REF: TC/73/5

28th June 1973

N E W S L E T T E R No. 4

1. GENERAL POINTS

1.1. Bibliography

This News Letter is a vehicle for the fourth instalment of the bibliography on conservation problems, covering items 71 to 127. This search of the recent literature has answered some of the questions asked recently; see sections 1.2 to 1.9.

1.2. Does water vapour attack glass?

Items 71, 106 and 115 leave no doubt that water vapour does attack glass rather slowly (at perhaps 100th of the rate of liquid water); it seems that all glass may deteriorate slowly unless it is kept in "dry" museum cases.

1.3. "Isothermal" glazing systems

Details of the methods of installing "isothermal" glazing, and the costs of doing so, are in items 72, 87 and 91. Calculations have been made (104) of the probability of condensation occurring on the ancient glass.

1.4. Will hydrophobic coatings prevent attack by water?

This may still be an open question but some siloxanes only delay the attack by water (86), perhaps by a factor of 4 to 10 (73, 101, 112, 120). It seems that the prevention of attack will involve rather complicated chemistry (85).

1.5. Inorganic coatings

These still remain a possible method of protecting glass (76, 92A, 95, 97, 105, 124) but they have yet to be tested on a glass with poor durability.

1.6. Ultrasonic cleaning

It seems that painted glass is not harmed by cleaning for three minutes in an ultrasonic bath (74, 126), even if the paint is "poorly fixed". The York Glaziers Trust report is now available as YG/73/3, dated 10th May.

1.7. Durability of medieval glass in relation to its composition

References 81, 84, 113, 115 and 127 relate the effect of glass composition to the way that it weathers. No. 84 throws light on crust formation and No. 127 investigates one case where the "colour" of the glass was claimed to affect the durability; in fact, differences in basic composition were involved.

1.8. Spontaneous cracking of glass

The spontaneous cracking of the outside surface of some medieval glass is still not completely understood, but it now seems likely to be due

to the effect of water, which extracts alkali ions and replaces them with hydrogen ions causing the surface to be in tension. Two papers (109, 115) describe what seems to be the same kind of phenomenon.

1.9. Environmental pollution

Information is being collected on the extent of pollution and the "fate" of sulphur dioxide and other atmospheric pollutants. It seems that more than half of the sulphur dioxide in the atmosphere comes from natural sources, and that it lasts for only a few days before it is destroyed (116, 118, 119, 122, 123). It has been thought that Geilmann (40) was the first to notice sulphates on medieval glass but it now seems that Scott (117) found gypsum on the windows of Wells Cathedral in 1932.

2. RESULTS FROM THE RESEARCH PROGRAMME

A. Tests on protective coatings

Some inorganic coatings are being applied to the poorly durable glass (No. 2) and another synthetic medieval glass (No. 3) with much better durability has been melted in case the consistent failures of protective coatings (Item A.1. of News Letter No. 3) may have been due to some feature of Glass No. 2 which prejudiced the results. Glass No. 3 has the following composition:-

	Molar percentage	Weight percentage
Silica	55.5	50.6
Lime	25.0	21.2
Potash	17.0	24.3
Alumina	2.5	3.9

B. Examination of medieval glasses

The identification of early medieval glass in York Minster, by attaching radiation monitoring films (page 3 of News Letter No. 3), has been successful; exposure for two months may be enough.

3. MISCELLANEOUS

The National Institute of Agricultural Engineering has surveyed methods of cleaning glasshouse panes and it was concluded that the only really effective method is to use dilute hydrofluoric acid (apparently a 1% solution of HF will remove a 15 μm layer of glass in three minutes). Experiments are in progress to discover whether fluorosilane compounds can be used to make glass self-cleaning under the influence of rainfall.

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This fourth bibliography on the conservation of painted glass supplements the three already issued, on 13th April (items 1 to 26), 22nd May (items 27 to 49) and 21st August 1972 (items 50 to 70); these three were supplied, in a yellow cover, to participants at the 8th Colloquium of the CVMA, held in York and Canterbury 25th September to 1st October 1972. The four bibliographies will be published, with an introductory section, by the British Academy and also, in an abbreviated form, in Art and Archaeology Technical Abstracts.

71. ADLERBORN, J (1971) "Investigation of weathered glass surfaces with the scanning microscope" OECD report on scientific research on glass (REF: DAS/SPR/71.35) dated 1 Dec. 1971, pp 244-254.

Glass surfaces were stored, either undried or dried by heating at 600°C in dry oxygen for two days, in dry or humid (50% relative humidity) gases for about a week and then examined with the scanning electron microscope. There are 22 photographs which show that specially-dried glass is not attacked by dry gases although gases with 50% relative humidity will attack the surface. Glass which has not been specially dried will show attack in one week when exposed to dry gases.

This paper is important because it shows that air or oxygen will attack glass if there is any moisture around. Especially-dry conditions must be achieved if the attack by water vapour is to be eliminated. Thus glass can be attacked by the atmosphere even though condensation of liquid water does not occur. In the presence of SO_2 part of the deposit was insoluble in water, suggesting that some calcium sulphate was formed in addition to sodium sulphate.

72. BACHER, E. (1972) "Exterior protective glazing" Compte Rendu du 8e Colloque du CVMA, held at York 25th to 27th Sept 1972, p. 27. (This abstract is based on a full paper made available by the author.)

In Austria it has been decided to use isothermal external protective glazing to protect her medeival stained glass, at least until the problem of an applied coating can be resolved. The panels are mounted inside the church, 6-8 cm away from the 4 mm thick modern glass which is set in the original rebate, and are mounted on bolts attached to cross-bars. As the jambs are splayed, the panels have to be widened (to fill the gap) by putting a metal border around them. Ventilation is achieved at the bottom by placing the bottom panel further in, and at the top by tilting the top panel inwards. The bolts permit easy removal for cleaning because there is a tendency for dirt to collect in the ventilated space.

This experience was gained in 1969/70 on two choir windows of the WaasenKirche in Leoben and in 1971/72 on four choir windows of the DeutschordensKirch in Graz; work is in hand at Maria am Gestade and at Lilienfeld. (The full paper gives much additional detail of a constructional nature.)

73. BASCOM, W. D. (1968) "The wettability of fluoro- and chloro-carbon trialkoxysilane films adsorbed on glass and metal surfaces" Journ. Colloid Interface Science, 1968, 27 (4) 789-796.

This is a scientific study of the effects of eight organic compounds (fluoro- or chloro-carbon trialkoxysilanes) on the wettability of glasses and metals. Briefly, the films of these compounds formed three-dimensional networks (polysiloxane) which formed siloxane bonds to the glasses, but the films did not achieve the maximum close-packing of the fluoro-carbon groups which had been reported elsewhere.

Two of the chloro-carbon compounds met the two basic requirements for adhesion promoters: (a) they form stable films on glass surfaces and (b) the films are sufficiently oleophilic (critical surface tension more than 40 dynes/cm) to be readily wetted by most adhesive resins.

74. BETTEMBOURG, J. M. (1972 a) "Nettoyage par voie chimique et par ultra-sons des verres de vitraux" (Chemical and ultrasonic means of cleaning painted glass). Compte rendu du 8e Colloque du CVMA, held at York 25th to 27th Sept 1972, p. 47.

The author reported on the different methods of cleaning which he had used; mechanical, chemical, and ultrasonic. From the chemical point of view, 10% aqueous solutions of sodium thiosulphate and sodium pyrophosphate were found effective for removing a weathering crust composed of gypsum and syngenite when the corrosion of the glass had been uniform. If, however, the surface of the glass is very pitted, the only procedure which he found efficacious was ultrasonic cleaning. If the painted decoration is in a good state of preservation it is not affected by any of these treatments.

75. BETTEMBOURG, J. M. (1972 b) "La restauration de vitraux brises. Veillissement accelere de colles" (The restoration of cracked windows - accelerated ageing of the adhesives) 8 pages of typescript, dated 3-11-72.

Thirteen adhesives were used for edge-to-edge gluing of cracked glass and then submitted to accelerated ageing tests in the Weatherometer. Each daily cycle consisted of immersion for one hour in water at 20°C followed by two hours at -20°C and then two hours in the Atlas Weatherometer (being 120 minutes of "illumination" of which 18 minutes involved spraying with softened water). The "illumination" could involve one arc lamp (which gave a temperature of 40°C) or two lamps (giving 70°C). Two series of tests were carried out; the first used six of the adhesives and involved 10 cycles with one arc, followed by 25 cycles with two arcs; the second test used seven adhesives and involved 45 cycles with two arcs. The nine epoxy resins had the worst performance of the 13 adhesives and the best performances were given by the two silicone resins. The two thiokol resins gave durable joints but they became grey and opaque.

76. BRACKLEY, G., LAWSON, K. and SATCHELL, D. W. (1972) "Integral covers for silicon solar cells" Photovoltaics Specialists Conference, 2-4 May 1972, in Maryland, USA. 6 pages and 4 figures.

Integral covers up to 0.3 mm thick have been produced by radio-frequency sputtering of Corning 7070 glass. The films have a low intrinsic stress and do not need to be annealed. Adhesion is good and transparency is very high with only a slight change after irradiation. Some pure silica (Corning 7940) films were also deposited. The edges of the cell are coated to a thickness of about 40% of that on the face of the cell. With a power input of 5 kW at 13.6 MHz the equipment can coat 70 cells, each 2 x 2 cm, with 7070 glass at a rate of 2.6 µm per hour. The coatings have been tested for 100 cycles between +130° and -180°C. Samples of 7070 glass on silicon have been immersed continuously in boiling water for many weeks but no delamination occurred and the films of glass could not be removed from the silicon. The cost of coating these cells is $1 per 4 cm^2, or about £100 per sq. ft. (say 10 000 DM per sq.m.).

77. BRILL, R. H. (1972) "Glass analyses" Compte rendu du 8e Colloque du CVMA, held at York 25th to 27th Sept 1972 pp 21-22.

Dr. Brill described the different methods used at the Corning Glass Center for analysing ancient glass (X-ray fluorescence, atomic absorption spectroscopy, emission spectroscopy, etc.), in order to establish their provenance and provide a link between their composition and their durability to weathering. Analyses of plant ash are also undertaken in order to rediscover the techniques used by medieval glassmakers. The provenance of the lead used for glazing can be established by isotopic analysis. He also recommended the airbrasive for cleaning the glass.

78 BROCKWAY GLASS COMPANY INC. (1967) "Corrosion retarding fluorine treatment of glass surfaces" US Patent No. 3,314,772 dated 18 April 1967.

This patent has been included to indicate the type of improvement of the durability of commercial glass bottles which is deemed worthy of patenting. The patent opens with a discussion of the mechanism of deterioration of glass and how the reaction with water can be greatly reduced by reacting fluorine atoms with the surface. In the practical examples given, the durability of the bottles is increased variously about 7-fold to 17-fold. Thus the attack is not inhibited, but only delayed by a factor of about 10 (depending on the kind of test carried out).

79. CAVINESS, Madeline (1972) "Saving Canterbury's medieval glass" Country Life, September 1972, pp 739-740.

The article points out that the stained glass windows painted between 1175 and 1220 had an impact on the slightly later windows at Chartres. Much of the glass had been repainted by three generations of the same family of craftsmen and "by now it is rare to find a panel in which half of the pieces of glass have not been replaced". About 100 years ago another restorer laid straps of lead across some glass to hold together the decaying original leading. "The marks of these straps, removed a hundred years later, can be seen because they protected the surface during what was evidently a period of accelerated decay". She also points out that extensive back-painting was used on the Canterbury glass and this increases the problems in conserving the windows.

80. COLE, F. W. (1972) "The state of 'Adam Delving'" Compte rendu du 8e Colloque du CVMA, held at Canterbury 30 Sept 1972, pp 31-32.

Mr. Cole described the history of the restorations at Canterbury Cathedral, which had been dominated by Mr. Caldwell for more than 50 years. The state of conservation of the glass was illustrated by the panel 'Adam Delving' which had been removed from the West Window and installed in the crypt so that it could be inspected closely by those attending the meeting. The holes in the glass were noted and it was the opinion of the experts that these pieces of glass would disintegrate in 10 or 20 years unless some action were taken to preserve them. As a start it should be put in an air-conditioned environment. Dr. Frenzel expressed the opinion that the glass was so fragile that doubling would be the best treatment.

81. DOUGLAS, R. W. and EL SHAMY, T. M. M. (1967). "Reaction of glasses with aqueous solutions" J.Amer. Ceram. Soc. 1967 50 1-7.

The kinetics of the reactions of various glasses with water was studied in a range of aqueous solutions, from strongly acid to strongly alkaline. The glasses varied from those easily decomposed by water to those having a durability comparable with that of commercial glasses. The rates of removal of various glass constituents were measured and potential mechanisms for the reactions are discussed. At the end of this paper the authors discuss the alkali-deficient leached layer which forms at the surface of glass attacked by water. In general the layer is thicker for glasses of low durability and may extend to include the whole bulk of the original glass.

82. DUFTY, A. R. (1972) "Through a stained glass less darkly" The Times, London, Saturday 23 September 1972, p.14.

This is a short article which draws attention to the many problems existing in the conservation of medieval stained glass and points out that the CVMA would be holding a meeting in York and Canterbury from 25th September to 1st October for the purpose of pooling knowledge about solving the problems. It mentions that "lost" inscriptions leave vestigial images which can be revealed by the use of suitable optical means.

83. EL-SHAMY, T. M. M. (1966). "Reactions of glasses with aqueous solutions" University of Sheffield Ph.D. thesis, September 1966, 145 pages.

The author studied the mechanism of decomposition by water of some very simple glasses (binary and ternary silicates). Alkali extraction was usually independent of the pH of the water until it reached pH = 9, when the alkali extraction decreased but the silica extraction increased. Leaching of alumina occurred in acidic solutions (pH less than 4 or 5). He showed that true phase equilibria do not exist when glasses are attacked by water, and the whole question is exceedingly complicated, especially as the various components do not pass into solution in the same proportion in which they occur in the glass. Silica continues to pass into solution as long as alkali is still present but the rate approaches zero when all the alkali has been removed from the glass. Hydrofluoric acid is shown to attack glass because it is a reagent having both a strong nucleophilic agent and a strong electrophilic agent.

84. EL-SHAMY, T. M. M. (1973) "The chemical durability of K_2O-CaO-MgO-SiO_2 glasses" Glass Technology 1973, February (in the press)

The authors point out that multicomponent silicate glasses are normally very resistant to attack by aqueous solutions but as the silica is replaced by potash, the quantities of potash, lime and magnesia extracted by water or hydrochloric acid increase considerably. In glasses with more than 15 mole % of potash, more than 10% of the potash can be leached out in one hour and the glass is completely dealkalised in less than 72 hours. It is considered that the glasses which form a weathering crust are those which have a ratio of silica to basic oxide (ie lime and/or magnesia) of less than 67:33. It thus seems that this work indicates the way in which a fuller understanding will be gained of the mechanism of crust formation.

85. EL-SHAMY, T. M. and DOUGLAS, R. W. (1972) "Kinetics of the reaction of water with glass" Glass Tech. 1972 13 (3) 77-80.

This is a rather technical paper concerned with the kinetics of reaction of a $K_2O.3\ SiO_2$ glass with water, but a point of special interest for the conservation of glass is the authors' comment that "experimental factors designed to eliminate the effect of accumulation of decomposed materials.....are far from successful.....the effect of increasing pH due to preferential extraction of alkali into solution is impossible to eliminate....". This remark emphasises the dangers inherent in allowing any water to remain for a prolonged period in contact with glass.

86. FRANCEN, V. L. and HEINE, R. F. (1965) "Fluorochemical glass treatments" Glass Industry 1965 46 594-597, 628-9.

The paper discusses the use of various fluorosilanes, marketed by the Minnesota Mining and Manufacturing Co, to make glass surfaces water-repellant. Two of the compounds (L-1653 and L-1668) make glass both oil-repellant and water-repellant and the coatings resist strong acids (except phosphoric and hydrofluoric) and organic solvents. However 5% caustic soda will remove the coating; "only reagents which chemically attack the glass surface will remove the fluoroalkyl coatings". (RGN: it thus seems that the coatings cannot be expected to provide long-term protection against the weather, or against condensed moisture.)

87 FRENZEL, G. (1972 a) "Gutachten über den Erhaltungszustand und Vorschläge zur Sicherung der Mittelalterlichen Glasmalereien, Munster zu Ulm" (Expert opinion on the state of preservation of the medieval stained glass of the Minster at Ulm and suggestions for protecting it) Report from Dr. G. Frenzel to the Department of Works of Ulm Minster, dated 6th June 1972. 11 pages of typescript and 24 photographs.

The author blames the poor state of the glass at Ulm Minster on air pollution (but see items 118 and 119) and he describes the process of corrosion. He recommends that external "isothermal" glazing should be installed, the medieval glass be rehung in the Minster, and that heating units and hygroscopic materials (Heizelementen und Trocken patronen) be placed on the sills if the air circulation is not sufficient to provide adequate protection for the medieval glass against moisture in the air space. Recommendations are also made for cleaning and for removing the overpainting.

In all, 736 panes require attention and the total cost is considered to be in the region of 3 million DM, spread over 10 years.

88. FRENZEL, G. (1972 b) "Preventative and conservational methods for preserving the Augsburg Prophet windows of 1130" Compte rendu du 8e Colloque du CVMA, held at Canterbury 30 Sept 1972, p. 54.

The author showed 35 colour slides which illustrated the type of decay that occurred between 1909 and 1972, with special emphasis on the increased rate of attack since 1945. Photomicrographs were used to illustrate the progress of corrosion, and increased concentrations of carbon dioxide and sulphur dioxide are considered to be responsible for the enhanced attack in the last decade. There was a comprehensive discussion of the materials required for cleaning and restoring the windows, and the vast effort required. It will need four years' work, and a total cost of 300 000 DM (say £40 000) to clean and preserve the five Augsburg Prophet windows.

89. FRODL-KRAFT, E. (1972) "Untersuchungen und praktische Erfahrungen in der Konservierung mittelalterlicher Glasgemälde 1963-1972" (Researches and practical experiences in the conservation of medieval painted glass 1963-1972).

Compte rendu du 8e Colloque du CVMA, held at York 25th to 27th Sept 1972, pp 27, 52.

Since the publication of (33), the Austrian department for ancient monuments has gained much experience and carried out systematic tests, including analyses of the glasses and of the weathering crusts which explained the influence of certain elements in the composition of the window; the crust consisted 50% of silica and 20 to 30% of SO_3. The question of cleaning and protection of the surface was a complex one and acids should be avoided because they could penetrate fissures in the surface and cause long-term damage. Solutions of polyphosphates were found satisfactory for removing weathering deposits. The use of films of resin to protect the outside of the glass had been tried and the results were encouraging.

90. GIBSON, Peter, (1972) "The activities of the York Glaziers Workshops" Compte rendu du 8e Colloque du CVMA, held at York 25th to 27th Sept. 1972, p.17.

On 26th September the delegates visited the workshops of the York Glaziers Trust. The Superintendent, Mr. Gibson, explained that the workshops were founded in 1962, before which the windows were cleaned solely in warm water. The 12th century panels exhibited the results of modern cleaning techniques, cleaning in an ultrasonic bath and removal of the weathering crust by grinding and polishing, although this latter procedure is used only in the most difficult cases. A "bank" of medieval glass permits the replacement of glass which has been too greatly damaged by weathering. If replacement is not possible, modern glass is used but it is never repainted. If the glass is very fragile it is doubled on both sides.

91. HAHNLOSER, H. (1972) "Restaurationsbericht von Konrad Vetter, Bern, betr. Scheiben von Hans Acker, 1441, Sowie Biel & Burgdorf" (Konrad Vetter's restoration report on the panels at Berne, Biel and Burgdorf, by Hans Acker, 1441). Paper for the 8th Colloquium of the CVMA at York (not included in the Compte rendu) 15 pages of typescript and 16 photographs.

The report is in six parts (A-F): A. Exterior glazing. This is isothermal protective glazing and engineering drawings are given to show the way the medieval glass is supported on bolts inside the church in such a way that the warm air can circulate around it. Laminated safety glass is installed in the original glazing grooves as a protection against stone-throwing.

B. Cleaning When the panels have been removed the outside must be cleaned with a brush, lye and pickling agent (Lauge, Abbeizmittel - Ebeco Rico R2, from Böhme AG). The inside is cleaned with a soft duster or, if the black enamel is in good condition, with water only.

C. Mending cracks. Araldite AY 101 is used with 10-12% addition of hardener HY 956 to mend the cracks. Never let the Araldite dry out completely on the surface, or splinters of glass will be detached when it is removed. With care cracks can be repaired without removing the glass from the leads.

D. Doubling - to be used only if the black enamel is intact, otherwise it must be fixed first. In this case only 9% of HY 951 is added.

E. Restoration of pitted glass. Remove the weathering crust by brushing with a glass fibre eraser. Then protect the rough surface with an Araldite-acetone solution:- mixture of AY 103 and HY 151, 1 part; acetone 15 parts. Paint this on the rough glass in 3 to 5 applications, allowing 12 hours to dry between applications.

F. Reversible restoration . Araldite protection can easily be removed by using the picking agent Cital paste (the hands and eyes must be protected). Doubled pieces of glass can be separated by heating to 150-180°C in the kiln, and then levering off with a thin blade.

92 HALL, E. T. and SCHWEIZER, F. (1973) "X-ray fluorescence analysis of museum objects: a new instrument. 1 A non-dispersive X-ray 'Isoprobe'" Archaeometry 1973 15 (1) 53-57, 74-76.

This paper describes the 'Isoprobe', a device for the "immediate" non-destructive analysis of materials, including glass. (It has been used for analysing glass from York Minster - see item 127). It will carry out an analysis in about 100 seconds. In its simple form (using an air path between the device and the sample) it will analyse for elements with atomic numbers down to 20 = calcium. If a helium path is used it will analyse elements with atomic numbers as low as 11 = sodium.

It seems likely that the equipment will provide valuable information about the composition of large numbers of pieces of medieval glass.

92(a) HAMMOND, V. J. Private comments, June 1973

A special calcium, alumino-silicate glass, type CAS 10 developed by G. V. Planer Limited in conjunction with Pilkington Brothers, can be used to coat substrates by vacuum deposition using an electron beam evaporation source. This low alkali glass was initially developed as a thin film dielectric for use in microelectronic circuit fabfication for which purpose it has been shown to have very acceptable characteristics, particularly extremely low incidence of pinholing in films even as thin as 250 nm. Films deposited from this glass are highly durable, resistant to high relative humidity and have very good wear characteristics at thicknesses of the order of 2 μm.

Although not yet evaluated in the context of protective layers for cathedral glass, Hammond of G. V. Planer considers that the material has a high potential for this application. Initial work is shortly to be put in hand to assess its interlayer adhesion prior to preparation of samples for non-permeability evaluation.

93. HEATON, Noel (1907) "Medieval stained glass: its production and decay" J.Roy.Soc. Arts, 1907 468-484.

This is the text of a lecture on the composition and manufacture of stained glass (pages 468-473) followed by a discussion on weathering (pages 473-477). Table I lists some of the materials used in making glass and Table II gives the analyses of 14th century glass from Sandiacre, Derbyshire and 13th century glass from Dale Abbey (also in Derbyshire) which had lain buried until 1882. His remark, that lead was not used in medieval glassmaking has since been disproved by Eva Frodl-Kraft. He believed that early medieval glass was made by pouring, or spinning or by the cylinder process.

On p. 472 he comments on the phosphate contents of medieval glasses and suggests first that the wood ashes were not lixiviated (Theophilus suggested that the ashes should be purified with water) and second that the phosphate content may account for the "peculiar opalescence or horniness" of medieval glass. On p. 474 he points out that potash glasses are hydroscopic and attract moisture to the surface, thus leading to their own decay.
There is a long discussion of the formation of pits on the surface but there is now no support for his suggestion (on p. 475) that crystallisation of glass occurs at room temperature. Moreover, it is difficult to understand his remark that decomposition of the glass occurs "until it reaches a point at which the strain set up in the glass by this molecular movement results in a crack forming around the area of decomposition and then the whole mass comes away, leaving behind a little hole or pit in the surface of the glass". It seems to RGN that pits are formed by attack from the surface and that the cracking away of a piece from the surface is quite a different phenomenon, possibly associated with fractures due to the formation of a hydrogen layer.

On p. 476 he refers to a piece of flashed purple glass "the flashed surface quite bright and free from corrosion but studded all over with numerous well defined pits, suggesting that such pits are internal rather than external in origin". Unfortunately this sample is not one of those illustrated and it is not possible to judge whether the pits are formed by corrosion or by fracturing.

Pages 477 to 488 are concerned with speculations about the nature of "geet", used for painting glass and with rejecting the suggestion that it was jet. Pages 480 to 484 record the discussion which took place, with comments about the relative durability of different pieces of glass and about the change from potash to soda in the sixteenth century. The glass used at Southwark in the sixteenth century is stated to have been of foreign origin.

94. HEATON, Noel (1910) "The foundations of stained glass work" J.Roy. Soc. Arts 1910 454-470.

This article deals with the analysis of glass and the composition and nature of the paint used, both modern and medieval, with special emphasis on the mutual understanding of the problems by the artist, craftsman and glassmaker.

Some items of particular interest in the conservation of glass are:- pp 455-6, a piece of glass from York Minster, dated 1310, was heavily pitted and badly disintegrated; analysis showed it to be mainly a soda glass. His analyses of modern glass used by artists, given on p. 457, is rendered invalid by the fact that he deliberately mixed many samples; thus the 1.52% of lead oxide may have been introduced by one piece of lead glass. On p. 464 he refers to the problems of using glass which has a "hydrated" surface, but his explanation of the difficulty seems to be inaccurate. The 'hydrogen glass" which can form on the surface of glass exposed to a humid atmosphere is actually under tension and causes the glass to craze; it does not seem likely that the water "will be driven off as steam during the firing". Poorly-fired paint seems to have been causing trouble for hundreds of years (p. 465).

95 HOLLAND, L. (1972) "The basic principles of sputter deposition" (Edwards High Vacuum International, UK - extract from a NATO conference on coatings held in London, 1972)

The release of material from elemental and compound targets by impact of energetic ions is discussed and related to the ion energy, mass and incidence angle. Practical sputtering systems for thin film deposition are divided into three kinds: cold cathode glow discharge, plasma/ion extraction and ion beam-target vessel. There are two systems:- in a high vacuum with the target material travelling direct to the substrate, or in a low gas pressure with diffusion of the sputtered particles in the residual gas, and the gas can modify the effects of the film.

96. HUSBAND, T. B. (1972) "A new type of mending lead". Compte rendu du 8e Colloque du CVMA, held at York 25th to 27th Sept 1972, p. 28.

The author described a new type of mending lead for restoring windows, based on the process of the Tiffany Company, used from the beginning of the century for assembling painted glass. The process consists of folding copper foil over the edges of the glass and then soldering them together to give the appearance of a strip of lead, a tin-rich solder being used. At the Cloisters Museum cleaning is restricted to the use of de-ionised water and the policy is to leave corrosion products in position.

Following this paper (on p.29) there was a discussion of the use of adhesives, during which M. Bettembourg pointed out that silicone-based adhesives were more reliable in damp conditions than epoxy resins, even though Dr. Frenzel had found epoxy resins to be satisfactory (in plated panels) for about 15 years.

97 JACKSON, G. N. (1970) "R. F. Sputtering" Thin Solid Films 1970 5 209-246.

The author refers to Wehner's work on sputtering of insulators in 1955 and shows how it has become an important field in thin film technology, being used on metals and semiconductors as well as on insulators. There is a detailed discussion of electrode systems and power generators, and of the sputtering process itself. The rate of deposition of the sputtered material depends on many items and, in any new application, the properties of the film have to be found by experiment, rather than by predicting them. The substrate (eg, the ancient glass, if this is to be protected) becomes heated, figures of 275°C (at 0.5 kW r.f. power) and 325°C (at 1 kW) are quoted (p. 235).

Discussions, held with the author of this paper, with special reference to the sputtering of medieval painted glass, elicited the following additional information. Coatings of one glass on another have been used to provide corrosion resistance when only 100 μm (0.1 mm) thick but this is probably a lower limit and experimental work should envisage the use of layers 300 μm (0.3 mm) thick. These do not show any delamination when boiled in water for a week but they would probably cost nearly £1 per square inch to produce (say £100 per sq. ft.). It seems likely that the edges of the sample can be covered if radio-frequency sputtering is used (because the sample becomes an "extended source"). Corning 7070 glass can be deposited on silicon to a thickness of 300 μm but silica can be deposited to only 80 μm or the intrinsic stress is too high. Corning 7070 glass has a coefficient of expansion of 32×10^{-7} whereas silicon is 30×10^{-7}.

Discussions held with Professor J. C. Anderson of Imperial College, London, show that radio-frequency sputtering can coat a sample 150 mm square in 3 hours to give a coating 0.3 μm thick at a cost of £40. The equipment is capital intensive (costing about £20 000) and thus the cost of depositing a coating is virtually independent of the material being applied. RF sputtering will also deposit material on the sides of a sample which is small enough. Vacuum evaporation can be used to deposit a similar range of materials and it is cheaper than RF sputtering by a factor of ten. However, it will not coat the edges of the sample. The sputtered deposits tend to be denser than those prepared by vacuum evaporation because the atoms are forced together rather better.

98. JACOBI, R. (1955) "Das Konservierungsverfahren für die Obergadenfenster des Kölner Domes" (The conservation process used for the upper storey windows of Cologne Cathedral). Kölner Domblatt 1955 9 122-130.

The author describes the precarious state of many medieval windows, particularly as regards the presence of many cracks (even 400 per sq. metre), and he recounts the disadvantages of using lacquers, mending leads, etc. He then points out that one way of repairing such windows is to laminate them, as is done for the laminated windscreens of cars. Pages 126-127 then give the history of the development of the "safety glass process" from 1937 to 1954, and pages 128-130 give the detailed instructions for carrying out the process, especially the method of bending the two cover plates to match the contour of the ancient glass before the lamination is carried out (German Patent No. 822015).

99. JACOBI, R. (1960) "Fehlurteile über die Restaurierung der Domfenster - Entgegnung auf einen Aufsatz von G. Frenzel" (Incorrect assessments of the restoration of the cathedral windows - reply to a paper by G. Frenzel). Kölner Domblatt 1960 18/19 167-170.

The author complains about some criticisms expressed by G. Frenzel in Z. f. Kunstges., 1960 23 (1), the latter apparently having failed to make clear distinctions between early laminating and cleaning techniques and those used 20 years later. These are detailed comments about alleged failures and it seems that there may have been misunderstandings about whether the Konhof window of the LorenzKirch was restored at Cologne or in the Zettler workshops. It seems that properly-applied laminated cover glasses can be removed more than once, by heating and levering off, without damaging black enamel that was in good condition before the cover glass was applied. It also seems that in some cases, both at Nuremberg and at Cologne, unsatisfactory materials had to be used and these gave rise to defects which would not normally occur.

100. JACOBI, R. (1972) Letter dated 28-9-1972.

This letter was a reply to a direct question about the costs of using Dr. Jacobi's technique. Between 50 and 130 pieces of safety glass can be bonded per hour, depending on the size, and the cost may be as high as 2 000 DM/m^2, or perhaps £20 per square foot. The Knorr window in the LorenzKirch, Nuremberg was stored during the War in crates, but too many crates were piled on top and this window was smashed. The Schidmaier window of the LorenzKirche cost about 500 DM/m^2 to fix by the safety glass method. The windows in Cologne Cathedral were in a very precarious condition and the cost of repairing and laminating was 2000 DM/m^2.

101. JAMES, D. I., NORMAN, R. H., and STONE, M. H. (1968) "Water attack on the glass-resin bond in GRP" Plastics and Polymers 1968 36 21-31.

The authors tried to identify the weak link in the glass/coupling-agent/resin interface of glass reinforced plastics (GRP) but the interest of the paper for conservation purposes is that they tested the material in boiling water and found that the glass is then appreciably hydrolysed and the layer of coupling-agent on the surface gives little protection. On p. 22 they say "It is commonly thought that one function of coupling-agents is to protect the glass against attack by water.... It was therefore of interest to see whether they prevented hydrolytic attack on the glass.....it is clear that although coupling agents do reduce the rate of hydrolysis (eg, to about one quarter) there is nevertheless considerable attack at the glass surface." The agent A 1100 (see item 120) was the most effective of those examined.

102. KING, Dennis, G. (1972) "Methods of cleaning medeival painted glass" Compte rendu du 8e Colloque du CVMA, held at York 25th to 27th Sept. 1972, pp 15-16.

Dennis King discussed the methods of cleaning used in his workshops at Norwich and demonstrated the results with numerous examples (1) Ultrasonic baths were very useful, the painted design being protected by a coating of latex; in difficult cases the dental ultrasonic descaler ("Cavitron") can be used to clean around the edge of the design. (2) The airbrasive is an effective means of removing the crust, the design again being protected by latex. (3) Resurfacing and polishing at the external surface of the glass. (4) Restoration of the design by copying it on thin modern glass and then plating it to the original. Yellow stain can be "restored" in the same manner. In the discussion Dr. Brill stated that the annealed surface of the glass is the best means of protection, and it should be retained.

103. LACY, R. E. (1970) "A note on the climate inside a medieval chapel" Studies in conservation 1970 15 65-80.

This paper describes calculations of the humidity in King's College Chapel, Cambridge, based on climatological data, and subsequent measurements of the temperature and humidity in the building for a period of 12 months. The humidities measured in the winter were greater than those expected because the structure absorbed moisture exhaled by summertime visitors. The interest for the conservation of stained glass lies in the closeness of the predicted values with those measured and the possibility that Mr. Lacy's technique might be used to calculate the conditions existing in "double-glazed" windows. He has now made such calculations (see item 104).

Other points in the present paper are (p.65) that the installation of heating in an ancient church in Sweden destroyed medieval wall-paintings in ten years because the increased evaporation from the walls caused efflorescence. It is also suggested that heating systems encourage greater damage by death-watch beetles. The humidity in the chapel was measured on 1524 occasions and on only four of these was the relative humidity less than 50%.

104 LACY, R. E. (1973) "Estimates of frequency of condensation on the windows of a large church or cathedral" Building Research Station Report dated 12 March 1973, 5 pp typescript.

Following a discussion with him of his paper (item 104) Mr. Lacy was asked if a similar theoretical study could be made of the frequency of condensation expected on the inner leaf of various kinds of double windows. The calculations were carried out for windows of three types, A, external protective glazing; B, "isothermal" glazing and C, a sealed double-glazed window, as if they had been installed in the relatively unheated Kings College Chapel Cambridge. He has calculated the percentage of the time, for different months of the year, when condensation might be expected to occur on the ancient glass. The figures are:-

Estimated frequency of condensation (percentage of all hours) on inner leaf of double windows in churches, with three different arrangements

Month	A: outer rainshield of modern glass	B: ancient glass free-standing within church	C: sealed double-window
January	22	6	14
February	23	3	12
March	16	3	11
April	7	1	3
October	11	2	7
November	16	3	10
December	22	6	15

He comments that the figures in column B are probably really all zero and that the values listed may represent occasions when the air in the building became saturated, or nearly so. All the figures would become smaller in a heated building. In this connection Mr. Bernard Feilden states that the temperatures inside York Minster, Norwich Cathedral and St. Paul's Cathedral are, respectively 14.4, 15.6, and 16.7°C (58, 60 and 62°F).

105. LINSLEY, G. F. (1972) "A possible method of conserving ancient glass" Compte rendu du 8e Colloque du CVMA, held at York, 25th to 27th Sept. 1972, p. 51.

The author reviewed the methods advocated for preserving restored glass from renewed atmospheric attack and found them wanting. He described a new approach involving the vacuum deposition of a silica-rich glassy layer only a few micrometers thick. It seemed that these invisible layers of durable glass might protect glass against humid atmospheres.

106. LÖFFLER, J. (1968) "Reaktionen zwischen Glas und Luft feuchtigkeit" (Reactions between glass and atmospheric moisture) Glastech.Ber. 1968 41 (12) 506-512.

This paper is largely concerned with the problems of chemical analysis of the water and the reaction products on glass surfaces but it makes the fact clear that air which has not been dried will attack glass, even though no liquid water has condensed. Once some reaction product has formed on the surface there is a likelihood of the formation of solutions, owing to the lower vapour pressure of the deliquescent material.

The author remarks that liquid water attacks glass at isolated points but water vapour attacks the surface uniformly. (RGN: This view is not supported by two other observations (a) some re-surfaced Winchester glass which had lain in Dennis King's workshops for 20 years can be shown - with the Normarski technique - to be covered with small circular areas with diameters between about 30 µm and 400 µm;(b) the electron-microscope pictures taken by Adlerborn(71) show that the initial attack occurs at isolated points.)

107 LOWE, John (1961) "The conservation of stained glass" The text of an address presented to the United Kingdom Group of the International Institute for Conservation of Historic and Artistic works, on 27th April 1961, 13 pages of typescript.

This is an interesting general account of the problems of cleaning and restoring ancient stained glass as seen from the point of view of a museum restorer, rather than a conservator of stained glass in churches. There are good descriptions of the different types of glass and decorating techniques, with special points, for example, that yellow stain is easier to apply to potash glass than to soda glass.

Details of cleaning techniques are set out on pages 3-5, and Bedacryl is recommended for "fixing" loose black enamel in museum situations; it could be dangerous to use if dampness were present.

Decay of glass is regarded as something which has been progressing continuously, and no mention is made of enhanced deterioration in the post-war enviornment. In 1647 a glass-painter's contract stipulated that the paint should not be "liable to injury from the moon"! He comments that there can be no simple explanation because there are cases where glass has survived in badly polluted towns but has decayed badly in country churches. (RGN: it is clearly important to obtain as many analyses of such glass as possible, eg, by using the 'Isoprobe'.)

His explanation for "back-matching corrosion" - that lead may alter the composition of the glass by absorbing some of the excess alkali in the glass - seems hardly tenable in view of the alternative explanation (see item 53). He gives credit to Dennis King for having first evolved the resurfacing technique used successfully at Winchester and other places, and refers to William Lowe's use of dental drills (see item 18).

Pages 8-10 are concerned with methods of repainting old glass and the aesthetics of so doing, or merely shading - in an indication of a head. Page 11 is concerned with "jumbled windows", how they arose and how they may be reconstituted.

108. MARCHINI, G. (1972) "L'affaiblissement de la grisaille le long des plombs"(Weakening of the painted decoration near the leading). Compte rendu du 8e Colloque du CVMA, held at York 25th to 27th Sept 1972, p. 46.

Professor Marchini drew attention to the many windows in Italy where a loss of painted decoration had occurred along horizontal parts of the leading, and he attributed this to corrosion by condensed water which contained atmospheric pollutants. Because the lead is a good conductor of heat (or of cold) there is a tendency for dew to condense on it to a greater extent than on the glass itself. He therefore recommends that the ancient glass should be protected by external glazing arranged so that there should be natural circulation of the air inside the building (isothermal protective glazing).

109 METCALFE, A. G., GULDEN, Mary Ellen, and SCHMITZ, G. K. (1971) "Spontaneous cracking of glass filaments. Glass Technology 1971 12 (1) 15-23.

Despite its title, this is an important paper from the point of view of the spontaneous cracking which has been noticed on the outside of many pieces of ancient glass. The damage to the medieval glass takes the form of cratering (which resembles pitting except that there are no corrosion products in the craters; they have smooth sides sometimes showing conchoidal fracture marks), and the craters are generally associated with fracture lines in the outer surface only, the glass being otherwise smooth and uncorroded.

The authors studied glass fibres, which they treated with acid. They found that the surface of the fibre remained glassy but that glass had a different composition, the alkali (soda or potash) being replaced by hydrogen ions. Because the hydrogen ion is smaller than either of the alkali ions, the surface is placed in tension and fractures occur in the surface, but only as deep as the modified glass which had been formed. Between the cracks, no general surface attack was found and another discovery was that the replacement of the acid by alkali reverses the effect, prevents loss of strength and cracking, and the "protected" glass does not crack even in concentrated acids.

The paper is rather technical but anyone who wishes to know more about the scientific basis of this spontaneous cracking should read this paper, and also the one by R. J. Charles "The origin of depression constants of glass thermometers", Glass Technology 1971 12 (1) 24-26. He showed that stress relaxation (really a kind of stress readjustment) can take place when there are "mixed alkalis" in the glass. There is a migration of the smaller and faster-diffusing ion to regions of the sample which are under lower compressional stress. There is also another effect in which the larger ions(in a mixed alkali glass),though slower-moving, are generally more responsive to the applied stress field. Both processes can modify the stress in the sample.

110. NEWTON, R. G. (1972) "Recent results from conservation studies" Compte rendu du 3e Colloque du CVMA, held at York 25th to 27th Sept. 1972, pp 48-50.

The author started by describing a study of a panel which had been damaged by cleaning with a strong detergent. The parts which had originally been painted were rougher than the surrounding parts, but only by about half a wavelength of light and special optical techniques were therefore needed. The Normarski differential interference contrast technique revealed the lost design quite clearly but it could only be used under a microscope. Differences in specular reflection could also be used, provided care was taken to remove reflections from the back of the glass.

Slides were shown which demonstrated how the air-brasive equipment can be used to remove weathering crust around painted decoration when the painted areas are protected by a deposit of rubber latex. The origin of the so-called "back-matching corrosion" was discussed and it was attributed to painted designs on the back of the glass, which matched the design on the front, where the paint had accelerated corrosion and (usually but not always) destroyed itself in the process.

The author discussed the evidence for the distribution of sulphur dioxide in the air in Britain and showed that the presence of gypsum and syngenite in the weathering crust was not evidence of air pollution. Both were present in the crust at Ely Cathedral, which was in an area of low sulphur dixoide. Moreover, there was enough sulphur dioxide present, from natural sources only, to convert all the weathering crust into sulphates. It seems likely that the enhanced deterioration of medieval glass, which has taken place since the war, may be due to adverse storage conditions when the windows were removed as a precaution against bomb damage. There was also a contribution which showed that some "forest-type" medieval stained glass was readily soluble in hydrochloric acid.

In the discussion Dr. Frenzel drew attention to the evidence for the back-painting and suggested that such pieces of glass should not be cleaned on the outside. There was also some discussion as to whether the corrosion products protected the glass surface or caused accelerated corrosion, and it was evident that opinions were in favour of removing the corrosion products, especially if it were found possible to protect the cleaned glass, for example by applying a resin having the appropriate refractive index.

111 NEWTON, R. G. (1973) "Notes on researches recently carried out" Yet unpublished work at the British Glass Industry Research Association.

Recent work, chiefly in conjunction with the York Glaziers Trust has dealt with the following topics:

(a) The technique of revealing faded decoration by means of specular reflection (see item 110) has been considerably improved by removing reflections from the back surface of the glass. This is done by using a liquid with a "matching" refractive index (glycerine is satisfactory) to stick black paper to the surface. The technique has been used successfully on a window in situ in the church of St. Michael-le-Belfry, York.

(b) Several examples of glass have been studied where the outer surface has many fracture craters. Superficially the craters resemble corrosion pits but examination under a microscope shows that the shape is quite different; there are often radiating cracks associated with them, and sometimes fragments of glass adhere to the bottom of the crater. The outside surface of the glass has been in a state of strain and the reason is still being investigated but it is possibly due to dealkalisation. (See item 109)

(c) The humidity has been measured inside the "double glazing" on the Great East Window at York Minster, and found to be in excess of 80% relative humidity (see also item 104).

(d) The isoprobe (item 92) has been used to analyse 12th century glass at York Minster (item 127) with most interesting results. It has also been used to "authenticate" a 17th century roundel, by showing that it contains much more potash than would a modern soda-lime glass.

(e) The problem of identifying potash-containing early medieval glass has been simplified by making use of the natural radioactivity of the potassium. Standard personal radiation-monitoring films will be appreciably darkened after exposure for two months, and it is hoped that a semi-quantitative analytical technique may be devised.

112. NORMAN, R. H. (1973) "The significance of the interface in glass reinforced plastics" Lecture given at the Eleventh Annual Conference on Adhesion and Adhesives, London, 12-13 April 1973.

E-glass fibres, 10 μm thick, were embedded in an 0.2 mm thick sheet of a thermoplastic resin chosen to have a refractive index close to that of the glass. When the samples were freshly prepared the fibres were almost invisible in transmitted light but immersion of the resin in water caused de-bonding to take place and this could be seen as visible spots at the interfaces which spread until they merged to give complete loss of adhesion.

The process took only minutes when the sample was immersed in boiling water but pre-treatment of the glass with a vinyl silane coupling agent, before embedding in the resin, would delay the start of de-bonding for several hours. If a better coupling agent was used (methacrylsilane) the de-bonding in boiling water could be delayed for several days.

The de-bonding is attributed to the diffusion of water through the resin, followed by reaction with the glass, and failure would be much slower at room temperature than in boiling water; (acceleration - factors are difficult to estimate but 10 000-fold might be a reasonable guess).

113 OLIN, J. S., THOMPSON, B. A., and SAYRE, E. V. (1972) "Characterisation of medieval window glass by neutron activation analysis" Pages 35-55, reprinted from Vol. 10 of Developments in Applied Spectroscopy, Edited by A. J. Perkins, E. L. Grove, E. F. Kaelble and Joan E. Westermeyer, Plenum Publishing Corporation.

The authors have used the technique of neutron activation analysis to ascertain its usefulness for deciding the provenance of medieval window glass, eg, which pieces are original and which are replacements. Forty-five samples were analysed; 32 were of scattered provenance, 11 were from one panel, and 2 were studied in detail to assess their homogeneity. The samples taken were in the range 10 to 100 mg and full details are given of the irradiation procedure in the nuclear reactor. In the case of sodium and manganese there was good sensitivity in the analysis and no interferences from other elements, so the precision of measurement was about ± 2%; potassium determinations were less reproducible. None of the samples showed inhomogeneities greater than the analytical limits.

Eighteen elements were analysed but most of them are trace elements and there are no figures for silica or magnesia. Of the glass-making elements, there was great variation among the 32 pieces of scattered provenance, eg, Na_2O, 0.30 to 19.4%; K_2O, 2.41 to 31.3%; MnO, 0.36 to 1.9% and Fe_2O_3, 0.34 to 1.2%. When the 11 pieces from one 13th century panel were analysed, the range of variation was much less and the samples fell into two compositional groups. Eight of the samples had:- Na_2O, 0.49 to 0.57%; K_2O, 25 to 31%; Cs_2O, 9.8 to 11.2% ppm; MnO, 1.23 to 1.43%; CeO_2, 15.2 to 22.4 ppm, etc. The other three samples had:- Na_2O, 0.61 to 0.62; K_2O, 21 to 22%; Cs_2O, 23 to 27 ppm; MnO, 0.86 to 0.94%; CeO_2, 17.2 to 30.3 ppm, etc. Within either of these two groups the compositions of the samples are so similar "as to raise the question as to whether they had all been products of a single batch of glass preparation...the second group...might have represented a second batch prepared in the same workshop.". There were slight but definite differences in appearance of the outer surfaces of the two groups, and these might correlate with differences in weathering related to the differences in alkali content.

114. SCHOLZE, H. and CORBACH, R. (1971) "Study of surface properties of glass in acidic aqueous solutions" OECD report on scientific research on glass (REF: DAS/SPR/71.35) dated 1 Dec. 1971 156-174.

The authors show that ion exchange occurs (H^+ for Na^+) and that in neutral and basic solutions bond-breakage occurs in the silica network. A leached layer develops which is thicker in poorly-durable glasses. As deterioration proceeds, condensation of SiOH groups can occur to form new Si-O-Si groups with elimination of water and the resultant surface possesses very fine pores, determined by the radius of the alkali ions (for soda-lime glasses the pore diameter is 0.3 to 0.4 nm).

115. SCHRÖDER, H. (1953) "Über de Angreifbarkeit des Glases durch Lösungen mit pH-Werten nahe 7" (The susceptibility of glass to attack by solutions with pH values of about 7). Glastech. Ber., 1953 26 (4) 91-97.

The author comments on the relatively small amount of work so far carried out on attack of glass by solutions of salts and describes his work on the leaching of certain optical glasses to produce surface layers with a different refractive index. Such layers have tiny pores in them, between 5 and 10 nm diameter, and the mechanism of their formation is discussed. He suggests (p. 94) that his results might in practice play an important part in the spontaneous weathering frequently observed (häufig beobachteten spontanen Verwitterung), eg when window glass is stored where it has not been fully protected against water vapour. It is particularly dangerous when the sheets are stacked closely together under conditions of fluctuating temperature and moisture, when even an invisible condensed water film can react with the alkali of the glass to produce highly concentrated solutions particularly likely to form layers. The prior washing of the glass with acids, frequently recommended as an antidote, can only postpone the process somewhat because the extremely thin dealkalised silica gel skin cannot prevent moisture from diffusing in. A somewhat more effective process might be that of annealing the glass in an atmosphere containing sulphur dixoide (see Angenot, Silic. Industr. 1952 17 41-45 and Coward and Turner JSGT 1938 22 309-323).

Certain additives (salts of barium, calcium and aluminium) will diminish the attack by water, even by a factor of 10, but the effects can be complicated by the presence of other agents (p. 94, col 2). There are some materials (salts of beryllium, and colloidal silica) which retard the etching process on glass but without activating the leaching process (p. 95, col. 2) and the great complexity of the processes gives some insight into possible reasons for the remarkably different weathering deposits which are encountered with different glasses and slightly different environments. (RGN: the layering of the crusts in excavated glass may have this kind of origin.) On p. 96 (col. 2) he points out that any impairment of the diffusion at a glass surface will affect the susceptibility to attack, and this must be borne in mind when considering what might take place between a "protective coating", and the glass it is intended to protect, if moisture enters the space. Another surface placed a very small distance from the glass (less than 0.1 mm) can significantly suppress leaching in favour of etching.

116. SCORER, R. S. (1972) "The management of sulphur dioxide" Quality (the bulletin of the Shell Committee for environmental conservation) No. 14, June 1972, pp 2-5.

Because sulphur is not easy to remove from fuels, and SO_2 is easy to measure in small quantities, it has become an indicator of the degree of gaseous pollution despite the fact that many surfaces remove SO_2 rapidly and therefore disturb the measurements, with the result that SO_2 values may vary 100-fold from day to day. Although the total emission of SO_2 has increased in the last 20 years, the concentration in the air has not increased, because much taller chimneys are being used and because (for other reasons) the SO_2 is mixed more completely in the air.

About half the SO_2 released in Britain is absorbed at ground level, or in rain, and ⅓ of the rest is absorbed by the sea. Perhaps ⅓ reaches neighbouring countries and has effects negligible in comparison with the SO_2 produced there. Leather, books, and paintings are harmed by SO_2, but the man-made SO_2 is less than that produced by nature. It seems that the H_2S released from the North Sea produces more SO_2 than blows across it from Britain. (RGN: it also seems that there is more SO_2 produced by natural sources than is needed to produce all the sulphate found on medieval windows.)

117. SCOTT, A. S. (1932) "Apparent decay of ancient glass at Wells Cathedral" BSMGP Journ. 1932 IV (4) 171.

The author analysed a scraping taken from the inside of the fourteenth century glass at Wells Cathedral and found it to consist of calcium sulphate. He was at a loss to explain its presence and, eventually, attributed the calcium content to dust rising from the limestone floor and the sulphur content to sulphur dioxide from the gas flames used for lighting the Cathedral. (RGN: it seems more likely that the deposit was gypsum derived from weathering of the glass.)

118. SHELL (1973) "Natural and man-made (air pollution)" "Quality" Jan 1973, No. 16, pages 1-2. (Bulletin of the Shell Committee for Environmental Conservation).

This is a brief summary of some of the conclusions from the Stockholm Conference. Sulphur dioxide emissions are estimated as 100 to 250 x 10^6 tons per year from biological decay and 33 to 45 x 10^6 tons per year from man-made sources. The release of carbon monoxide from natural sources (3.5 x 10^9 tons per year) is estimated to be 10 times the emission from man's activities. Similarly, the natural emissions of oxides of nitrogen and reactive hydrocarbons is many times greater than from human sources.

119. STANFORD RESEARCH INSTITUTE (1968) "Sources, abundance, and fate of gaseous atmospheric pollutants" Stanford Research Institute Report, PR-6755, February 1968.

This comprehensive report discusses all the gaseous pollutants. Table III on p. 18 shows that the annual emission of sulphur into the atmosphere is about 220 million tons but about two-thirds comes from natural sources and only one-third from man-made sources. As regards carbon dioxide, it is increasing, but only slowly. Between 1860 and 1940 the CO_2 concentration increased by 7.9%, and in 1962 by 15.2% (compared with 1860). It seems that the increase is continuing at about 1.4% per year; in 1962 the average CO_2 content of the air was 315 parts per million.

See also "Man's influence on the environment" UK Scientific Mission Report No. 73/6, March 1973; CO_2 has increased from 295 ppm in the middle of the 19th century, to 323 ppm. It may become 380 ppm by 2000 AD.

120. STONE, M. H. (1971) "A new test for the glass-to-resin bond life in GRP; comparison of typical systems exposed to water" Japan Plastics April 1971 15-21.

This paper is primarily concerned with the behaviour of glass reinforced plastics but the author has used an electrical conductivity method for learning about the attack by water at the bond between a coating and the glass. He concludes that the weakening of the bond "results from the combined effect of hydrolytic degradation in the glass and in the resin" - thus water gets between the glass and the resin (despite all their efforts to improve glass reinforced plastics) and this is the thing we want to avoid when coating ancient stained glass.

He also states that the use of a siloxane primer (actually A 1100 from Union Carbide - gamma-aminopropyl triethoxy silane) increases the life of the bond by a factor of four, and he concludes that the bond remains good for 0.9 days at 100°C and 190 days at 60°C (RGN: IF the same relationship holds down to room temperature, the bond life might be 100 years at 20°C!).

121. VICTORIA AND ALBERT MUSEUM (1973) "Some materials and commercial products used in the conservation of art objects"

This 20-page duplicated document can be obtained free-of-charge from the Conservation Department of the Museum. It is a most useful compendium of about 150 materials used in the conservation of art objects, including many of value for conserving and restoring painted glass.

122. WARREN SPRING LABORATORY (1971) "The investigation of air pollution. National survey of smoke and sulphur dioxide, April 1970 - March 1971" Warren Spring Laboratory, Stevenage, Hertfordshire SG1 2BX. 213 pages of typescript.

This document records the measurements of smoke and sulphur dioxide each month at about 1250 sites in the UK. For each site the monthly average figure is quoted, together with the number of days on which the SO_2 concentration exceeded 500, 1000, 1500, 2000 and 3000 $\mu g/m^3$. It is clear that the SO_2 can vary greatly from day to day because most average figures lie between 80 and 300 (μg SO_2/m^3 of air) yet some towns (such as Bootle, near Liverpool) had 10 days where it exceeded 500, with 1 day exceeding 1000 (all in January 1971) and only 3 other days in the whole year (all in the winter) where it exceeded 500.

The highest daily values were found in industrial areas:- Cardiff (1569), Middleton (1412), Prestwich (1381), Wandsworth (1381), Salford (1320), West Drayton (1301), etc. The lowest average values for the whole year were generally in coastal towns in the north and west, eg, Kirkwall (8), Pembroke (11), Ambleston - near Haverfordwest (13), Weymouth (16), Camborne (19), etc, but not necessarily so because low values were found from Ironbridge (26) and Kettering (34), about 50 km and 80 km from Birmingham.

This document, and the supplementary "Directory of sites" should be consulted by anyone who is concerned about the amount of SO_2 released in the vicinity of any stained glass in which he is interested (see also item 123).

123. WARREN SPRING LABORATORY (1972) "National survey of air pollution 1961-1971. Vol. I. Introduction, United Kingdom South East, and Greater London) HMSO London 195 pages.

This is the first (and only one which has yet appeared) of a series of volumes in which the smoke and sulphur dioxide data (see item 122) are summarised and discussed. It points out that pollution by smoke has been decreasing over the last ten years, and that domestic fires still account for a high proportion of the smoke. Sulphur dioxide has been decreasing since 1970 and there is now only a small probability that Londoners will be subjected to concentrations above the accepted limits; there has in fact been no serious pollution episode since 1962.

The annual average SO_2 concentration for urban areas (μg SO_2/m^3 of air) was 177 in 1958-59 and 97 in 1970-71. In the latter year the figures were:- London, 132; N.W. England, 125; Yorkshire and Humberside, 121; S.E., 74; S.W., 63; Wales, 48; it would seem that a figure of 40 $\mu g/m^2$ represents a concentration of SO_2 which will be improved upon only in coastal areas.. The SO_2 concentration in the winter months is always higher than in the summer months, eg, Central London, 327 and 166; low-density open space in London, 157 and 82, etc. The book is a mine of information, and detailed maps are given for all the counties and towns, showing where the measurements were taken, where the sources of pollution exist, and what factors affect dispersal. For example, on pages 36 and 42 there is a discussion of the effect of the Bedfordshire brickworks on the town of Bedford.

124 WEINIG, S (1972) "Applications of sputtering - past, present and future" (Materials Research Corporation, USA - extract from a NATO conference on coatings held in London, 1972)

By means of sputtering, a thin film of almost any material which can be formed into a target (sacrificial element) can be placed on almost any substrate; thus combinations of metals, ceramics and even organic materials can be sputtered on to metal, ceramics, cloth and paper. The film is very thin (0.1 to 5000 nm) and there is a high degree of surface adherence because the sacrificial material is ejected at energies of 2-10 eV. It seems to have been first used in 1928. In the 1960s very thin corrosion-resistant films of Cr, Cr-Pt and Ti-Cr alloys were deposited on the edges of razor blades. Coatings have been applied to optical lenses to provide scratch-resistance; corrosion-resistant coatings have been applied to objects d'art, and coins.

125. WOLLAST, R., Van Damme, CHARLET, and JELLI, A (1971). "The corrosion of glass by aqueous solutions" OECD report on scientific research on glass (REF: DAS/SPR/71.35) dated 1 Dec 1971, 188-231.

The authors discuss the attack of solutions, including hydrofluoric acid, on glass and conclude that the attack takes place inhomogeneously. This is attributed to the inhomogeneous nature of the glass structure (in the modern sense, as contrasted with the earlier ideas that macroscopic inhomogeneities were the cause of uneven corrosion, such as pit formation).

126. YORK GLAZIERS TRUST (1973 a) "Preliminary report on cleaning painted and enamelled glass with the ultrasonic bath" York Glaziers Trust Research Programme Report YG/73/3, dated 10th May 1973, 11 pages of typescript.

This project was carried out to provide objective data on the effects of ultrasonic cleaning on 18 selected pieces of glass, 9 with "loose" paint or enamel and 9 with "firm" paint or enamel. Many photographs were taken (666 in all) of the samples, before cleaning, after cleaning for ½ minute, after cleaning for 3 minutes and for 6 minutes.

It was concluded that half a minute in the ultrasonic bath is inadequate for cleaning because there seems to be an "induction period" of that order of time, especially if the glass is not very dirty. Periods longer than 3 minutes did not seem to increase the effectiveness of cleaning in a useful manner and in a few cases some dirt remains even after 6 minutes. Periods as long as 6 minutes did not seem to cause damage to painted lines, at least if the paint has been well-fired. There was no evidence that the density of well-fired decoration was impaired, but unfired "overpainting" was removed by treatment for 3 minutes in the bath. Three minutes seems to be an optimum period for cleaning dirty painted glass.

127 YORK GLAZIERS TRUST (1973 b) "Use of the 'Isoprobe' for studying the chemical composition of some 12th century glass from York Minster" York Glaziers Trust Research Programme, Report YG/73/4,

In one 12th century panel all the pieces of green glass had deteriorated worse than any of the pieces of pink glass. The panel was known not to have been tampered with and the pieces of glass were thus contemporary. It had therefore been assumed that the basic glass composition had been constant and only the colouring agents had been altered. It was difficult to believe that this could have been the case and the eight pieces of glass (4 pink and 4 green) were analysed using the Isoprobe (see item 92).

It was found that the pink and green glass differed in their basic composition as regards the potassium/calcium ratio in the direction which would support the suggestion that the pink glass would be the more durable of the two. They also differed in colouring agents, the green glass being coloured with copper and the pink glass by manganese.

The four pieces of pink glass had almost identical compositions, suggesting that they had been melted at the same time. Three of the four pieces of green glass had identical compositions, again suggesting that they had been melted at the same time, but the fourth piece had a composition nearer to that of the pink glass and it was also more durable than the other pieces of green glass.

It was also found that the black paint used on the four pieces of pink glass, and on the three pieces of green glass, had the same composition, but the paint on the fourth piece of green glass had a different composition. It was therefore concluded that this fourth piece of green glass was melted and painted at a different time from the other three pieces.

The panel was quite unaffected by all these analyses and it is now on exhibition in the Undercroft.