REF: TC/74/3

6th May 1974

N E W S L E T T E R No. 8

1. GENERAL POINTS

1.1. Visits to conservation workshops in Europe

I shall visit Switzerland, Italy (Florence) and Austria in the period 5th to 15th May. Mr. Ian Addy (from the York Glaziers Trust Workshop) will be with me most of the time, and will then go on to Nuremberg.

1.2. Conservation workshop at Canterbury

Mr. Frederick Cole tells me that he now has four assistants in his workshop, Derek White who has worked for John Piper and Patrick Reyntians; Andrew Small; Carolyne Blake and Anne Marsh, and some restoration work is therefore now in progress.

1.3. My retirement

On 1st July I shall become an Honorary Visiting Professor at the University of York, to assist in planning the work with their new "Isoprobe" (see item 1.2 of News Letter No. 6) and in interpreting the results.

2. ISOTHERMAL GLAZING

There has been an encouraging response to item 3 of News Letter No. 7, and two correspondents have sent me comments which I gladly quote below.

2.1. The problem of heating the air-space in an isothermal glazing system. (Probleme der Beheizung des Luftzwischenraumes von Aussenschutzverglasungen)

Dr. J. C. Ferrazzini of Zurich (see item 1.3 of News Letter No. 7) has kindly sent me three pages of comments which, when translated and edited, are set out below.

2.1.1. Why the air-space has to be heated

The behaviour of the air and its moisture content in the space between the protective glazing and the painted glass depends on the temperatures outside and inside the church. The condensation of water on the panes (and possibly also the formation of ice) is related both to the temperature gradients produced in the air-space and by the relative humidity of the air in the church.

There are three quite distinct cases:

Case No.	1	2	3
Season	Winter	Winter	Summer
Temperature in the church T_1	heated +12°C	unheated +4°C	unheated +12°C
Outside temperature T_2	-20°C	-20°C	+30°C
Temperature difference $T = (T_1 - T_2)$	32 deg C	24 deg C	18 deg C
Average temperature in air space	-4°C	-8°C	+21°C

This leads to the build-up of the following situations which, if the ventilation is poor, cause condensation on the panes as follows:- Case No. 1, condensation on the inside of the protective glass (face No. 2, counting from the outside). Case No. 2, condensation on faces Nos. 2 and 4; case No. 3, condensation on the outside of the painted glass (face No. 3). In the winter, ice-formation is likely to occur as well as condensation, especially in central Europe.

2.1.2. Possible methods of preventing condensation

2.1.2.1. Chemical By using chemicals which absorb water, eg, silica gel filters, the excess moisture can be extracted from the air, but this method is not practicable because the absorbent rapidly becomes saturated and would have to be renewed too often.

2.1.2.2. Physical.

2.1.2.2.1. Injection of hot air. This process is impracticable because the hot air must be injected with relatively high pressure (this is governed by the geometry of the airspace and the resulting noise (whistling) would not be tolerated. On the other hand, the injection of a weaker stream of air leads to the formation of turbulence and pressure gradients in the airspace so that the air cannot flush the whole surface of the glass.

2.1.2.2.2. Electrical heating of the air-space over its full height Some glasses have heating filaments sealed into them and are possibly very good for special applications (supplier: Verres Industriels SA, Quart. Verrerie 25, CH-2740 Moutier, Switzerland) but the possibility of using such a glass for the outer protective glazing is really ruled out on the grounds of cost (800 Swiss francs per m^2).

Another possibility would be to span horizontal heating filaments at certain intervals (approx. 25 cm apart) in the air-space. This method is based on the principle of utilising the upward movement of the heated air to maintain the circulation. It is noiseless and Dr. Ferrazzini is investigating it more closely.

2.1.3. Request to our readers

If any of our readers know of other methods, Dr. Ferrazzini and I should be most grateful if they would let us know of them.

2.2. Grasliof and Prandtl numbers in the air-space

Mr. Ted Bowman, of the National Institute of Agricultural Engineering, at Silsoe, Bedfordshire, has sent the following comment about the minimum spacing between the two sets of glazings to ensure adequate air circulation in the air-space between the old glass and the protective glazing. The assumption, that non-turbulent natural convection will occur, is satisfied theoretically when the product of the Grasliof and Prandtl numbers lies between 10^3 and 10^7. For air at a mean temperature of 20°C and a surface to surface gradient (ie between faces Nos. 2 and 3, counting from the outside) of [redacted] 10 deg C, the Gr.Pr. product varies, according to the width of the air space, as follows:-

Air space (mm)	Gr.Pr.
10	2×10^3
20	1.6×10^4
40	1.3×10^5
80	1.0×10^6
160	8.3×10^6
320	6.6×10^7
640	5.3×10^8

He suggests, therefore, that natural convection should start even with a gap as narrow as 10 mm, and if this proves to be correct many of the aesthetic problems might be overcome. He also suggests that there would be no gain in having a gap greater than 160 mm since the flow would then be fully turbulent.

Mr. R. E. Lacy (cf item 3.2.2. of NL No. 7) commented on these calculations and suggested that the Grasliof and Prandtl relations apply strictly to conditions in which there is a temperature difference across the line of fluid flow, whereas the isothermal glazing situation is concerned with flow of fluid induced by differences in stack pressure at the ends of an elongated space. The experiments to be carried out in Sheffield will help in resolving these questions.

3. BIBLIOGRAPHY SUPPLEMENT

Twenty-three more abstracts (Nos. 146 to 168) are given below to supplement Nos. 128 to 145) given in NL No. 5. The first 129 abstracts will shortly be published for the British Academy by the Oxford University Press, together with three research papers, at a cost of £4.00. The abstracts will be in alphabetical order of authors' names (hence the numbering will be quite different) and translations of the introduction are available in French and in German. Much shortened versions of the first 130 abstracts have been published as a supplement to Volume 10, No. 2 (Winter 1973) of AATA but the abstracts are arranged in date order and the numbering is again quite different.

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146. ANON (1973) "SO_2 monitoring system in the Milan area" Quality, Nov. 1973, No. 19, pp 5-7 (Bulletin of the Shell Committee for Environmental Conservation).

In August 1971, Shell Italiana and the Milan Polytechnic started an investigation of air pollution in the Milan area and the article gives a brief description of the results from the first two years' work. The survey was principally concerned with sulphur dioxide and it was continuously monitored at six points and the average concentration was recorded every 30 minutes.

The mean concentrations of sulphur dioxide measured during the winter in the area of the Shell refinery were lower than those measured in the centre of Milan. In the summer, when there is little or no domestic heating in Milan the SO_2 is below the Italian legal limits (0.30 ppm/30 minutes or 0.15 ppm/24 hours).

147. BOLIN, B. and GRANAT, L. (1973) "Local fallout and long distance transport of sulphur" Ambio 1973 11 (Swedish Royal Academy of Sciences).

The overall residence time of sulphur gases in the air is such that 50 percent, or more, is deposited within 100 km from the source.

148. BLOKKER, P. C. (1969) "The atmospheric chemistry and long-range drift of sulphur dioxide". Institute of Petroleum, 21 October 1969.

The paper discusses the sources of sulphur gases in the atmosphere and shows that on a global basis 50% comes from natural sources but in small industrial areas (such as the Netherlands) 14% can come from 0.7% of the land area, corresponding to a 95% emission from "unnatural sources".

Sulphur dioxide is destroyed more rapidly in polluted atmospheres than in pure atmospheres and many details are given in the paper. It is concluded that during the last decade the atmospheric pollution over Central Europe and Scandinavia has substantially increased but it is still an open question as to whether this is partly due to a drift of sulphur dioxide and sulphuric acid aerosol from Central Europe.

149. BREWSTER, Sir David (1863) "On the structure and optical phenomena of ancient decomposed glass" Phil. Trans. Roy. Soc. Edin., 1863 23 193-204.

This paper, which is more than 100 years old, is of interest because he describes the actual observation of weathering, and its cessation in a dry atmosphere, over a period of 50 years. On p. 194 he describes a fine plate glass prism "made for Mr. Talbot by Fraunhofer at Munich" which had three iridescent spots which "must all have been formed during a period certainly not greater, but probably very much less, than 20 years". He made accurate drawings of these spots in March 1833, including the interference colours, and re-examined the prism "after an interval of thirty years, I cannot observe any change in the rings and colours..... and, what is very remarkable, two long irregular streaks of decomposition, one an inch long, and the other nearly two inches, have entirely disappeared."

He concludes that deterioration which had occurred in the first 20 years was halted or reversed in the next 30 years when the prism was kept in dry air. He also quotes another instance (Phil. Trans.,1816, p.73) where a fissure disappeared in the course of a day. (This could have been the healing of a fracture, rather than the healing of corrosion - RGN.)

150. FERRAZINI, J. C. (1974) "Die Überwachtung der Korrosion mittelalterlicher Glasgemälde - Ein Vorschlag" (The observation of the corrosion of medieval painted glass - a suggestion.) Typescript 9 pp Jan 1974.

He puts forward a suggestion for following the corrosion which occurs on freshly-restored painted glass, using the electron microscope as a sensitive method for recognising the corrosion phenomena even in the initial stages. Surface replicas are taken from known places on the surface of the newly-restored glass and observed with the scanning electron microscope. The paper gives full technical details of the ways in which the replicas are taken and studied. He points out that it is advisable to produce ten successive replicas, and throw the first nine away, before the surface of the glass can be regarded as being satisfactorily freed from adventitious dust, etc.

The same spot should be re-examined after intervals not exceeding five years but he admits that there are still difficulties in finding exactly the same spot on the next occasion. He does not give any results from the use of this suggestion on an actual window.

151. FREY, P. (1973) "Luftverunreinigung oder Verwitterung?" (Air pollution or normal decay?) Umwelt (Dusseldorf) 1973 3 22-23.

The article discusses the decay of stonework at Cologne Cathedral. Limestone which is continually exposed to rain containing sulphur dioxide shows little deterioration and the decay is concentrated at places where the stone is protected from direct rain. It seems that the rain can wash contaminants away before they become effective.

152. LAFOND, Jean (1969) "Was crown glass discovered in Normandy in 1330?" J. Glass Studies, 1969, 11 37-38.

It has generally been thought that crown glass was invented by Philippe de Caqueray in 1330, but excavations at Gerasa and Samaria have brought to light crown glass discs dating from the 4th century. The ruins of the castle of Quasr el-Heir el-Gharbi, abandoned in 750, contain coloured crown fragments. Pontil marks are clearly visible on a 13th century window from Rouen Cathedral. Theophilus describes only the cylinder method.

153. MORA, Paolo and Laura (1972) "Une méthode d'elimination des incrustations sur les pierres calcaires et les peintures murales" (A method for removing incrustations from limestones and wall paintings). Communication to the ICOM Committee for Conservation, Madrid 2-7 Oct. 1972, 5 pages of typescript.

The procedure recommended for cleaning limestone has been found useful for removing hard weathering crusts from medieval glass and the details are given in item 2.4(b) of News Letter No. 7. The method is regarded as satisfactory because it dissolves the crust, probably by the combined action of HCO_3^- and the EDTA, with Ca^{++}. Perhaps, also, the $CaSO_4$ is transformed into the more-soluble $(NH_4)_2SO_4$. Moreover, the action can be controlled by altering the concentration of the solution and the progress of cleaning can be observed because the paste is transparent.

154. NEWTON, R. G. (1974, a) "Conserving medieval stained glass" Spectrum, March 1974 No. 115 6-8.

This is a general article which points out that medieval window glass has a different composition from modern glass and is therefore much less durable. The compositions of different pieces in the same window can be distinctly different and hence the durabilities will also be different. Equipment has been installed at the University of York which will enable the glass to be analysed without damaging it and the next two years' work will provide much understanding of the weathering problems at York Minster.

The author was at pains to explain that he believes that air pollution is not the major cause of deterioration but the editor of the journal included two photographs concerned with air pollution!

155. NEWTON, R. G. (1974, b) "Cathedral chemistry - conserving the stained glass" Chemistry in Britain, 1974 10 (3) 89-91.

This is a general article which discusses the development of window glass since Roman times and describes the process of weathering in chemical terms. The possibility of using an organic coating to protect the glass is discussed and is dismissed in favour of the use of "isothermal" glazing. The problem of accelerated weathering in recent years is also discussed and is attributed to adverse war-time storage of the windows, rather than to any increase in air pollution.

156. NEWTON, R. G. (1974, c) "A problem arising from the weathering of poorly-durable glasses" 10th International Congress on Glass, Kyoto, July 1974.

Glasses which have poor durability present problems in their conservation and safe storage. Some Venetion glass has a relatively low "RO" content and the surface may then "weep", especially if potash is present as the alkali, and the glass must then be kept in a cabinet having a relative humidity below 42%. Other ancient glasses have remarkably good durability but poorly-durable medieval window glasses are unlikely to be completely protected by means of a coating, either organic or inorganic. Experiments are however in hand, both in Austria and in England to assess coatings and to predict weathering behaviour.

157. NEWTON, R. G. (1974, d) "The spontaneous surface fracturing of some medieval window glass" 10th International Congress on Glass, Kyoto, July 1974.

Some types of medieval window glass show spontaneous cracking on one surface only. The cracks may penetrate to a depth of about 500 μm in a glass typically 2 to 5 mm thick and they may link up to permit a fragment of glass to be ejected from the surface. The cavity which then remains will usually display conchoidal fracture marks, and there may even be microscopic fragments of glass attached to the bottom of the cavity, but little or no strain can be demonstrated anywhere in the glass and the other surface may remain quite undamaged.

A theory can be put forward to explain this fracturing (found in a church at Thornhill, Yorkshire; in the Library of Trinity College, Oxford; and St. Michael's, Coventry) on the basis of ion exchange (hydrogen entering the glass and potassium coming out) which would put the surface in tension, but experimental studies using X-ray fluorescence or electron microprobe analyses have failed to show any difference in alkali ion concentration between the two surfaces. At present, therefore, the theory is unconfirmed and the phenomenon must still be regarded as a mystery.

158. PATERSON, M. P. (1974) "Quality control in the measurement of air pollution and air chemistry". Quality, March 1974, No. 20 pp 2-5 (Bulletin of the Shell Committee for Environmental Conservation).

He discusses the considerable problems of measuring the minute proportions of pollutants in the atmosphere, with special reference to modern methods of monitoring the sulphur dioxide in the atmosphere, some of which will give a reading in a few minutes.

159. RIEDERER, J. (1973) "Die schädigende Einwirkung Tuftverunreinigender Stoffe auf Kunstwerke" (The harmful effects of atmospheric pollution on works of art pages A86-A89). Paper presented to a German conference on air pollution by Dr. Josef Riederer, of the Doerner-Institut, 8 Munich 2, Meiserstr. 10.

In 1968 the VDI Commission on Clean Air, set up a working party to investigate the damage caused to works of art and three projects have been undertaken:- on bronze (1969); on stone (1972); and on painted glass (1972). Sulphur dioxide causes damage to bronze sculptures and 80 bronze test-bars have been coated with synthetic resins, waxes, or oils and exposed in the centre of Munich (see Maltechnik 1972 1 40-41).

In the case of building stone, other forces, especially frost, wind, sunshine and driving rain, also cause damage. Salts, rising damp, and micro-organisms also cause damage (for preservation of historic gravestones see Schönere Heimat 1972 61 287-291 and Steinmetz u. Bildhauer 1973 (5)). There are doubts as to whether air pollution causes damage to stonework (Staub-Reinhaltung der Luft 1973 33 (1) 15-19; also La Rochelle Conference Papers 1972).

In the case of painted glass, sulphur dixoide certainly converts the weathering products of glass into a hard crust of various sulphates but little more is said about glass, the remainder of the article being concerned with wall paintings, which are especially difficult to clean.

160. ROSS, F. F. (1973) "Anhydride sulfureux (1970-1972)" (Sulphur dioxide, 1970-1972). Centre Belge Etude Doc. Eaux, 1973 25 456-460.

This is a review of problems caused by sulphur dioxide and it is concluded that emissions from high chimney stacks probably cause no harm at all. Farmlands and forests are said to need 0.5-3 t/km^2 per year of sulphur, of which man-made SO_2 can supply 1-2 t/km^2, corresponding to an atmospheric concentration of 20 μg/m^3 in summer. In Sweden soil acidification by SO_2 may be due to lack of alkaline ashes and dust. In Britain the average emission is 12 t/km^2.

161. SANDERS, D. M., and HENCH, L. L. (1973, a) "Environmental effects on glass corrosion kinetics" Ceramic Bulletin, 1973 52 (a) 662-665, 669.

They studied the effects of environmental conditions, including relative humidity, on the weathering of a very unusual glass (33 mole % Li_2O-SiO_2), and hence the results may not be appropriate to window glass, but they found that attack by 100% relative humidity leads to the same corrosion as attack by liquid water. However, attack by 85% RH produced a different effect.

162. SANDERS, D. M., and HENCH, L. L. (1973, b) "Surface roughness and glass corrosion" Ceramic Bulletin, 1973 52 (9) 666-669.

Again using the unusual glass described in Ref. 161 they found that the initial formation of a silica-rich layer was fastest for the smoothest surfaces but later the roughest surfaces had the thinnest silica-rich layer, apparently because the corrosion solutions remain in the "pockets" where the surface is rough.

163. SCHMIDT-THOMSEN, K. (1973) "Steinzerstörung und -konservierung in Westfalen-Lippe" (Corrosion and conservation of stone in Westphalia-Lippe). Paper to the same conference as Ref. 159, but pages A93-A97. The author's address is: Landesoberverwaltungsrat im Landesamt für Denkmalpflege von Westfalen-Lippe, 44 Münster/W., Erbdrostenhof, Salzstr. 38.

This article is concerned with the great deterioration of the stonework which has occurred during the present century in the great German Cathedrals of Bamberg, Regensburg and Cologne. The deteriorating agents are the same as those set out in Ref. 159. Photographic evidence of deterioration is available for Westphalian buildings because Albert Ludorff systematically photographed them between 1892 and 1915; some sculptures are now unrecognisable compared with his photographs, especially the tympanum from the transept of the 12th century church at Opherdicke (near Unna). Several other examples are given in detail. Ethyl polysilicate dissolved in alcohol has been used as a preservative by the Münster workshop for eight years. It is considered that Methyl triethoxysilane should also be used to produce a hydrophobic effect.

164. TICHANE, R. M. (1966) "Initial stages of the weathering process on a soda-lime glass surface" Glass. Tech. 1966 7 26-29.

He used the internal surfaces of machine-drawn tubing made from Corning glass No. 0080 which is expected to be durable. The electron microscope showed, however, that the surface of the glass had "weathered" even before it was examined. It was therefore cleaned in boiling distilled water for one minute and wiped with lens tissue. A few minutes' heating in air at 400-700°C produces "bumps" visible under the electron microscope which were readily soluble in water and were believed to be sodium carbonate. Moist sulphur dioxide also produced soluble excrescences on the surface.

165. WATTS, D. C. (1973) "Understanding the colour of old glass" 14 pages of typescript, privately printed by Dr. D. C. Watts, of the Biochemistry and Chemistry Department, Guy's Hospital Medical School, London, SE1 9RT.

This article is mainly about the colour of old glass, and about the medieval glass-making practice which led to the introduction of the iron. It is a well-documented history of glass making from early times, and the iron-content of the glass in the period 1680-1830.

166. WOLFF, A, and LUCKAT, S. "Untersuchungen zur Einwirkung von Luftverunreinigungen auf die Baumaterialen des Kölner Dones" (Investigations into the effect of atmospheric pollution on the building materials of Cologne Cathedral). Paper to the same conference as Ref. 159, but pages A90-A92. The first author's address is Dr. Ing. Arnold Wolff, Dombaumeister in Köln, 5 Köln 1, Roncalliplatz 2.

It is stated that Cologne Cathedral is an important example of a building threatened with collapse because of the weathering of the stonework. The building is ideal for research into preservation of stonework because it is in the centre of an industrial city and close to one of the busiest railway stations in Europe with 500 trains per day for several decades.

In 1907 sulphur dioxide was regarded as the main cause of weathering, and this was again thought to be the case in 1927. It was hoped that the electrification of the railway, after the war, would lead to a reduction in chemical attack, but the reverse occurred. Some research was initiated in 1972 and it is suggested that fluorine in the atmosphere may have been responsible for the rapid decay of the medieval painted glass in the cathedral! (Fluor dürfte für den raschen Verfall der mittelalterlichen Glasgemälde des Domes mit verantwortlich sein).

The atmosphere is monitored for hydrogen chloride, sulphur dioxide and hydrogen fluoride and levels of all three are similar to those in industrial towns, with a sharp rise in the winter months; at the end of December they were three times as much as at the end of August. The levels also increase with height; on the central tower (at 65 m height) they are double the values above the aisles (20 m).

167. YORK GLAZIERS TRUST (1974,a) "A simplified method for comparing the compositions of medieval window glass samples from the point of view of their durability" York Glaziers Trust Research Programme, Report YG/74/1, dated 28th January 1974, seven pages of typescript.

A description is given of a method of comparing glass compositions for their relative durability by meams of a triangular diagram.

168. YORK GLAZIERS TRUST (1974, b) "A means for the identification of early medieval glass by the detection of its natural radioactivity. Part I: The preliminary studies, and use of the technique on the inside of windows" York Glaziers Trust Research Programme, Report YG/74/2, dated 28th January 1974, seven pages of typescript.

It is shown that early medieval glass can be distinguished from later glass, used in restoration work, by attaching radiation monitoring films. In York Minster an exposure period of two months gave adequate darkening with the early glass, and none with the replacement glass. In other buildings the background radioactivity from the stonework would have to be assessed.