EUREKA PROJECT E!1319 - EUROCARE MED-GLASS

1. General description

Project	E! 1319 - EUROCARE MED-GLASS	**Status**	Finished - 26-MAR-2001
Title	**Weathering Of Mediaeval Stained Glass**		
Class	Sub-Umbrella	**Technological area**	Environment
Start date	01-JAN-1995	**End date**	01-FEB-2001
Duration	73 months	**Total cost**	0.1 Meuro
Partner sought	No		

Summary

The Aim Of The Project Is The Quantitative Characterisation Of The Influence Of Air Pollutants On The Weathering Mechanism Of Mediaeval Potash-Lime-Silica Glasses Used As Window Panes In Historic Buildings.

Budget and duration

Phase	Budget(Meuro)	Duration (Months)
Full Exploitation	0	56
Implementation phase	0.1	18
Total	**0.1**	**73**

Member contribution

Member	Contribution	Position	Since
Austria	**90.00%**	**Notified Finished**	**26-MAR-2001**
Germany	10.00%	Notified Finished	26-MAR-2001

Participants

Company	Country	Type	Role
Akademie Der Schoenen Kuenste Wien	**Austria**	**University**	**Main**
Tu Wien/Institut Fuer Analytische Chemie	Austria	University	Partner
Technische Universitaet Wien			
Johann-Wolfgang-Goethe Universitaet/Institut Fuer Kernphysik	Germany	University	Partner

2. Project outline

Project description

Mediaeval stained glass used for window panes in glass paintings of Romanesque and Gothic cathedrals, chapels or minsters, is characterised by a high sensitivity towards atmospheric attack. Systematic investigations carried out on artifacts all over Europe have revealed that for the majority of the glass, silica, lime and potash (instead of soda, which was used for ancient as well as common modern glass) are the main ingredients. The high content of modifier ions such as potassium and calcium and the low amount of silica compared to ancient as well as modern glass are the main reasons for the low chemical durability of the mediaeval artifacts.
It was found that, depending on the chemical composition, some mediaeval glass decays predominantly by forming pits on the surface, while other types decay predominantly by crusting, with the entire surface of the panel turning opaque and being covered by a layer of corrosion products called "weathering crust."
In general, mediaeval stained glass exposed to the ambient atmosphere for approximately 600 years shows weathering phenomena indicating chemical reactions during the weathering process similar to the corrosion of silicate glass in acidic solutions. In acids as well as in neutral aqueous media a selective leaching of alkali ions, and to some extent alkaline earths also, predominates, at least in the first stages of the attack. Therefore, an ion exchange mechanism according to the chemical reaction:
Si-O(-)M(+) + H(+)(aqu) <------> Si-OH(aqu) + M(+)
has been assumed, where the network modifiers are replaced by hydrogen or hydrogen bearing species. A surface layer enriched in hydrogen and depleted in network modifiers is built up during leaching in aqueous solutions as well as during the weathering of the glass.
The leaching behaviour of potash-lime-silica glass with mediaeval glass composition has been investigated in several research projects supported by the AUSTRIAN SCIENCE FOUNDATION ("FONDS ZUR FOERDERUNG DER WISSENSCHAFTLICHEN FORSCHUNG IN OESTERREICH"). Glass specimens with a chemical composition similar to original mediaeval glass were treated in acidic solutions and the amount of modifier ions removed from the silicate material was determined. On the other hand, the surface layers formed were characterised by surface analytical techniques such as SEM (Scanning Electron Microscopy), SIMS (Secondary Ion Mass Spectrometry), RBS (Rutherford Backscattering Spectrometry) and NRA (Nuclear Reaction Analysis).
The research projects were carried out in cooperation with the Institute of Chemistry at the ACADEMY OF FINE ARTS, the Institute of Analytical Chemistry at VIENNA UNIVERSITY OF TECHNOLOGY and the Institute of Nuclear Physics at the J.W. GOETHE UNIVERSITY in Frankfurt, GERMANY.
The EUREKA project will study the behaviour of the mediaeval potash-lime-silica-glass in defined atmospheres. The influence of moisture and predominantly the role of pollutants such as NO2 and ozone will be characterised. Systematic investigations have already been carried out under controlled atmospheric conditions with a defined

content of water as well as air pollutants in cooperation with the ISCA (Institute of Silicate Chemistry and Archaeometry at the UNIVERSITY OF APPLIED ARTS IN VIENNA). The corrosion products formed at the glass surfaces are analysed by x-ray diffraction analysis and scanning electron microscopy with energy and wavelength dispersive analysis. The main interest is focused on the surface layers built up during the weathering process. Therefore, the surface analytical techniques SIMS, RBS and NRA are used.
In-situ measurements are also being carried out by AFM (Atomic Force Microscopy). Information on the kinetics of the corrosion reactions taking place on the glass surfaces can be obtained by leaching experiments under liquids as well as by weathering tests of the potash-lime-silica glass with mediaeval glass composition.
Glass specimens are exposed under natural conditions, where the physical and chemical parameters of the ambient atmosphere are registered. The expositions take place within the International Cooperative Programme on Effects on Materials Including Historic and Cultural Monuments. This project is supervised by the ECONOMIC COMMISSION OF EUROPE at the UNITED NATIONS (UN ECE).
The international cooperation of the project has already been built up and the financial support by the AUSTRIAN SCIENCE FOUNDATION is completed (Project No. 9220-TEC).
References:
* M. Schreiner: Deterioration of stained mediaevel glass by atmospheric attack - Glastechn. Ber. 61/7 (1988) 197-204 and 61/8 (1988) 223-230.
* M. Schreiner: SIMS analysis of potash-lime-silica glasses leached in HC1 and H(2)SO(4). J. Am. Ceram. Soc. 72/9 (1989) 1713-15.
* M. Schreiner, M. Grasserbauer, P. March: NRA and SIMS depth profiling of hydrogen in naturally weathered mediaeval glass. Fres. J. Anal. Chem. 331 (1988) 428-432.
* M. Schreiner: Glass of the past - the degradation and deterioration of mediaeval glass artifacts. Microchim. Acta II (1991) 255-264.
* I. Schmitz, T. Prohaska, G. Friedbacher, M. Schreiner, M. Grasserbauer: Investigation of corrosion processes on cleavage edges of potash-lime-silica glass by atomic force microscopy. Fres. J. Anal. Chem. in press.

Technological development envisaged

The chemical reactions occuring during the weathering of glass are described in principle in the literature, where a leaching process similar to the corrosion of silicate glass in aqueous solutions is assumed. However, the mechanisms of reactions are not necessarily analogous to those which take place when complex glass is degraded by the atmosphere which, in addition to water vapour, contains reactive gases such as COy, SOy, NO(x), etc. No information at all is available in the literature concerning the synergistic effects when the various air pollutants are present in different concentrations, at different temperatures and at varying contents of water vapour.
On the other hand, restoration, conservation and preservation of mediaeval glass paintings, which are still

in-situ and exposed to the ambient atmosphere, require information about the weathering mechanism of this type of potash-lime-silica glass for various reasons:
* The knowledge about glass corrosion has been achieved on modern soda-silica glass and cannot be transferred to the potash-lime-silica glass without any additional investigations.
* Usually, the corrosion products (weathering crusts) formed on the glass surface such as syngenite, gypsum, hydrated silica and dust are removed mechanically or by liquids in order to achieve a high transparency and translucency of the objects. It is assumed that some of these cleaning methods also attack the leached layer formed during the centuries, which will change the weathering durability of the mediaeval glass.
* In many cases outdoor glazing has been used to protect the original mediaeval glass from further attack from the ambient atmosphere. This treatment usually slows down the weathering process but in some cases corrosion of the silicate glass can still be observed.
* In addition to outdoor glazing coating of the mediaeval glass objects is proposed and tested at several places. Organic compounds such as acrylates or heteropolysiloxanes are applied in the form of a lacquer in order to reduce the contact of the glass surface with moist air. The knowledge of the synergistic effects of the various constituents in the ambient atmosphere will make it possible to apply the most sufficient protecting material for this type of glass.

Markets application and exploitation

* Only a small part of the project will be exploited.
* The initial exploitation will be done by the project leader, the ACADEMY OF FINE ARTS in Vienna.

Project codes

BSI

AUY	conservation
EIC.OM	weathering (weather action)
GC/GF	pollution
VVL/VVV	glass

NACE

7310	Research and experimental development on natural sciences and engineering

3. Main participant

Company	**Akademie Der Schoenen Kuenste Wien** Schillerplatz, 3 1010 Wien Austria Tel +43 1 588 16 261 Fax +43 1 588 16 137
Contact	**Prof. Manfred Schreiner** Assistant Professor Tel +43 1 58816 261 Fax +43 1 58816 137
Organisation type	University
Participant role	Main

Contribution to project

Project coordination. Sample preparations, X-ray diffraction analysis and the evaluation of all analytical results has to be carried out as well as the correlation of the data with environmental measurements (statistical evaluation).

Expertise

Several research projects concerning the corrosion of mediaeval potash-lime-silica stained glass were carried out with support from the Austrian Science Foundation (FONDS ZUR FOERDERUNG DER VISSENSCHAFTLICHEN FORSCHUNG IN OESTERREICH). During these projects international cooperation links were forged with the Institute of Nuclear Physics in Frankfurt and the Institute of Analytical Chemistry in Vienna.

4. Partner

Company	**Tu Wien/Institut Fuer Analytische Chemie Technische Universitaet Wien** Waehringerstrasse, 38 1090 Wien Austria Tel +43 1 4277 52301 Fax +43 1 4277 9523 www.anc.univie.ac.at
Contact	**Prof. Manfred Grasserbauer** Director Of The Institute Tel Fax

Organisation type University
Participant role Partner

Contribution to project

All surface analytical investigations will be carried out on the naturally and artificially weathered glass samples. The methods are: SIMS, SEM, AFM (Atomic Force Microscopy) etc.

Expertise

One of the leading institutes in Europe on surface analysis. Investigations on semiconductors, highly pure materials and coated tools were carried out in cooperation with research institutes and the Industry. In addition, other hand working groups are involved in international proejcts on optical sensors and environmental research. In the past, several research projects have been carried out with the Institute of Chemistry at the ACADEMY OF FINE ARTS. As a result of this cooperation, several theses for Ph.D. and Graduate theses have been done by chemistry students.

4. Partner

Company **Johann-Wolfgang-Goethe Universitaet/Institut Fuer Kernphysik**
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Organisation type University
Participant role Partner

Contribution to project

Surface analytical investigations by NRA (Nuclear Reaction Analysis) and RBS (Rutherford Backscattering Spectrometry) will be carried out.

Expertise

Located at the J. W. GOETHE UNIVERSITY in Frankfurt, this Institute is known worldwide. Professor Rauch's working group is experienced in NRA and RBS measurements on glass have worked on several research projects with the German glass industry, with companies such as SCHOTT in Mainz, GERMANY. The project leader of this EUROCARE project has been cooperating with Professor Rauch's group for

several years.