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Abstract

The preservation of the world's cultural heritage requires a thorough knowledge of its constitutive material (wood, stone, glass, etc.), the degradation processes, and an understanding of the properties of the materials used in its conservation. In this chapter, we explore inorganic and organic–inorganic sol-gel formulations of interest to conservators, for potential uses on stained glass, stone, or metal substrates exposed to corrosive outdoor environment. Regarding inorganic sol-gel materials, the use of tetraethoxysilane (TEOS) in conservation is not new, and the use of silicon precursors in the treatment of stone can be traced back to 1926. Another application is the removal of toxic organics within the wood using a TiO_2 precursor, based on its photocatalytic properties to decompose the organics.

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Regarding hybrid sol-gel materials, methyltrialkoxysilanes are probably the most studied alkoxy-silanes in conservation. More complex alkoxy-silanes such as (3-alkoxypropyl) triethoxy- and (3-alkoxypropyl) diethoxy-methylsilanes were studied as hydrophilic, elastic stone consolidants. In the treatment of organic surfaces such as wood, some alkoxy-silanes can provide some antimicrobial properties, as for example 3-(trimethoxysilyl) Pr di-Me octadecyl ammonium chloride in combination with TEOS. A case study is also explored: the use of organic-inorganic hybrids applied in the treatment of a medieval glass in an outdoors mosaic in Prague.

Introduction

The preservation of the world's cultural heritage requires the use of the most advanced materials and technologies. More specifically, conservation of an object necessitates a thorough knowledge of not only its constitutive material (wood, stone, glass, etc.), but also of the degradation processes to which it is subjected and, most importantly, an understanding of the properties of the materials used in its conservation. In this respect, an argument can be made that materials science is intrinsic to conservation science. Over the years, advances in materials have allowed conservators to use increasingly sophisticated materials, better suited for each specific application. Advanced polymers have certainly been responsible for much progress in this field. Lately, however, there has been increasing interest in the use of sol-gel precursors for a variety of conservation applications. Reports of the use of metal-organic precursors in various aspects of conservation, from the treatment of wood to the consolidation of stone or the protection of glass or metal surfaces, have appeared. In this review, we summarize the most recent advances, listing some of the advantages that sol-gel materials hold over polymeric materials in the field of conservation. We also point to some of the shortcomings and offer some yet unexplored prospects for the technique.

The corrosion of glass enamels, decay of limestone, or the rotting of wood are very challenging issues for which there is no single unique solution. Each conservation situation requires thorough analysis of the degradation processes, as well as a careful review of what materials are available to solve or alleviate the problem. Therefore, materials science is arguably a core discipline of conservation (Scherrer et al. 2001). First, the physics and chemistry of the degradation process must be understood. Second, the properties of the material used in the conservation must be known; and third, the interactions between substrate and conservation material must be considered. The conservators must, therefore, remain keenly aware of advances in materials science.

For example, there are many factors that one should consider in designing a coating for a protective application. Parameters like elastic modulus, coefficient of thermal expansion, both for the substrate and the coating, must be known before a suitable coating material can be chosen. In the case of sol-gel coatings,

the key role of some of these factors was recently reviewed (Mackenzie and Bescher 2003).

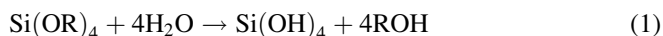
Proper selection of materials is a central issue in the success of a particular conservation effort. Polymers has revolutionized the field of conservation because they may be applied as liquids, and can be polymerized in situ using various techniques such as UV or thermal catalysis; they are generally flexible materials that are easy to use. However, they also have some shortcomings, such as poor UV resistance, limited chemical and thermal stability, high permeability to various gases, etc. Therefore, in some cases, even the best polymers may not be suitable for a specific conservation problem. Inorganic oxides may be desirable but they are difficult to apply at or near room temperature. Sol-gel-derived materials can, and they have been proposed as suitable materials for the artist (Smy 1998). But beyond this, the sol-gel process has also been proposed as offering unique advantages in the conservation of artifacts.

Sol-gel materials have already found many successful applications as functional coatings. A number of patents have been awarded for the use of colloidal particles in siloxanes as abrasion-resistant coatings on soft organic polymer for ophthalmic use (Ashlock et al. 1980). The colloidal silica improves the mechanical properties while allowing good optical transparency. One would expect that the porosity and permeability of a membrane made of this material would be much lower than that of an undoped matrix. Some sol-gel coatings have otherwise already been proven to be effective permeability barriers (Amberg-Schwab et al. 2000) or anticorrosion coatings. The protection of cultural heritage is likely to benefit from such recent advances in this field.

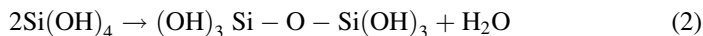
In this chapter, we explore inorganic and organic–inorganic sol-gel formulations of interest to conservators, for potential uses on stained glass, stone, or metal substrates exposed to corrosive outdoor environment.

The Sol-Gel Process

The sol-gel process involves the reaction of liquid precursors at room temperature for the fabrication of glasses and ceramics (Brinker and Sherrer 1990). It has been used for the fabrication of many amorphous and crystalline oxides such as SiO₂, Al₂O₃, and many rare-earth doped oxides. Usually, the process involves hydrolysis and condensation of organometallic precursors. In the case of silica, a silicon alkoxide such as tetraethoxysilane (TEOS) is mixed with an alcohol, such as ethanol, in the presence of water. A reaction of hydrolysis follows, during which alcohol is released:



This step is followed in solution by condensation of the silanols to form Si–O–Si links:



As reaction (2) proceeds, the viscosity of the solution increases until a solid network is formed, at which point the solution has “gelled”. Equations 1 and 2 are oversimplified compared to the actual processes, but they provide a basis of the essential advantage of the sol-gel process, which is that an inorganic oxide framework is derived from a solution. Upon careful drying, organics are removed, and an amorphous oxide is usually formed, which can be converted to the corresponding crystalline phase upon further heating. The advantages of the sol-gel process over conventional ceramic processes have been described as being related to:

- the improved purity of the precursors
- the lower processing temperatures
- the ease of fabrication of coatings, films,
- the possibility of intimate mixing of components (“homogeneity at the molecular level”)

An advantage of the sol-gel process in the case of coatings on inorganic oxide substrates is that the large amounts of hydroxy groups present in the solution facilitate easy bonding between coating and substrate. Obviously, this is an advantage when the substrate is a stone that exhibits large surface hydroxyls concentration.

Inorganic oxides tend to have several advantages over polymeric materials. Many polymers tend to be chemically unstable. Some have a tendency to become brittle and yellow with age. Their thermal stability is limited. Due to their open structure, they often exhibit permeability for water vapor or other gases. Inorganic oxides, on the other hand, are thermally and chemically resistant, often have low permeability. From this standpoint, they would be highly desirable materials for the conservator. However, they typically have to be processed at high temperatures. With the sol-gel process, they can be processed at ambient conditions, like polymers. They become attractive for the conservator. Recently, the field has been widened to include organic–inorganic hybrids (Mackenzie and Bescher 1998), in which the inorganic structure of the material is modified through the inclusion of organic moieties.

Sol-gel materials, from the purely inorganic system to the organic–inorganic containing various types of organics, present an opportunity for the field of conservation that we shall review next.

Inorganic Sol-Gel Materials

The use of tetraethoxysilane (TEOS) in conservation is not new. In fact, the use of silicon precursors in the treatment of stone can be traced back to a 1926 patent describing the use of a silicic ester in the preservation of stone (Laurie 1926). TEOS has since been applied in the treatment of a variety of organic objects, such as wood, basketry, and paper (Paleos et al. 1981; Grattan 1982). Its suitability in the treatment of

inorganic objects, such as stone, stems from the similarity between the structure of the dried gel and the structure of the stone (Wheeler et al. 1992a; Sattler and Schuh 1995).

In such treatment, the type of stone appears to have an important role to play. Clay from ruins excavated in El Salvador was successfully consolidated with TEOS solutions (Ohta et al. 1998). Increased hardness after 60 days exposure in the tropical atmosphere was observed. Cervantes et al. (1998) used TEOS to consolidate porous stones of historical buildings in Central Mexico, in order to prevent stone degradation by smog, acid rain, and moisture. Some of the problems of the use of TEOS and its derivatives, such as ethyl silicate, have been discussed (Kotlik 1987). One of the main issues is that the thickness of a coating from a TEOS application is limited. A related drawback of the impregnation of stone by TEOS consolidants is that they tend to form brittle and highly cracked gels inside the stone, because of the high shrinkage that occurs during drying (Lewin and Wheeler 1985). Esquivias et al. made the distinction between gels that dry within the stone, where capillary pressure controls the drying process and where such pressure (around 40 MPa for pores of 1 nm) will cause cracking of the network, and gels drying on the surface of the stone.

As with all sol-gel systems, a coating exceeding a few hundred nanometers in thickness will tend to crack upon drying. Therefore, the effect of a TEOS treatment is bound to be limited as far as mechanical properties are concerned. Some improvements in the mechanical properties of a highly friable material are possible, however. Another shortcoming of pure TEOS is that its low molecular weight and high vapor pressure means that it might evaporate before hydrolysis. When partially hydrolyzed, its molecular weight increases and it may be used in the consolidation of stone (Mosquera et al. 2003; Wheeler et al. 1992b; Scherer and Wheeler 1997).

The use of colloidal silica has been investigated as well. Kozłowski et al. (1992) have used colloidal silica to form a protective coating on calcareous stones. Silica particles were deposited within the pores of the stone. The passage of water through the pores was impeded by the presence of the particles. The results of field trials have not yet been reported.

For the protection of metal surfaces against corrosion, many sol-gel derived inorganic coating materials have been tested. For examples, SiO₂ coatings (de Sanctis et al. 1990; Izumi et al. 1993; Simões et al. 2000) or alumino and borosilicates (Maliavski et al. 1995) on stainless steels have been proposed. The main shortcoming of such coatings is that, as we discussed above, they undergo severe cracking when their thickness exceeds several hundred nm. Here again, using a nanoparticulate approach as opposed to a molecular approach allows the formation of thicker films (up to 2 μm) that do not crack as easily and provide more effective protection against gaseous attack (Mennig et al. 1998). A review of the potential uses of inorganic sol-gel coatings was published by Colby et al. (1988).

Wood may also be treated with TEOS and its derivatives. TEOS was shown to improve some wood properties such as dimensional stability, fire resistance, and durability, without any increase in weight (Okawa et al. 2002). Removal of various toxic organics within the wood using a TiO₂ precursor was also investigated (Leclaire 1991). The goal was to use the photocatalytic properties of TiO₂ to decompose the organics. Various other metal alkoxides have been used in the

treatment of wood in order to improve various properties including water repellency, antibacterial properties or resistance against termite attacks (Saka 2001). The fire resistance of wood was also enhanced by impregnation of sodium methoxide to a TEOS solution. A glassy $\text{Na}_2\text{O}-\text{SiO}_2$ layer forming over wood was deemed superior to a SiO_2 layer (Miyafuji and Saka 2001).

Textiles containing wooden fibrous materials have also been coated with TEOS solutions, in a two-step process, to enhance the stability of the fibers (Koga 2001).

The Barium Hydroxide Process

The use of barium hydroxide solutions in various aspects of conservation has attracted much attention. Although not strictly speaking a sol-gel process, because the system appears to involve crystallization rather than gelation, the technique is closely related and deserves to be briefly mentioned. Lewin (1968) and Sayre (1970) have developed methods intended to precipitate barium carbonate and barium sulfate deeply within a stone. Barium carbonate is precipitated from a solution of barium hydroxide and urea (Lewin and Baer 1979). The urea slowly hydrolyzes producing ammonia and carbon dioxide. The liberated ammonia and carbon dioxide dissolve in the water, forming ammonium carbonate. When a certain pH is reached, barium hydroxide reacts with the carbonate ion and barium carbonate is precipitated. The reaction rate can be controlled, so the barium carbonate precipitate forms days after a stone is treated. The formation of barium carbonate gives a crystalline solid solution with the calcite crystals of calcareous stone. Barium sulfate can be precipitated in a stone by a similar method. The process has been applied successfully to the conservation of wall paintings (Botticelli et al. 1984; Matteini 1991). The usefulness of the method in stone consolidation is not always demonstrated (Toniolo et al. 2001) and the method is nonreversible, but it is elegant and useful nonetheless.

These are but a few examples of the application of inorganic precursors on various substrates of interest to the conservator. In spite of some of the limitations of the technique, mainly related to the maximum thickness allowable in a brittle inorganic system, it is clear that opportunities abound. It is useful to remember that as is the case with all sol-gel systems, the role of catalysts and other solution parameters is very significant (Brus and Kotlik 1996), so there is much room for improvement and further research. An area of research that has attracted attention lately is the organic modification of inorganic precursors to fabricate organic-inorganic hybrids that exhibit properties that are intermediary between that of ceramics and polymers.

Organic Inorganic Hybrids

Alkoxysilanes have been used extensively as coupling agents to improve the adhesion between an inorganic surface and an organic coating, or between glass and an adhesive. The alkoxy groups in the silane react with the surface of the glass or ceramic, leaving the organic ligand available for cross-linking with the polymer applied subsequently.

Trialkoxysilanes in alcoholic solutions (typically 5% solution) are typically used for this purpose.

When alkoxy silanes are extensively polymerized or condensed, they form silicones, which are dissolved in organic solvents, and may be used as water repellents (Bosch 1972). Commercial silicones have been used extensively in materials conservation (Roth 1988; Molteni 1987), either pure or combined with other organic polymers such as polyurethanes (Puterman et al. 1996) or isocyanate prepolymers (Jansen et al. 1993). Some of their shortcomings involve high oxygen diffusion rates and high water uptake.

Molecular alkoxy silanes have also been used extensively in conservation and stone consolidation (Wheeler et al. 1992c; Amoroso and Fassina 1983). They have been shown to suitably impregnate stone to significant depths (Price 1975). Marschner reported (Marschner 1978) that alkoxy silanes improved the resistance of sandstone to sodium sulfate crystallization. Some alkoxy silanes have been used in a treatment strategy combining the use of calcite coupling molecules to passivate the surfaces against new weathering (Brinker et al. 1998).

Methyltrialkoxysilanes are probably the most studied alkoxy silanes in conservation. They have been used to render stone water-repellent or to consolidate stone such as marble (Moncrieff 1976). However, such monomeric solutions may evaporate before hydrolysis and condensation takes place, thereby preventing effective penetration of the material within the stone. Several approaches have been used to prevent this phenomenon, such as using low vapor pressure solvents (Moncrieff and Hempel 1977), using a protective lining preventing evaporation (Hempel 1976) or modifying the surface of the stone prior to treatment. There was some debate as to whether a MTMOS treatment was as suitable for calcareous stone as it is for quartz-based stones (Danehey et al. 1992). However, Butlin et al. (1995), reporting on the performance of silanes in field trials over a period of some 15 years, states that consolidation of limestones appeared at least as effective as consolidation of sandstones. Beyond hydrophobicity, MTMOS may also affect other properties of the stone. For example, the role of MTMOS as an antimicrobial or fungicide has also been investigated (Koestler et al. 1987). A mixed cultures of a fungus, a cyanobacterium, and an alga was performed on a sample of MTMOS. After 5 months, no evidence of microbiological attack was observed. It was concluded that the use of the material in the consolidation of a dolostone monument in the Metropolitan Museum of Art's collection would not encourage the growth and spread of the microorganisms present in the stone.

The effect of other organosilanes on deteriorated limestone was investigated. Particular attention was paid to the depth of penetration, effects on color, and the degree of consolidation. A solution of acrylic silane in methyltrimethoxysilane was found to be the most suitable consolidants for use on limestone (Bradley 1985). It was also shown that organosilanes do not encapsulate salt in stone and that soluble salts could be removed by a poulticing technique following consolidation.

More complex alkoxy silanes such as (3-alkoxypropyl) triethoxy- and (3-alkoxypropyl) diethoxy-methylsilanes were studied as hydrophilic, elastic stone consolidants. The addition of (3-alkoxypropyl) diethoxymethylsilanes to stone

consolidants reduced the cracking of the resulting SiO₂-gel. Application of (3-alkoxypropyl) triethoxysilanes without any additives even offers the opportunity to produce hydrophilic, elastic consolidants for natural stones (Fabis et al. 1996).

In the treatment of organic surfaces such as wood, some alkoxysilanes have been shown to provide some antimicrobial properties. 3-(trimethoxysilyl) Pr di-Me octadecyl ammonium chloride was used in combination with TEOS to render wood antimicrobial. The wood composites revealed some antimicrobial activities, but with the use of 2-heptadecafluorooctylethyltrimethoxysilane in a small quantity, the wood was also rendered water-repellent, which further improved its resistance against both brown and white rot fungi (Tanno et al. 1997). Hexadecyltrimethoxysilane (HDTMOS) and methyltrimethoxysilane were used in the treatment of wood (Tshabalala et al. 2003). Previous testing had shown that the reaction between moisture-conditioned wood and low molecular weight alkoxysilanes led to the deposition of SiO₂ gels within the wood cell walls (Saka 2001). The wood treated with the HDTMOS and MTMOS contained a polysiloxane network that bonded to the wood via condensation with surface hydroxyls. As a result, the wood was shown to exhibit lower liquid and vapor water intake.

Organically modified transition metal alkoxides can be used in the consolidation of stones as well. Most transition metal alkoxides are highly reactive to moisture and oxygen. However, some metal alkoxides such as Zr alkoxides have been used because they can make transparent coatings and preserve the porosity (Bradley et al. 1999). The stability of TMO alkoxides can be improved by the use of chelating agents such as acetylacetone to prevent precipitation. Wheeler et al. (2003) have used Zr-*n*-propoxide stabilized with acacH and ethylacetoacetate (eaaH) as vehicles to impregnate coupling agents to calcite powder. The sols can be used to reduce the porosity of limestone. Such alkoxysilane coupling agents can increase the modulus of rupture of limestone (Wheeler et al. 2000). The role of the Zr alkoxides was to bond the functional groups of the coupling agents (phosphate, amino, and acryloxy) to the calcite surface. FTIR studies showed that such bonding took place.

Another variation is the use of MTMOS combined with an organic polymer such as B72 acrylic resin (Wheeler et al. 1991, 1992). B72 is a copolymer of methyl and ethyl acrylates widely used in conservation. The prospects for such systems for the consolidation of stones is unclear, as the conclusion of the study was that the composites formed by this technique were less suitable for preservation of stone than either of their components. TMOS appeared to be better suited as a stone consolidant for sandstone than for limestone. Nevertheless, it illustrates the diversity and the flexibility of the technique.

Ormocers (Organically Modified Ceramics) were used by Stoch et al. (1994) in the waterproofing and consolidation of the surface of limestone and sandstone. Wetting angle, porosity, and water absorption were measured prior to and after treatment.

Such Ormocers may be used on glass surfaces. The deterioration of colored historical gold enamels at the Gurenes Gewoelbe museum in Dresden, Germany, was caused by corrosion of the enamel layers affected by indoor air pollutants. Mechanical damage occurred due to the different thermal expansion of glass and

metal or previous restoration measures. Sol-gel organic–inorganic hybrids cured at ambient conditions showed good adhesion to the enamel surface and protected the samples during artificial aging (temperature and humidity cycle, high pollutant levels). The viscosity of the conservation materials was adapted to provide effect penetration into micro- and macrocracks of the enamel layer (Pilz and Troll 1998).

A similar treatment was proposed by Römich et al. in the protection of bronze surfaces. Several alkoxy network formers such as glycidoxypopyltrimethoxysilane (GLYMO) or g-methacryloxypropyltrimethoxysilane (MEMO) were used (Pilz and Roemich 1997). The authors pointed out the obvious compromise that must be found between total reversibility of the coating (the ability to dissolve the coating with a liquid solvent) and the stability of the cured coating. This kind of organic–inorganic approach has the obvious advantage of a range of reversibility characteristics depending on the amount and the nature of organic groups in the system and on the amount of cross-linking undergone by the system. Out of 13 different compositions tested, the most promising one on bronze substrates was a diphenyl derivative.

A similar system was used by Bescher for the treatment of glass tesserae on an outdoors mosaic, as will be discussed in “[Case Study: Conservation of the Last Judgment Mosaic in Prague](#)”.

Case Study: Conservation of The Last Judgment Mosaic in Prague

The use of organic–inorganic hybrids was applied in the treatment of an outdoors mosaic in Prague (Bescher et al. 2000). The conservation of a medieval glass, such as the one found in a mosaic, is a complex problem caused by the unstable nature of the medieval glass. An example is the Last Judgment mosaic in Prague. Because of limitations of the glass melting technologies in the thirteenth century, large amount of alkali were used in the processing of the glass. While the high alkali content allowed processing of the glass at relatively low temperatures, it also caused extensive weathering of the glass surface in the Prague climate. High-alkali glass is well known to be highly prone to a complex corrosion process leading to progressive the dissolution of the glass into more stable, insoluble compounds on its surface. The unstable glass can react with water vapor and rains, as well as with sulfur dioxide in the atmosphere. As a result of these reactions between the glass and its environment, the mosaic deteriorated and the tesserae were covered with a thick (>1 mm) layer of gray corrosion salts. When the corrosion salts were removed mechanically, they revealed a highly irregular glass surface, replete with corrosion pits and cracks. Traces of original and twentieth century gilding were visible, as well as replacement tesserae. Previous conservation treatment involving polymers had consistently failed.

It was obvious that a complete treatment of the mosaic would require removal of corrosion salts, in a process not described here, and the design and application of a coating system that, if it could not stop corrosion completely, would at least make it manageable.

Fig. 1 The final coating system used in the conservation of the Last Judgment mosaic

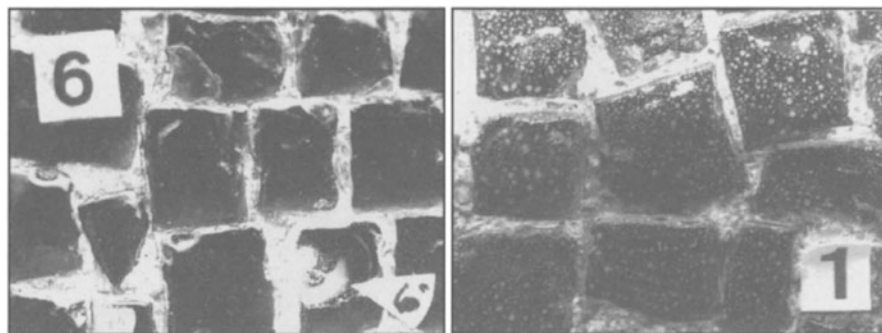
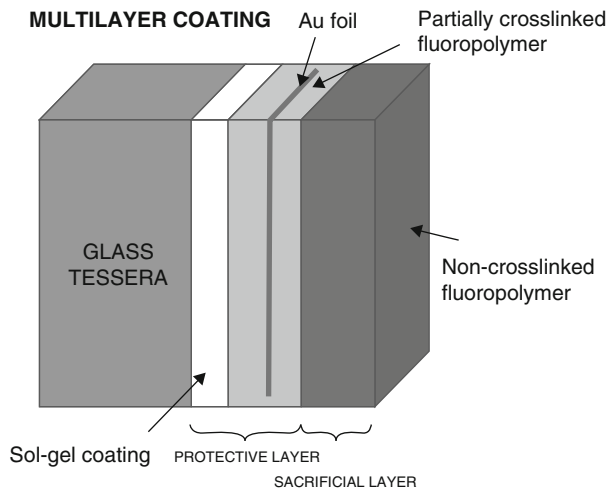


Fig. 2 Onsite testing panel of the Last Judgment mosaic after 2 years of outdoors exposure. *Left (6)* is the sol-gel/functionalized fluoropolymer coating combination. *Right (1)* is an epoxy polymer exhibiting delamination

In order to prevent corrosion of the glass tesserae, it was desirable to design a protective coating that would slow down significantly the diffusion of water and sulfur reactants toward the surface of the glass.

The selection of materials for conservation was made after a series of laboratory and onsite testing that included several polymers and sol-gel compositions, including multilayers. The final coating systems that passed the accelerated weathering test was a multilayer coating including glycidoxo and methyl silanes in combination with a fluoropolymer (Fig. 1). The other systems failed due to cracking or delamination (Figs. 2 and 3). The advantages of this system are that the organic-inorganic hybrid is better suited than the polymer for a direct contact with the glass surface. The polymer coating is easily reversible and can be re-applied every few years, which improves the performance of the underlying hybrid. It was found during the

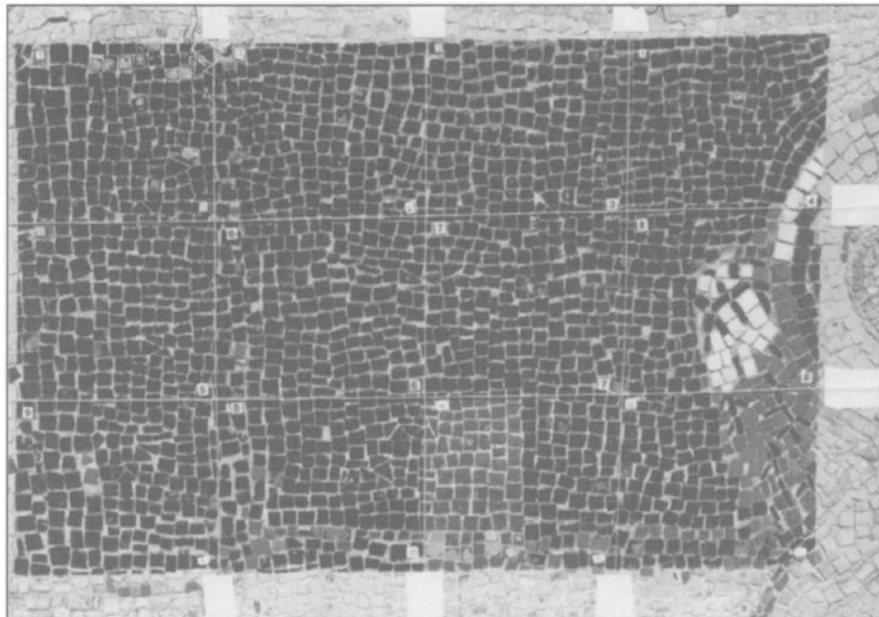


Fig. 3 Onsite testing panel for a variety of sol-gel materials on the Last Judgment mosaic

testing phase that the multilayer combination performed better than either single coating alone. A similar system was also effective in the protection of metallic surfaces (Bescher and Mackenzie 2003).

Conclusion

The opportunities afforded the conservator by the use of metal-organic precursors are unique, diverse, and exciting. Whereas, simpler systems like inorganic silicates have been known for some time, some of their limitations can now be overcome with the use of more advanced materials like organic-inorganic hybrids. However, much additional work must be done in this field in order for conservators to be aware of these possibilities. It is interesting to quote C.A. Price (Price 1996) on the development of the sol-gel process in the field of conservation:

Although the literature contains many papers describing the use of silanes on stone, there are very few that even attempt to come to grips with the underlying chemistry or the associated sol-gel technology. One gets the uncomfortable impression that few conservation scientists have the ability to utilize the extensive chemical literature in this area, and that this is preventing the transfer of valuable knowledge to the conservation field.

There is no doubt that without this transfer of knowledge, the benefits of the sol-gel process cannot be fully realized. However, it is clear that recent work in this field indicates that as more conservators acquaint themselves with the technique, the number of successful applications will grow.

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