Alkoxysilanes Consolidation of Stone and Earthen Building Materials

Isil Öztürk
University of Pennsylvania

Follow this and additional works at: https://repository.upenn.edu/hp_theses

Part of the Historic Preservation and Conservation Commons

https://repository.upenn.edu/hp_theses/264

Copyright note: Penn School of Design permits distribution and display of this student work by University of Pennsylvania Libraries.
Suggested Citation:

This paper is posted at ScholarlyCommons. https://repository.upenn.edu/hp_theses/264
For more information, please contact repository@pobox.upenn.edu.
Alkoxy silanes Consolidation of Stone and Earthen Building Materials

Disciplines
Historic Preservation and Conservation

Comments
Copyright note: Penn School of Design permits distribution and display of this student work by University of Pennsylvania Libraries.

Suggested Citation:

This thesis or dissertation is available at ScholarlyCommons: https://repository.upenn.edu/hp_theses/264
ALKOXY SILANES CONSOLIDATION OF STONE AND EARTHEN BUILDING MATERIALS

Isil Öztürk

A THESIS

in

The Graduate Program in Historic Preservation

Presented to the faculties of the University of Pennsylvania in
Partial Fulfillment of the Requirements for the Degree of

MASTER OF SCIENCE

1992

Jeanne Marie Teutonico, Lecturer, Historic Preservation Advisor

Frank G. Matero, Associate Professor of Architecture in Historic Preservation Reader

David G. De Long, Professor of Architecture
Graduate Group Chairman
# TABLE OF CONTENTS

CHAPTER 1: OVERVIEW OF STONE CONSOLIDATION MATERIALS ........................................... 1

1.1. Introduction ................................................................................................................. 1

1.2. Inorganic Stone Consolidants .................................................................................... 3

   1.2.1. Siliceous Consolidants ......................................................................................... 4

      1.2.1.1. Alkali Silicates .............................................................................................. 4

      1.2.1.2. Fluorosilicon Compounds ............................................................................. 5

   1.2.2. Alkaline Earth Hydroxides ................................................................................. 6

      1.2.2.1. Calcium Hydroxide (Limewater) ................................................................. 6

      1.2.2.2. Barium Hydroxide ....................................................................................... 8

1.3. Alkoxysilanes ............................................................................................................. 10

1.4. Synthetic Organic Polymers ...................................................................................... 12

   1.4.1. Acrylic Polymers ............................................................................................... 13

   1.4.2. Acrylic Copolymers ............................................................................................ 14

   1.4.3. Epoxies .............................................................................................................. 16

1.5. Waxes ......................................................................................................................... 18

CHAPTER 2: ALKOXYSILANES ............................................................................................. 26

2.1. Performance Criteria ................................................................................................... 26

   2.1.1. Performance Criteria for Stone Consolidants ..................................................... 26

   2.1.2. How Alkoxysilanes Meet the Performance Criteria ........................................... 29

2.2. Chemistry of Alkoxysilanes ....................................................................................... 30

   2.2.1. Chemical Structure of Alkoxysilanes .................................................................. 31

   2.2.2. Polymerization of Alkoxysilanes: Hydrolysis and Condensation .................... 33
2.3. Application Methods ........................................ 39
2.4. Protection and Maintenance ................................ 41
2.5. Evaluation Techniques ........................................ 42
   2.5.1. Laboratory Testing Program ............................... 43
   2.5.2. Field Testing Program ................................. 47

CHAPTER 3: REVIEW OF USE OF ALKOXY SILANES
IN CONSERVATION ............................................. 54
3.1. Consolidation of Stone ....................................... 54
   3.1.1. History of the Use of Alkoxysilanes for Stone Consolidation 54
   3.1.2. Recent Experiments with Alkoxysilanes in Stone Consolidation 56
3.2. Consolidation of Earthen Building Materials .............. 65

CHAPTER 4: CONCLUSIONS AND RECOMMENDATIONS .................. 77

APPENDIX A: COMMERCIALLY AVAILABLE ALKOXY SILANE
CONSOLIDANTS .................................................. 80

APPENDIX B: TEST METHODS FOR THE LABORATORY
EVALUATION OF STONE ......................................... 84

APPENDIX C: SELECTED PROJECTS TREATED WITH ALKOXY SILANES . 87

APPENDIX D: MEETINGS ON THE CONSERVATION OF
EARTHEN ARCHITECTURE ....................................... 94

BIBLIOGRAPHY .................................................... 95
CHAPTER 1
OVERVIEW OF STONE CONSOLIDATION MATERIALS

1.1. INTRODUCTION:

The increasing interest in the conservation of historic structures and the accelerating deterioration of the stone of exposed sculptures and buildings have necessitated an understanding of the mechanisms responsible for stone decay to develop the possibilities of optimum stone protection. In response to this, numerous research projects, publications and conferences dealing with stone have been facilitating the world wide exchange of information.

As is the case with other materials, stone experiences change upon exposure to natural weathering. As long as stone is in contact with any kind of environment, it undergoes chemical, mechanical, physical or biological weathering processes. Weathering is the natural disintegration and erosion of stone caused by the action of water, wind, and atmospheric gases. When used in building construction or for outdoor sculpture, stone is subject to other decay processes in addition to natural weathering due to its interaction with polluted urban-industrial environments, to improper selection or positioning of stone material, etc.

The factors considered responsible for the deterioration of exposed stone include salt crystallization, chemical attack by acidic substances which are either naturally occuring constituents of the atmosphere or introduced by industrial and automotive combustion, freezing of water in pores and capillaries in the stone, microbiological growth on stone such as bacteria, algae and fungi, repeated wetting and drying of stone, thermal stresses caused by differential thermal expansion of some mineral constituents, and abrasion due to
wind or windborne particles or human contact.

Water is the most aggressive agent which acts as a vehicle for weathering processes. Water dissolves and transports soluble salts within the stone causing efflorescence on the surface and salt-induced spalling. The combination of water with gaseous pollutants results in acidic precipitation. Water is responsible for frost damage in climates where freezing temperatures can occur. It is also water which favours the growth of microorganisms. Disintegration, surface erosion, cracking and crust formation are the commonly observed symptoms of stone decay.

As a consequence of the combined effects of chemical and mechanical weathering, stone can lose its cohesion to such a degree that its physical survival is imperilled and a treatment is necessary to restore its integrity. In such cases, consolidation could become part of the conservation process. Consolidation is an in-depth treatment that re-establishes the cohesion between particles of deteriorated stone. The consolidant is usually applied as a liquid which is intended to penetrate deeply into the stone and deposit an additional binding agent which will reinstate the stone's cohesion. Besides its consolidating value, a consolidant should meet basic performance requirements concerning compatibility with stone, effect on moisture transfer, effect on stone porosity, durability, depth of penetration, and effect on appearance. These factors will be discussed in Chapter 2.

Consolidation should not be considered as a single operation. It is a part of a series of processes which include diagnosis, cleaning, preconsolidation, consolidation, surface protection, and maintenance. Additionally, consolidation should be performed only in specific cases when the degree of deterioration threatens the integrity of the material and after considering other less invasive treatment options.

The stone consolidants reviewed in this chapter are divided into four groups according to their chemistry. They are inorganic consolidants, alkoxy silanes, synthetic organic polymers, and waxes.
1.2. INORGANIC STONE CONSOLIDANTS:

Inorganic materials, such as soluble glass, waterglass, limewater, barium hydroxide, etc., have been used as stone consolidants since the 19th century. Despite more than a hundred years of experience in the application of various chemical substances to consolidate stone, little success has been achieved with inorganic materials. Although well-intended, their use often accelerated the deterioration process rather than reducing it. There is still not much known about efficient inorganic substances or feasible application methods. Recent improvements in the application of some inorganic consolidants such as calcium hydroxide and barium hydroxide have renewed interest in inorganic consolidants.

The use of inorganic materials as consolidants is an effort to produce a decay-resistant phase in the pores of deteriorated stone from aqueous solutions. The deposition, that will bind stone particles together, can result from evaporation of the solvent or chemical reactions with the stone. It has been assumed that the binding agent of the consolidant should be similar in nature to the original cement of the stone. For example, it is generally agreed that calcareous stones such as limestone and marble should be consolidated with consolidants which result in the formation of calcium or barium carbonate; sandstones, on the other hand, should be consolidated with consolidants which deposit silica as an end product.

Despite their ability to structurally regenerate stone and remain stable over time, inorganic consolidants have failed to meet many of the performance requirements of a consolidant. In general, their drawbacks include insufficient penetration and formation of shallow and hard surface crusts, formation of soluble salts as by-products in the consolidation reaction, the growth of precipitated crystals, inability to improve the mechanical properties of stone, and possible change in the color of stone.

Siliceous consolidants and alkaline earth hydroxides are the primary inorganic
materials used in stone consolidation. Other inorganic materials, including hydrofluoric acid, aluminum sulfate, zinc and aluminum stearates, phosphoric acid and phosphates have been used to a lesser extent to consolidate stone.\(^9\)

1.2.1. **SILICEOUS CONSOLIDANTS:**

Siliceous consolidants have been used to consolidate sandstone and limestone based upon the principle that formation of silica or insoluble silicates occurs within the pores of the stone to give the grains of the stone a protective coating and bind them together.

Silica (SiO\(_2\)) is an inorganic compound of the chemical element silicon (Si). Hydrated silicon oxides, which is the combination of silica and water, form salts called silicates, such as sodium silicate and potassium silicate. The reaction of those silicates with water, which is called hydrolysis, results in the formation of silicic acid (Si(OH)\(_4\)) and a caustic by-product, sodium or potassium hydroxide, better known as caustic soda or caustic potash. It is this silicic acid that is considered responsible for the consolidation of stone.\(^10\) The silicic acid condenses rapidly precipitating silica gel in the stone pores under the influence of acidic oxides from the air, such as CO\(_2\), SO\(_2\), NO\(_2\), etc.\(^11\) If silicic acid is formed inside a stone which carries hydroxyl (-O-H) groups on its surface, a reaction takes place between the acid and the stone in which water is released. As a result of that, chemical bonds are formed, improving cohesion of the stone.\(^12\)

Siliceous consolidants include alkali silicates and fluorosilicon compounds.

1.2.1.1. **ALKALI SILICATES:**

Alkali silicates have been known since about 1500 B.C.\(^13\) Around 1830, the chemist Von Fuchs began to manufacture sodium silicate or soluble glass (Na\(_2\)SiO\(_3\)). Initially, the consolidation of stone with soluble glass had a big success, but then met serious criticism and was progressively abandoned.\(^14\) Soluble glass was used around 1857
to treat the stone of Westminster Abbey in England, however there is no information available about the long-term effectiveness of this treatment.\textsuperscript{15}

On the other hand, a closely related chemical potassium silicate (K\textsubscript{2}SO\textsubscript{3}), known as "waterglass" has been marketed for stone preservation to the present day. Although some success was reported in the use of waterglass in Germany,\textsuperscript{16} in general alkali silicates are not recommended for stone consolidation. (It is essential to note that the term "waterglass" is a colloquial term used to refer to potassium and/or sodium silicates.)\textsuperscript{17}

One of the drawbacks of alkali silicates is the formation of water soluble salts, such as sodium carbonate and potassium carbonate, as a result of carbonation. These salts can be deleterious to the stone by migrating and forming efflorescence on the stone surface, or causing typical subflorescence damage, e.g.

\[
\text{K}_2\text{SiO}_3\text{.aq} + \text{CO}_2 \rightarrow \text{SiO}_2\text{.aq} + \text{K}_2\text{CO}_3
\]

(water solution of atmospheric silica gel potassium carbonate potassium silicate carbon dioxide)

Alkali silicates also produce impervious surface crusts, since silicates precipitate relatively rapidly and they are deposited near the surface of the treated stone. Formation of silica gel at the surface prevents the further absorption of atmospheric carbon dioxide and therefore prevents the complete and deep carbonation of the silicated solution. In addition, their high viscosity is also responsible for insufficient penetration.

Despite the poor performance of alkali silicates, these types of stone consolidants have never completely disappeared from the market. Some recent attempts at improving waterglass application have been made, but unsatisfactory results were obtained.\textsuperscript{18}

\section*{1.2.1.2. FLUOROSILICON COMPOUNDS:}

In 1883, L. Kessler suggested the use of metal salts of fluorosilicic acid as an
alternative method to the use of waterglass.\textsuperscript{19} Fluorosilicates react with calcium carbonate and form silica gel and insoluble fluorides which have consolidating and waterproofing properties, e.g.

\[
\text{MgSiF}_6 + 2\text{CaCO}_3 \rightarrow 2\text{CaF}_2 + \text{MgF}_2 + 2\text{CO}_2 + \text{SiO}_2
\]

(magnesium fluorosilicate) (calcium carbonate) (calcium fluoride) (magnesium fluoride) (silica gel)

Many soluble types of fluorosilicates, such as magnesium, zinc, and aluminum fluorosilicates have been used to consolidate limestone and sandstone. In Italy, a mixture of magnesium and zinc fluorosilicates has been used for the restoration of several stone monuments by P. Sampaolesi and some success has been achieved.\textsuperscript{20}

However, similar to the alkali silicates, only a surface hardening of the stone is achieved by the use of fluorosilicates which may lead to future spalling. In addition, a tendency to discolor the stone and to form soluble salts which damage the stone through salt crystallization are other undesirable effects of the fluorosilicates. Deposition of magnesium fluorosilicate salts forms a whitish color on the treated stone.

A systematic study of several stone treatments, carried out by B. Penkala in 1964, indicated that fluorosilicates were not effective consolidants.\textsuperscript{21} In most countries, the use of these consolidants in conservation is not allowed.\textsuperscript{22}

1.2.2. ALKALINE EARTH HYDROXIDES:

Alkaline earth hydroxides include calcium hydroxide and barium hydroxide.

1.2.2.1. CALCIUM HYDROXIDE (LIMEWATER):

Limewater is a clear saturated calcium hydroxide solution. It has been used for centuries to treat limestone. When in solution or wetted, calcium hydroxide reacts with carbon dioxide in the air and forms insoluble calcium carbonate which is chemically identical to limestone. The precipitated calcium carbonate in stone may bind detached
limestone particles together. It is, therefore, believed that limestone consolidated with limewater retains its original properties and behavior.

Repeated applications of limewater are necessary to produce sufficient calcium carbonate for consolidation, due to the low water solubility of calcium hydroxide.\textsuperscript{23} In addition, the calcium hydroxide solution should be fairly dilute to prevent the formation of calcium carbonate on the surface of stone and allow deeper penetration.\textsuperscript{24} The precipitation of calcium carbonate begins at the surface as it is dependent on the absorption of carbon dioxide from the air.

Recent improvements in consolidating the mediaeval figure sculptures of Wells Cathedral, England, with lime poultries and limewater have attracted new attention to limewater as a stone consolidant. In the early 1970's, Prof. Robert Baker developed a lime-based technique for the conservation of the west front of Wells Cathedral, known as the "lime method", or the "Baker" or "Wells " method.\textsuperscript{25} The lime method is mainly a series of procedures, which are in sequence: cleaning, consolidation, repair, and surface coating. The application of a hot lime poultice to the pre-wetted Doulting limestone for cleaning is followed by repeated applications of limewater (almost forty applications), flooded onto the surface over a period of days for consolidation. When necessary, lime mortar is used for surface repairs. Finally, all the cleaned and repaired stone is given a shelter coat consisting of lime, sand and stone dust to provide some protection after treatment.

According to some advocates of the process, the lime poultice alone has a noticeable effect in consolidating the stone.\textsuperscript{26} It has been claimed that the lime poultice makes the surface more receptive to the lime water applications and also achieves some initial strengthening of friable areas.\textsuperscript{27} However, most practitioners agree that the limewater applications rather than the lime poultice play the major part in consolidation.

Although no further signs of decay have been reported after the treatment at Wells, the subsequent experiment carried out by C. Price and K. Ross on the same weathered...
stone in laboratory conditions replicating the Wells method did not provide any conclusive evidence of consolidation either with the poultice or the limewater. In 1988, another experiment carried out by Price et al., using a radioactive tracer to monitor the deposition of lime, demonstrated that more than half of the lime deposited is in the outer two millimeters of the stone. The radioactive tracer has the advantage of differentiating between the calcium already present in the stone and calcium deposited from the calcium hydroxide solution. Further results of this experiment showed that the limewater deposits four to five times as much lime as the lime poultice, although there was evidence that the poultice may facilitate the efficacy of the limewater treatment.

Despite its long history of use as stone consolidant, the effectiveness of the lime water technique is, thus, still open to debate. The question remains whether it is the skill of the conservator or the chemical properties of limewater, the lime poultice, or treatment as a whole which accounts for the success of the lime technique in certain cases.

1.2.2.2. BARIUM HYDROXIDE:

Barium hydroxide [Ba(OH)₂], formerly termed baryta, solution has been used in place of calcium hydroxide solution for the purpose of hardening and protecting weathered stone since the 19th century. In 1862 Prof. A. H. Church obtained a patent for the use of barium hydroxide solution in stone preservation. Similar to calcium hydroxide, barium hydroxide reacts with carbon dioxide resulting in the precipitation of insoluble carbonates. However, the treatment with barium hydroxide also somewhat transforms soluble calcium sulfate, which is present in the stone after years of attack by atmospheric sulfur oxides, to much less soluble barium sulfate. Barium sulfate is more resistant to atmospheric erosion. Thus, stone treated with barium hydroxide may be protected against further weathering.

Although initially no failure in the use of barium hydroxide solution on calcareous
stone was reported by Church, the treatment later met considerable criticism from other conservators. Most importantly, it has been claimed that no marked hardening effect is produced with this technique, since Church’s method allows the barium hydroxide solution to dry out shortly after application, resulting in the deposition of a very fine, non-adherent powder of barium carbonate. According to A.R. Warnes and J.E. Marsh, crystalline inorganic precipitates, such as barium carbonate and barium sulfate, do not have a long-term consolidating effect. With the use of barium hydroxide solution, only a surface hardening is produced and eventually this dense surface layer exfoliates. The crystal growth of barium carbonate or barium sulfate can also cause exfoliation, because these crystals have a larger molecular volume than the calcite crystals of calcareous stone and deteriorated stone might not accommodate these relatively large crystals. Additionally, this technique has been found to alter the surface color or texture of stone in many cases.

Despite such negative judgements, in 1966, S. Z. Lewin re-proposed the use of barium hydroxide solution in a revised form for stone treatment. Lewin’s initial proposal includes the use of an homogenous solution of barium hydroxide and urea. This procedure was proposed only for use by immersion. In 1971, Lewin made modifications to the process by adding glycerine to the barium hydroxide-urea solution which would allow in situ application. The addition of urea and glycerine to the barium hydroxide solution fundamentally differentiates this new method from the previous technique. The aim of this revised method is to achieve the deposition of barium carbonate as a binder deeply within the pores of the stone by keeping the barium hydroxide solution in contact with the stone for a prolonged period, usually 2 to 3 weeks. The glycerine prevents the solution from drying out for that period, while the urea facilitates deep penetration of the hydroxide and constitutes a source of carbon dioxide through its hydrolysis in the solution.

The process occurs in two phases. First of all, an exchange of calcium for barium ions occurs on the surfaces of the calcium carbonate grains in the presence of barium
hydroxide.

\[ \text{CaCO}_3 + \text{Ba(OH)}_2 = \text{BaCO}_3 + \text{Ca(OH)}_2 \]

Exchange Process

During the second phase, relatively large crystals of barium carbonate are formed directly on those surfaces and molecularly bonded to them. Thus, the expected long-term consolidation will be produced. Carbonation of the stone surface results from the reaction of the barium hydroxide with atmospheric carbon dioxide, whereas carbonation of the interior of the stone takes place by the reaction of barium hydroxide with carbon dioxide which is released during the hydrolysis of urea.

\[ \text{Ba(OH)}_2 + \text{CO}_2 \text{ (atmospheric)} = \text{BaCO}_3 + \text{H}_2\text{O} \]

Carbonation of Surface

\[ \text{Ba(OH)}_2 + \text{CO(NH}_2)_2 \text{ (urea)} = \text{BaCO}_3 + 2\text{NH}_3 \]

Carbonation of Interior

Crystal Growth Processes

Lewin has suggested that the barium hydroxide technique is very suitable for certain types of calcareous stone\textsuperscript{41} and contends that it is safe and effective in consolidation when applied to an appropriate stone using a suitable technique.\textsuperscript{42} Although the new method has been applied to a number of large projects in the field, it is still experimental. In the building industry, the markedly caustic nature of barium hydroxide is its major drawback since this may result in attack of other building materials including aluminum, zinc and glass.\textsuperscript{43} Discoloration may occur through the formation of white barium salts.

1.3. ALKOXY SILANES:

Alkoxysilanes have received the most attention recently due to their successful performance as stone consolidants. The use of alkoxysilanes for stone consolidation is not a recent development. The possibility of using tetraethoxysilane (TEOS) or ethyl silicate for stone conservation was first suggested in 1861 by A.W. Hoffman.\textsuperscript{44} It was produced as
an industrial chemical around 1924 and A. P. Laurie received a patent for its use as a stone preservative in 1925. During the 1960's, in Germany, extensive laboratory research and field tests with ethyl silicate were carried out and favorable results were obtained. Since then, alkoxysilanes have been commonly used on deteriorated sandstones in Germany. Ethyl silicate and its combination with organo-silicon hydrophobic agents has been commercially available in western Europe since 1972 and thereafter in the United States and Canada. These developments have brought a considerable interest to the use of tetraethoxysilane and also related molecular species, such as alkylalkoxysilanes and alkoxy silane-acrylic polymer mixtures, in stone consolidation.

Alkoxysilanes are a family of monomeric molecules that have the ability to hydrolize with water to produce either silica or chains of alkylpolysiloxanes. The types of alkoxysilanes commonly used as stone consolidants are tetraethoxysilane (ethyl silicate or silicic acid ester), triethoxymethylsilane, trimethoxymethylsilane. When the alkoxysilanes are deposited in the stone, polymerization proceeds by two steps which are hydrolysis and condensation. At the end of that process siloxane linkages (-Si-O-Si-) are formed which provide the strengthening effect.

However, the formation of the final product is not very simple. There are several factors that control the rate of polycondensation and the structure of the forming products, such as the amount of water used in the reaction, the type of the catalysts, and the type of solvents. Alkoxysilanes with methyl groups (CH₃) provide water repellency as well as consolidation.

Even though alkoxysilanes have been commonly applied to the consolidation of sandstones, there have been attempts at using them on marble and limestone, as well. In addition, since 1969 ethyl silicate has been used in the consolidation of exposed adobe surfaces and predominantly satisfactory results have been observed to date.

Besides forming a binder similar to that in siliceous sandstone, alkoxysilanes have
the ability to penetrate deeply into porous stone because of their low-molecular weight. On the other hand, their high cost and tendency to darken the color of the stone and the possibility of their evaporation from the surface before hydrolysis can take place are some of the problems encountered in their use. Alkoxysilane treatments are irreversible.

Alkoxysilanes will be discussed in detail in later chapters.

1.4. SYNTHETIC ORGANIC POLYMERS:

Since the use of synthetic organic polymers as stone consolidants is a recent development, dating back to the early 1960's, there is not much known of their long-term effects. According to J. Riederer, consolidation with polymer materials works well for a considerable period, but not more than twenty years.

Synthetic polymers are formed by polymerization of monomers which are the low-molecular weight compounds. There are two types of application methods of synthetic organic polymers to consolidate stone. The simple procedure is to polymerize the monomeric organic molecules first, dissolve this polymer resin in an organic solvent and then apply it to the stone. When the solvent evaporates, the polymer remains in the stone. However, many solvents have a tendency to draw the dissolved resin back to the surface of the stone. In another application method, monomers either pure or dissolved in a solvent are polymerized in the pores of the stone after the solution has penetrated into the stone. Initiators and activators are also dissolved in the solvent to ensure that polymerization takes place after penetration. Deeper penetration can be achieved with monomer solutions, since they are less viscous than the diluted polymer resins and the size of a monomer molecule is very small.

Although some synthetic organic consolidants significantly improve the mechanical properties of disintegrated stone, their weakness lies in the fact that they slowly deteriorate in the presence of oxygen and light. Discoloration, loss of tensile strength, and
brittleness are the symptoms of that process. Poor penetration is also among the disadvantages of synthetic organic polymers. Additionally, most synthetic resins have high thermal expansion coefficients larger than that of all stones and adobe. This negative factor can cause the development of a stress at the interface leading to possible detachment of the consolidated stone from untreated stone. Different types of decay regarding some stone structures in Germany, which had been consolidated with organic polymers, was reported by Riederer. Deep channel erosion caused by rainwater occurred on the consolidated stone within ten years of the treatment.

Synthetic resins can be divided into two main groups which are thermoplastic and thermosetting resins. They both have been used for stone consolidation, even though their structure is fundamentally different. Thermoplastics are composed of monomeric units, which are linked together by weak molecular forces to form two-dimentional linear chains. They are reversible at least in principle and they remain soluble in appropriate solvents. However, they do not penetrate easily into small pores due to the large size of their molecules and tend to accumulate near the surface. The most widely used thermoplastic synthetic organic polymers are acrylates, polyethylene, nylon, and polyvinyl acetate.

In contrast to thermoplastics, thermosetting resins are irreversible, because the monomeric units are linked together by strong chemical bonds to form a three-dimentional network. Once they set, they can not be remelted or reformed. Thermosetting resins are harder and stronger than thermoplastics, however they are also more brittle. Examples of thermosetting synthetic organic polymers are epoxies, polyesters, and polyurethanes.

1.4.1. ACRYLIC POLYMERS:

Methyl methacrylate and butyl methacrylate are the acrylic monomers that have been most widely used to consolidate stone and concrete. Several methods of polymerizing
acrylic monomers in situ have been investigated. They polymerize by means of heating with an initiator, ultraviolet radiation or gamma radiation. However, occasional destruction of the stone, such as cracking, is the serious problem which has been encountered during polymerization when the polymerization temperature is lower than 50°C or when using radiation. It seems that the formation of cracks is related to polymerization temperature. However, it is not clear that the type of monomer or initiator and presence or absence of solvents have an influence on the appearance of cracks. A study on the polymerization of methyl methacrylate in sandstone by P. Kotlik et al. concurs with the above findings.

Depending on the type of initial monomer, the resulting polymer can have different properties. Methyl methacrylate monomers form quite hard polymers, polymethyl methacrylate (PMMA), while butyl methacrylate produces a relatively elastic product. Stone consolidated with methyl methacrylate and other acrylic based polymers may exhibit a brittle behavior. If adequate impregnation and complete polymerization are achieved, methyl methacrylate can improve the mechanical properties of porous stone. Acrylic resins have better resistance to oxidation and UV radiation than thermosetting resins.

Acrylic resins have been used to consolidate sandstone, limestone and marble. Pre-polymerized methyl methacrylate in methylene chloride was tested to impregnate Egyptian limestone bas-reliefs, the Abydos reliefs. The reason for choosing this solution was that appropriate impregnation had been achieved with it on limestones. In this case however, penetration was not considerable and also a glossy coat formed on the surface.

1.4.2. ACRYLIC COPOLYMERS:

The joining of two or more different acrylic monomers, such as methyl acrylate, ethyl acrylate, methyl methacrylate, and butyl methacrylate, in a polymer chain forms the acrylic copolymers. The combination of different monomers rather than one monomer
variety introduces the possibility of modifying the properties of the resultant polymer to fit the condition of the stone. For example, the addition of ethyl acrylate or butyl methacrylate to methyl methacrylate improves chemical strength, hardness and weathering.  

All the acrylic copolymers are dissolved in organic solvents and then applied to stone. The amount of penetration and actual impregnation resulting after the solvent evaporates depend on the choice and amount of solvent used. When too much solvent is used, evaporation will draw the acrylic copolymer back to the stone's surface forming a hard crust; when too little solvent or an improper solvent which evaporates too quickly is used, the acrylic copolymer will not penetrate deeply into the stone.

A copolymer of ethyl methacrylate and methyl acrylate, commercially known as Paraloid B-72 (Acryloid B-72 in US), has been widely used for surface consolidation of stone and reattachment of plaster and flaking stone in Italy. The surface of the Carrara marble Lunette of the SS Giovanni and Paolo church in Venice was treated with a solution of Paraloid B-72 in nitro solvent as an interim measure to prevent further loss of disintegrated stone, in 1974. G.Torraca indicates that Paraloid B-72 shows a good resistance to the ageing process and its life span is 3-10 years in external exposure. De Witte et al. studied different polymerization methods on limestone by using Paraloid B-72 in solution and a mixture of the monomers methyl methacrylate and ethyl acrylate, which are polymerized in situ under the influence of either gamma radiation or heating supposing that a polymer basically similar to B-72 would result. It was concluded that the best results were obtained with the thermal polymerization of a mixture of monomers, whereas the treatment with Paraloid B-72 resulted in only 4% impregnation which cannot be considered successful.

It is important to note that around 1975, the physical presentation of Paraloid B-72 changed from white irregular lumps to regular transparent globulas. Although the manufacturer of Paraloid B-72 confirmed that there was no change in its chemical structure,
De Witte et al. claimed that the analysis of old and new Paraloid B-72 showed a small but definite difference between the two resins. They are both copolymers of ethyl methacrylate and methyl acrylate, but the old B-72 contains 2% more methyl acrylate than the new. Conservators should be aware of the fact that even this small difference in composition results in some changes in the physical properties of the resins.76

Copolymers of acrylic/silane, acrylic/silicone, and acrylic/fluorocarbon have also been studied for stone conservation. Acrylic/silane mixtures will be discussed in Chapter 3. Gauri and Rao77 reported that fluorocarbon-acrylic copolymers increase the resistance of stone to atmospheric attack, as a result of their study on epoxies, fluorocarbon-acrylics, and silicones. They recommended the use of fluorocarbon-acrylic mixtures for surface application rather than impregnation. Fluorocarbon-acrylic copolymers, however, are generally avoided in conservation practice today.

1.4.3. EPOXIES:

Epoxies have been used to consolidate limestone, sandstone, and marble in addition to their use as adhesives, paints, varnishes, and constituents of synthetic mortars and concrete. An epoxy resin system consists of an epoxide group and a curing agent or hardener, which modifies the physical properties and chemical structure of the resin and transforms it into an insoluble and infusible solid thermosetting cross-linked polymer. During hardening no by-products are released. Frequently used curing agents are primary, secondary and tertiary amines, amides, Lewis acids, phenols, anhydrides, Lewis bases, and inorganic hydroxides.78 Hardening can be achieved at room temperature or may require higher temperatures depending on the type of hardener. For example, aliphatic amines and amides are for room temperature use, whereas aromatic amines and acid anhydrides are for high temperature curing.79 The type and quantity of curing agent is rather important to obtain a well-hardened final product. A resin and hardening agent with low-molecular
weight is recommended to get sufficiently deep penetration into porous stone.\textsuperscript{80}

Epoxies are generally too viscous to achieve significant penetration. Therefore, they are usually dissolved in organic solvents to reduce the viscosity. The choice of solvent to be used with epoxides is also very important. The presence of solvents has an essential influence on the speed of the cross-linking reaction which should take place slowly to gain time for the diffusion of the resin molecules into the pores of stone. A solvent with hydroxyl groups (-OH) facilitates the cross-linking, whereas a solvent with a carbonyl group (\textendash C=O) in the molecule slows the hardening reaction down.\textsuperscript{81} The solvents also affect the color of the resulting product.

After epoxy resin impregnation, the resin tends to migrate back to the surface as the solvent evaporates. In the case of small objects, the epoxy impregnated stone can be wrapped with polyethylene or aluminum sheets to prevent premature evaporation of the solvent and reverse migration before cross-linking of the resin. This is not practical on large building surfaces.

The most commonly used epoxy resins are epichlorohydrin and bisphenol A. Epoxy resins based on bisphenol A are found to protect the stone from carbon dioxide and sulfur dioxide, but are too viscous to penetrate stone deeply.\textsuperscript{82} Their viscosity can be lowered by addition of low viscosity hardeners. Epoxy resins are now commercially available with satisfactorily low viscosities.

Epoxy resins improve the mechanical properties of stone after correct hardening. They have a good adhesion to stone and are resistant to water and several chemicals. Two main drawbacks of the epoxies are their tendency to age and discolor (yellowing) upon exposure to light and their insolubility in ordinary solvents after setting. When exposed to sunlight, many epoxies tend to chalk, forming a white powdery surface.\textsuperscript{83} Epoxy also tends to fill completely the pores of stone which is extremely undesirable, since apart from preventing air and water vapour transmission through the treated stone, the stresses caused
by differential thermal expansion of epoxy will eventually deteriorate the stone. Because of these negative features, the use of epoxies is not recommended for the surface consolidation of historic buildings. In conservation practice, epoxies are used most successfully as adhesives.

1.5. WAXES:

Waxes have been used to treat and protect stone for many centuries. In the first century B.C., impregnation of stone with wax was already described by Vitruvius. The most common natural waxes used for consolidating stone are beeswax and paraffin wax. Beeswax is obtained from the hives of honey bees. Paraffins are petroleum-derived mineral waxes. They have been found effective in increasing the water repellency and the tensile strength of porous stone. Microcrystalline wax, which is the modern equivalent of paraffin wax, has the same chemical composition but smaller crystals than those of paraffin waxes. Therefore, in contrast to brittle paraffin waxes, microcrystalline waxes have good plasticity and adhesion. They appear to be effective as superficial consolidants.

Waxes have been used in the form of a solution or in the form of melted mixtures. By either application, the stone is heated to keep wax molten during impregnation and to increase the depth of wax penetration into the stone. However, the high temperature needed to assist the penetration may damage the stone by causing, for example, spalling. Small objects such as statues and architectural museum pieces are impregnated by immersion in a bath of molten wax and deep penetration can be achieved. But, where total impregnation is not possible, depth of wax penetration into the stone is always very shallow. Therefore, waxes can be considered as protective coatings rather than impregnants. The other drawbacks of waxes are their tendency to soften at high temperatures and to collect dirt. Waxes may cause yellowing of the treated surfaces. In addition, the impregnated wax can rarely be removed when there is a need for application of other materials.
A wax-based protection has been recommended on non-porous stone and on good quality limestone. Cosmolloid 80H, a commercial name for a microcrystalline wax, was successfully used as a surface coating on the non-porous Istrian limestone of the Loggetta of the Campanile, Venice. A paraffin wax with a low melting point was applied to Cleopatra's Needle in London to waterproof the surface of the granite. Unfortunately, it discolored the stone. Another failure has been reported in the use of a wax dissolved in turpentine on Westminster Abbey in London.

In general, waxes are no longer widely used or recommended for stone consolidation.


Pollution, Cleaning, Consolidation and Protection, p. 308.


19. Ibid., p. 569.


37. Ibid.


64. Ibid.


72. Ibid., p. 13.


74. G. Torraca, "General Philosophy of Stone Conservation," p. 263.


81. Ibid., p. 77.


84. T. B. McDonald, "Coatings, Sealers, Consolidants," p. 78


88. Ibid.


CHAPTER 2
ALKOXY SILANES

2.1. PERFORMANCE CRITERIA :

2.1.1. PERFORMANCE CRITERIA FOR STONE CONSOLIDANTS :

The effectiveness of a consolidation treatment depends on the proper selection of the consolidating substance, what is expected of it and how it is used. There are basic performance requirements that all consolidants must fulfill regardless of the specific application. The establishment of performance criteria for stone consolidants through years of experience provides a framework for evaluating any proposed consolidant and makes the selection of the appropriate consolidant easier for the conservator.

The following criteria have been suggested by several authors for an effective consolidation treatment :

o Consolidating Value : The primary requirement of a stone consolidant is to restore the physical integrity and mechanical properties of the decayed stone to an acceptable level by re-establishing the bonds between adjacent grains. A consolidant may perform this function through the deposition of a new and durable binding agent within the pores of stone.1

o Durability of Consolidated Stone : The consolidated stone is expected to be as durable as the unweathered stone. A consolidant should form a compact front against atmospheric pollutants, dust, biological agents, and wind at least for some time.2 If the consolidated stone is less durable than unweathered stone, the replacement of the deteriorated stone with a new one is suggested.3 Furthermore, in terms of appearance, the weathering rate of the treated stone should be nearly the same as the untreated stone.
Depth of Penetration: The consolidating substance should have the ability to penetrate easily and deeply into the weathered stone. Several authors have suggested that a stone consolidant should penetrate to such a depth that all the deteriorated zone is solidified and attached to the unweathered sound core of the stone. C. Price, on the other hand, has proposed the specific depth of penetration to be at least 25 mm. Ideally, a consolidant should penetrate uniformly into the stone pores and not accumulate at the surface forming a surface crust.

There are many factors affecting penetration of the consolidant. They are related to the properties of the treating agent including its surface tension, viscosity, rate of evaporation and gel rate, as well as the characteristics and temperature of the porous material to which it is applied. Porosity, pore size distribution and moisture content are the most important properties of the stone that also control the penetration of the consolidant. Low viscosity and high surface tension of the impregnating fluid are desirable to achieve good penetration.

Stone Porosity: The consolidant should not adversely affect the pore structure of the stone. Treating stone with consolidating material can reduce the mean size of the pores and make the stone more susceptible to frost and salt damage due to the increased proportion of fine pores.

Moisture Transfer: Consolidants should be water vapor transmissive so that the treated stone can allow water vapor and air circulation to prevent the accumulation of moisture and salts behind the treated layer which will ultimately cause the deterioration of the stone. Therefore, complete filling of the pores with an organic hydrophobic consolidant is not recommended.

Compatibility of Consolidant with Stone: The consolidant should have similar thermal-dimensional properties as the untreated stone. It should not have deleterious chemical or physical interactions with the stone which can form harmful by-products such
as soluble salts. Similarly, it should not disrupt the microstructure of the stone, for instance, through crystal growth from the precipitation of an inorganic consolidant. When the thermal expansion of consolidated stone is very different from untreated stone, it may produce important tensile stresses leading to cracking at the interface between the consolidated and untreated stone. The crystal growth of precipitate may also produce internal tensile stresses causing microcracks and eventual macrocracks in the stone.

o Effects of Consolidant on Appearance: The consolidant should create no or minimal alteration in texture, color and reflectance of the stone either initially or after exposure to the environment. If the treatment alters the natural appearance of the stone, the conservator responsible for the preservation of the structure will have to evaluate its acceptability.

o Ease of Application: During handling or application, a consolidant should not introduce health and safety hazards. If the consolidant is toxic, volatile, flammable, etc., adequate safety precautions should be taken for applicators which includes use of protective clothing, goggles and respiratory masks. All consolidants should be applied by experienced applicators. Environmental considerations regarding protection of surrounding landscape and sidewalk areas should also be taken into account.

In addition to the primary performance requirements, a specific application may necessitate secondary requirements, as well. These requirements may be encapsulation of salts or extraction of salts from stone, prevention of further microbiological growth, providing water repellency, reversibility to allow future treatment, etc.

It is important to note that the reversibility of a consolidation product is considered by many conservators to be more theoretical than practical. Even if the treatment is reversible, it is an impractical and difficult operation to remove a consolidant from immovable stonework on buildings, especially after it has been in place for a certain period of time. The consolidation treatment may not be reversible, but may be retreatable so that
the future application of the same treatment or another treatment may be possible as it is needed. The cost also should not be disregarded in selecting the appropriate consolidant.

In 1921, the characteristics of an ideal stone preservative had already been described by Heaton.\textsuperscript{11} It can be easily seen that his criteria are still relevant and valid to stone consolidants today:

1. It must penetrate easily and deeply into the stone, and remain there on drying.
2. It must not concentrate on the surface so as to form a hard crust, but must, at the same time, harden the surface sufficiently to resist erosion.
3. It must prevent penetration of moisture, and, at the same time, allow moisture to escape.
4. It must not discolour or in any way alter the natural appearance of the stone.
5. It must expand and contract uniformly with the stone so as not to cause flaking.
6. It must be non-corrosive and harmless in use.
7. It must be economical in material and labour of application.
8. It should retain its preservative effect indefinitely.

However, there is no one product that is able to fulfill all the requirements for stone consolidation at the same time, because these requirements can be contradictory. A variety of inorganic, organic and organosilicon consolidants are commercially available today, each accompanied by scientific data regarding production and use. Different cases will require different products and treatments and some no consolidation at all.

2.1.2. HOW ALKOXYSILANES MEET THE PERFORMANCE CRITERIA:

Alkoxysilanes have received increased attention as stone consolidants and are considered by many conservators to be the most promising stone consolidating materials available today. What makes the alkoxysilanes so attractive is that some of them, notably the alkylalkoxysilanes and silicic acid esters, meet several of the performance requirements.

One of the most important properties of alkoxysilanes is their ability to penetrate deeply into porous stone. This advantageous property differentiates alkoxysilanes from their many predecessors. Their low viscosity and small constituent monomeric molecules
give the alkoxy silanes a substantial penetrating power. They can penetrate certain porous stones to a depth of between 20 to 25-30 mm, thus eliminating the problems of shallow treatments.

When alkoxy silane monomers are polymerized, the structure of the cured polymers provides chemical stability through strong silicon-oxygen-silicon bonds and produces a high strengthening effect. Alkoxy silanes can cure at normal outdoor temperatures. Hydrolysis reactions of the alkoxy silanes produce alcohols as by-products which are not deleterious to stone and evaporate as soon as they are generated, thus leaving the solid polymer in the stone. It has been reported that solidified material does not seem to fill the entire pore space, but instead coats the pores, therefore permitting the transmission of moisture. This would also allow the treated stone to absorb a further treatment when necessary. Alkoxy silane consolidation is not reversible, but permits retreatment.

On the other hand, alkoxy silanes do have disadvantages. They have been reported to cause some slight changes in the color of treated stone, such as an initial darkening, and also formation of white spots on the stone. Alkoxy silanes are likely to evaporate from the surface before hydrolysis can take place. Additionally, alkoxy silanes are expensive materials and the consumption of material is high in order to achieve deep penetration. High cost may, thus, restrict their use to small objects and limited surface areas. Necessary precautions in application are not convenient for large projects. All of the alkoxy silanes may be regarded as hazardous for human health. They can cause kidney damage and injury to the eyes leading to blindness, if proper safety precautions are not taken.

2.2. CHEMISTRY OF ALKOXY SILANES:

Alkoxy silanes are monomeric organo-silicon compounds containing silicon, oxygen, carbon and hydrogen atoms. Most of these compounds are colorless, low
viscosity liquids with relatively low toxicity\textsuperscript{21} and moderate to low volatility.\textsuperscript{22} They react with water to give a solid polymer varying in nature from silicone resin to fine powder or glassy silica. The physical properties and chemical composition of the resulting product depend on the specific conditions which exist during the total process that will be further discussed in this section.

2.2.1. CHEMICAL STRUCTURE OF ALKOXYSilanes:

Alkoxysilane refers to a silane containing at least one alkoxy group. A silane is a compound based on a silicon backbone to which the alkyl groups and/or alkoxy groups are attached directly through a silicon-carbon link (Si-C, silane link) or an ester link (Si-O-C). Some alkoxysilanes can contain both silane and ester links at the same time, such as triethoxymethylsilane and trimethoxymethylsilane.

An alkyl group is a compound of carbon and hydrogen atoms, such as methyl (-CH\textsubscript{3}) and ethyl (-C\textsubscript{2}H\textsubscript{5}) groups. Those hydrocarbon groups are often represented by the letter R. An alkyl group bonded to an oxygen atom forms an alkoxy group, such as methoxy (-OCH\textsubscript{3}) and ethoxy (-OC\textsubscript{2}H\textsubscript{5}).

It should be emphasized that the term silane was originally applied to silicon hydrides that are the compounds formed by silicon and hydrogen. Since then, silane has been used to refer to many of the monomeric organo-silicon compounds including ethyl silicate.\textsuperscript{23}

Alkoxysilane is used here as a principal term describing the major types of consolidants that are commonly used to consolidate stone. A list of commercially available products in each category is presented in Appendix A.

1. ETHYL SILICATE (TETRAETHOXYSILANE) [Si(O\textsubscript{2}C\textsubscript{2}H\textsubscript{5})\textsubscript{4}]:

Ethyl silicate is the best known alkoxysilane, also referred to as tetraethoxysilane. Silicic acid ester, silicon ester, tetra(ethyl)orthosilicate (TEOS) have also been used in the
literature to refer to ethyl silicate. Ethyl silicate is produced industrially by the reaction of silicon tetrachloride (SiCl₄) with ethyl alcohol (C₂H₅OH). Its chemical structure may be represented as:

\[
\begin{align*}
\text{O(C}_2\text{H}_5) \\
(\text{H}_5\text{C}_2)\text{O} & \quad \text{Si} & \quad \text{O(C}_2\text{H}_5) \\
\text{O(C}_2\text{H}_5)
\end{align*}
\]

Ethyl silicate has an extremely low viscosity (0.60 centipoises at 20°C) that is lower than the viscosity of water (1.0 Nsm⁻²x10⁻³ at 20°C). Thus, ethyl silicate is more mobile than water. This desirable property for a consolidant provides ethyl silicate with excellent penetration in porous materials. However, large quantities of the material are required in order to get sufficient penetration which makes the treatment rather expensive. Ethyl silicate is volatile, so conditions must be controlled to prevent excessive evaporation before consolidation takes place.

2. PARTIALLY POLYMERIZED ETHYL SILICATE:

Ethyl silicate that is partially hydrolized and condensed to produce small polymers capable of further polymerization is called partially polymerized ethyl silicate. It is produced by including water during the synthesis of ethyl silicate. Partially polymerized ethyl silicate is widely marketed. It is called "ethyl silicate 40 " in the US which indicates the specific degree of polymerization.

The liquid may be yellow or brown and more viscous than the monomeric ethyl silicate. Partially polymerized ethyl silicate is less expensive than monomeric ethyl silicate.

3. TRIETHOXYMETHYLSILANE [(CH₃)Si(O C₂H₅)₃]:

This compound is chemically similar to ethyl silicate except for the substitution of a methyl group for one ethoxy group. The term is sometimes used in inverted order as methyltriethoxysilane (MTEOS).
Its chemical structure may be represented as:

\[
\begin{align*}
O(C_2H_5) \\
H_3C - Si - O(C_2H_5) \\
O(C_2H_5)
\end{align*}
\]

The viscosity of triethoxymethylsilane (0.6 Nsm\(^{-2}\)x10\(^{-3}\) at 20\(^{\circ}\)C) is lower than that of water (1.0 Nsm\(^{-2}\)x10\(^{-3}\) at 20\(^{\circ}\)C).\(^{30}\) In addition to their consolidating effect, triethoxymethylsilanes also provide water repellency through the exposed methyl groups of the cured product.

4. TRIMETHOXYMETHYLSILANE \[\text{[(CH}_3\text{)Si(OCH}_3\text{)\_3} \]:

Trimethoxymethylsilane is structurally similar to triethoxymethylsilane except for the substitution of methoxy groups for the ethoxy groups. Some authors use the term in inverted order as methyltrimethoxysilane (MTMOS). Its chemical structure may be represented as:

\[
\begin{align*}
O(CH_3) \\
H_3C - Si - O(CH_3) \\
O(CH_3)
\end{align*}
\]

Trimethoxymethylsilanes are also low viscosity monomers (viscosity 0.5 Nsm\(^{-2}\)x10\(^{-3}\) at 20\(^{\circ}\)C)\(^{31}\) and provide water repellency as well as consolidation. However, trimethoxymethylsilane may be toxic.\(^{32}\)

Methyl(trialkoxy)silanes or, more generally, alkyl(trialkoxy)silanes, have been used to refer to triethoxymethylsilane and trimethoxymethylsilane as well. They may be more expensive than ethyl silicate.

2.2.2. POLYMERIZATION OF ALKOXYSilANES:

HYDROLYSIS AND CONDENSATION

The application of alkoxy silanes to stone consolidation is based upon the fact that
the initial liquid compound can be converted into a consolidating solid deposit within the stone through interaction with either liquid water or water vapor. When the alkoxy silane is applied to stone as a monomeric molecule, its polymerization is initiated by a hydrolysis reaction.

Hydrolysis is the chemical reaction of an alkoxy silane with water or with the hydroxyl groups (-O-H) on the surface of a mineral grain. Several types of stone, brick and clay have reactive hydroxyl groups on their surface. The alkoxy groups (-O-R) of alkoxy silanes are capable of reacting with hydroxyl groups.

The hydrolysis reaction produces a silanol and an alcohol as a by-product which is harmless to stone and rapidly evaporates. In the course of polymerization, this partially hydrolized molecule can then undergo either further hydrolysis or condensation.

Two silanol molecules, which are the products of the hydrolysis reactions, can react with each other and condense to form a dimer molecule. Water is produced as well. Further hydrolysis and condensation proceed simultaneously and beyond the dimer stage trimers, tetramers and eventually a network of polymers having a -Si-O-Si-O-Si- backbone, called siloxanes, is formed. It is the silicon-oxygen-silicon linkages that produce the consolidation and strengthening effect.

An alkoxy silane is a mobile liquid. As hydrolysis and condensation reactions proceed, the liquid changes into a glassy solid. The network polymer that first forms is a soft gel; the gel shrinks and becomes harder; the shrinkage continues and it changes into a hard, brittle glass; in the end, it shrinks to small, glassy particles or crumbles to a fine powder.

If the alkoxy groups react with the hydroxyl groups present on the surface of the stone grains, they become molecularly bonded to the substrate. One end of the siloxane chain is bonded to the surface of one mineral grain, while the other end is attached to an adjacent grain. If the reaction takes place with the hydroxyl groups of water molecules, the
resulting network of polymers is not bonded to the grains of the stone, but fill the intergranular spaces of the stone. There are conflicting opinions among conservators and scientists regarding the importance of the molecular bond in strengthening stone. According to A.E.Charola et al., the lack of chemical interaction with the substrate may be an advantage.\(^\text{36}\)

When alkoxy silanes with alkyl groups [alkyl(trialkoxysilanes)] polymerize, unlike the Si-O-C link (ester link), the Si-C link (silane link) resists hydrolysis and the final product retains alkyl groups attached to the siloxane backbone. It is the alkyl groups that present a non-polar aspect to the surroundings and therefore provide water repellency in addition to the consolidating effect of the alkyl(trialkoxysilanes). For instance, trimethoxymethylsilane is polymerized as follows:

1. The methoxy groups are hydrolyzed to form a silanol, and methanol is liberated:

\[
\begin{align*}
\text{OCH}_3 \\
\text{H}_3\text{C} \quad \text{--- Si ---} \\
\text{OCH}_3
\end{align*}
\begin{align*}
\text{OH} & \quad \text{H}_3\text{C} \quad \text{--- Si --- OH} \\
\text{OCH}_3 & \quad \text{OCH}_3
\end{align*}
\]

\[
\text{Trimethoxymethylsilane + Water} \quad \text{Methyl Dimethoxy Silanol + Methanol}
\]

2. Two methyl dimethoxy silanol molecules react and condensation takes place. As a result, silicon-oxygen-silicon bonds are formed and water is released:

\[
\begin{align*}
\text{OCH}_3 \\
\text{H}_3\text{C} \quad \text{--- Si ---} \\
\text{OCH}_3
\end{align*}
\begin{align*}
\text{OH} + \text{HO} & \quad \text{H}_3\text{C} \quad \text{--- Si --- O} \\
\text{OCH}_3 & \quad \text{OCH}_3
\end{align*}
\begin{align*}
\text{Si} \quad \text{CH}_3 & \quad \text{H}_3\text{C} \quad \text{--- Si --- CH}_3 + \text{H}_2\text{O} \\
\text{OCH}_3 & \quad \text{OCH}_3
\end{align*}
\]

It is apparent that water is produced and consumed in the course of polymerization.

3. Further hydrolysis and condensation reactions convert -Si-O-C linkages into -Si-O-Si-linkages and generate a three dimensional cross-linked polymer which has some similarity to the chemically very stable compound, silica:
It is easily seen that methyl groups are left exposed and provide water repellency.

The conversion reaction of alkoxysilane monomers into a cross-linked polymer does not occur spontaneously; certain conditions are necessary for the course of the reaction. These are:

- **Presence of Water:** One of the most important conditions is the presence of water, since the partial reaction of the alkoxysilane liquid with water initiates polymerization. It has been suggested that sufficient water must be present in the initial solution along with the silane to produce gelation, because one can not rely on the hygroscopic moisture content of the building material itself, or atmospheric humidity to achieve a complete reaction.\(^{37}\) The amount of water used in the reaction markedly affects the mechanism of the gel formation. As a result of their study on the polymerization of tetraethoxysilane, S.Z. Lewin and G.E. Wheeler have suggested that the molar ratio of water to silane should be at least 2:1 to produce gelation. They also reported that even the order of mixing one in another gives a different set of reaction products. For example, tetraethoxysilane added to a water-alcohol solution gives a more predictable product than water added to a silane-alcohol solution.\(^{38}\)

- **Solvents:** The solubility of water in alkoxysilanes or alkoxysilanes in water is very small, therefore it is necessary to employ a mutual solvent in the starting solution. For instance, ethyl alcohol is often used as the mutual solvent to achieve the miscibility of ethyl
silicate and water.\textsuperscript{39} Methanol and cellosolve are two examples of solvents which are used with methyl(trialkoxy)silanes (MTEOS,MTMOS)/water mixture.\textsuperscript{40} Solvents are frequently added to alkoxy silanes to reduce their viscosity as well.\textsuperscript{41} In this way, the depth of penetration into the stone can be controlled.

- **Catalysts:** Catalysts are often employed to speed up the rate of hydrolysis and condensation reactions so that the evaporation of the monomer before polymerization is avoided. In the absence of catalysts, the polymerization is too slow for practical field use. Acids (e.g. especially hydrochloric acid and phosphoric acid), alkalis and metallic salts have been used as catalysts for both reactions. Solvent and catalyst choice is important. When choosing a solvent and catalyst to increase the rate of polymerization, one should be aware of the fact that they must not react with the substrate and leave any soluble residue in it which can cause future decay.

The rate of polymerization has an essential impact on the structure and quality of the forming product. The penetration of the impregnating liquid into the stone's pore system requires a time period varying from several hours to a day. However, if the liquid is too volatile, it will evaporate before a sufficient penetration is achieved. On the other hand, if the polymerization is too fast, gelation will occur before an effective penetration is obtained and consolidation will occur only at the surface, creating a potential source of future failure. Adjusting and controlling the rate of polymerization is obviously the most complicated and difficult problem in the application of alkoxy silanes to stone conservation. Besides employing catalysts and solvents, some other factors also influence the polymerization rate such as the type of the hydrocarbon group (methyl, ethyl, etc.) that is attached to the silane molecule\textsuperscript{42} and the relative humidity at which the reaction is carried out.\textsuperscript{43} The rate of the hydrolysis reaction is slower when the hydrocarbon group is larger and bulkier.\textsuperscript{44}

An experiment on uncatalyzed polymerization of trimethoxymethyl silane, carried out by A.E. Charola et al., revealed that the rate of polymerization and the quality of the
polymer are sensitive to the relative humidity (RH). The relative humidity should be between 50% and 30% for the application of trimethoxymethyl silane. Above 50% RH, the rate of hydrolysis is too rapid, and during condensation, stresses are developed leading to cracks and defects. Below 30% RH, the reaction rate is too slow, permitting excessive evaporation of the silane. The evaporation of liquid monomer has also been found to be RH dependent. More trimethoxymethylsilane evaporates at lower RHs. However, it is extremely difficult to control relative humidity in the field. Even though the ambient RH may be ideal, the moisture content of the porous stone varies at different depths, thus introducing a non-homogeneous polymerization environment.

For the effective application of alkoxysilanes in conservation, in addition to providing appropriate conditions for the reaction, application of the impregnating liquid on an appropriate type of stone is very important. The physical and chemical nature of the substrate also influence the polymerization process. Alkoxysilanes do not give the same results with all types of stone. As mentioned before, the presence of reactive -OH groups on the mineral grains of the stone can lead to a molecular attachment of the siloxane chains to the mineral grains. Thus, it has been claimed that the alkoxysilanes are most effective for porous, fine-grained, weak stones with surface hydroxyl groups, such as many types of sandstone and clay rich stones. According to many conservators, mudbrick and other earthen substrates are particularly suited to consolidation with ethyl silicate.

Nonetheless consolidation of calcareous stones, such as limestone and marble, with alkoxysilanes has been achieved. Although the chemical affinity of silanes for calcareous stones is minimal, a network of polymer may fill the intergranular spaces of the stone and having a consolidating effect without forming a chemical bridge between the grains.

The mechanism of alkoxysilane polymerization is very complicated and is still not completely understood.
2.3. APPLICATION METHODS:

An alkoxysilane consolidant is usually sprayed with low pressure or brushed on to the substrate in repeated applications referred to as "cycles" by some manufacturers. The number of applications and the waiting time between cycles or applications can vary for different products, therefore each product should be applied in accordance with the manufacturer's recommendations. In the initial stages, applications are absorbed very rapidly. Further applications should normally take place until no more is taken up. When necessary, absorbent pads of tissue should be placed below the treatment area to prevent excess silane from running down. Adjacent surfaces not designated for treatment and/or non-masonry surfaces should be protected from overspray of consolidant with sheets of polyethylene fixed firmly to these surfaces or by other protective materials such as adhesive tapes, non-oily modeling clay, etc. Following final application of the consolidant, excessive material should be washed immediately with a cleaning solvent from the masonry surface in order to prevent a possible surface discoloration.

Choosing the right application method very much depends on the type of surface to be consolidated, the porosity of the material and its dimension. Application by hand operated spray is very convenient and least damaging to friable surfaces, whereas application by brush is suitable on very firm surfaces. In addition, small surfaces can be treated with simple spray bottles, while larger surfaces require spray devices, such as spray-guns, etc.

Other application methods for alkoxysilanes include immersion of the substance in the consolidating solution, absorption by capillary suction and the use of compresses. Immersion can be accomplished under vacuum or at atmospheric pressure. Obviously, this method is only applicable to mobile and moderate size objects such as sculptures and architectural pieces.

During the course of the immersion technique at atmospheric pressure, the object is
completely immersed in a basin filled with the consolidant. It is recommended that in order to get the maximum depth of penetration the object should be removed from the bath occasionally.\(^4^9\) This will allow air which is trapped within the pore spaces to escape and provide a homogenous distribution of the consolidant. After immersion, the impregnated object is covered with an impermeable wrapping to avoid the evaporation of the impregnant. This wrapping must be kept in place from several days to a week depending on the case.\(^5^0\) The advantage of the immersion technique utilizing vacuum is that substantially deep penetration can be achieved. In order to increase the absorption of consolidant, a gas pressure (e.g. nitrogen gas) can be applied to the system.

The use of compresses is also suitable for mobile objects. The object is wrapped in a poultice and sealed air tight by means of a polyethylene film. The consolidant is injected into the poultice at a slow rate.

Certain specific conditions should be provided before the application takes place. Alkoxy silanes should be applied to a clean, dry and absorbent surface to get an adequate penetration. Obviously, a wet masonry substrate whose pores and capillaries are full of water will not have absorbency for the impregnated agent. Therefore, the consolidant should not be applied during rain or when there is chance of rain within 24 hours after application. In addition, rising damp problems should be corrected before consolidation. Control of other surface conditions for example, surface and air temperatures, wind and sun exposure is essential for proper performance of an alkoxy silane. Prior to application, masonry to be treated should be protected from direct sun radiation to keep the surface relatively cool and prevent rapid evaporation of the alkoxy silane. Application should be avoided when wind is sufficient to carry airborne chemicals to unprotected surfaces. For an adequate penetration, surface and air temperatures should not be too warm or too cool. It has been suggested that air and surface temperatures should be from 50 degrees F to 85 degrees F during application.\(^5^1\)
Clean surfaces will improve the absorbency of the masonry. Surface contaminants such as salts, carbon crusts, atmospheric stains, and bird droppings must be removed to assure thorough penetration. Additionally, all repairs to the masonry should be completed before the consolidating agent is applied because treated surfaces will not bond to cementitious or synthetic repair materials. The repair work may include pinning, mortar filling, fracture grouting, repointing, adhering detached pieces, and application of biocides, etc. It is important to know that silanes will not fill large cavities nor bridge large gaps. They can be used only for specific aspects of a conservation project.

Most importantly, alkoxy silane consolidants should only be applied by trained applicators who are familiar with these types of chemical preparations. During the application of alkoxy silane consolidants, adequate precautions should be taken to avoid contact with skin and eyes. Safety glasses should be worn at all times for eye protection. In addition to protective clothing, the use of rubber gloves for the applicators is recommended because the silane has a degreasing effect on the skin. The alkoxy silane is volatile and should not be inhaled. Therefore, the use of a respiratory mask is necessary. (Obviously, the material must also not be swallowed or ingested, since it is toxic.) Smoking must be banned in the working area, because alkoxy silane is flammable. Surrounding landscape, lawn and sidewalk areas should be protected from contact with cleaning materials and consolidating treatments through the use of polyethylene sheeting or these areas should be continuously washed with a steady mist of water.

2.4. PROTECTION AND MAINTENANCE:

If an alkoxy silane does not provide water repellency along with its consolidating effect, treated surfaces will be susceptible to weathering influences by absorbing water. Application of a water-repellent material might be indicated to protect treated surfaces from rain or damaging moisture. Alkoxy silane consolidants have a limited service life like other
conservation treatments. After a certain time period, re-application of the same consolidant or a different one will be required for a continuous protection of the masonry substrate.

Above all, buildings, monuments or sculptures can not be preserved by a single treatment. Regular inspection and maintenance of all protective systems are also necessary. Routine maintenance includes improvement of all the systems of protection against rainwater such as roof coverings, gutters, downpipes and flashings, control of rising damp in masonry, repointing of joints with a suitable material, cleaning, removal or control of vegetation, re-application of plaster if it had been used originally for protection of the masonry or earthen substrate. Moreover, careful records of the inspections including monitoring of the consolidated area and detailed description of the treatments which have been applied should be collected in a maintenance manual which establishes a maintenance program for future conservation references.

2.5. EVALUATION TECHNIQUES:

Prior to the application of alkoxysilanes or any other consolidation treatments, it is necessary to conduct a number of laboratory and field tests to understand the ongoing deterioration processes and to identify the most appropriate consolidation treatment for the masonry conditions present at the job site. Although the long-term effectiveness of the reported alkoxysilane applications will help to evaluate them as masonry consolidants, it can not be assumed that their overall performance will be similar for each project which shows a unique set of problems and requirements due to differences in environment, type of stone, degree of stone decay, etc. Additionally, because the value of a preservative is proven with time, there is a lack of performance data for the materials that have recently been used as consolidants. Therefore, there is a need for laboratory test programs to provide the rapid evaluation of any consolidation treatment. Following the complete laboratory tests, on-site test applications are also necessary to confirm the laboratory test
results and specify application procedures.

2.5.1. LABORATORY TESTING PROGRAM:

Laboratory testing programs are designed to assess the physical and chemical properties of the stonework and to identify the factors contributing to its decay. Furthermore, they assist in evaluating the ability of materials to meet the performance criteria for stone consolidants so that the number of available consolidants can be reduced to one or two most promising alternatives. Besides providing a short-term evaluation of the recommended consolidation treatment(s), laboratory programs have the advantage that test conditions can be adjusted to simulate the specific environment and climate to which the consolidant will be exposed. The laboratory test program is conducted in two phases:

1. A complete laboratory evaluation of the untreated masonry samples.
2. A complete laboratory evaluation of the treated masonry samples.

The comparison of the test results derived from tests run on treated and untreated stone samples is the most practical method of evaluating the effectiveness of stone consolidants. Such a comparison will demonstrate how well a consolidation treatment maintains the properties of the treated samples relative to the untreated samples and evaluate the improvement to the material offered by the recommended treatment. There are various test methods which have been developed to measure the durability and physical and chemical properties of natural stone and the effects of exposure to weathering factors. Some of these methods have been standardized by the American Society for Testing and Materials (ASTM), the Deutsche Industrie Norms (German Industrial Standards - DIN), and RILEM Committee (Reunions Internationales des Laboratoires d'Essais et de Recherches sur les Materiaux et les Constructions). A list of these standard test methods which might be used in a laboratory test program is presented in Appendix B.

Selection of samples is critical to a proper laboratory evaluation. For a complete and
reliable laboratory evaluation, samples should represent the variety of decay processes. Therefore, samples should be taken from weathered stone at various locations where degree of stone decay and condition of the stone is different. The number of samples provided for laboratory evaluation is also important to get a comprehensive evaluation. The conservator responsible for the preservation of the structure should be able to judge whether the number of samples submitted for laboratory testing is representative enough of the condition of the masonry. The form and size of the samples for testing can vary depending on the test method. Drill core samples are usually taken from the representative areas. Larger sized specimens, like test bars, are required by some test methods established by ASTM Standards. On the other hand, E.M. Winkler has introduced thin discs for testing the durability and strength of stone. He suggests that the use of small quantities of stone for testing is preferable, because the natural heterogeneity of the stone can lead to inconsistencies in test results. In addition, problems can be faced regarding the total penetration of most stone consolidants when large sized test samples required by some ASTM standard test methods are used.

The following tests are recommended for a comprehensive and reliable laboratory evaluation of untreated masonry samples to determine the suitability of the masonry for consolidation treatment:

- Petrographic Analysis: The material composition of untreated masonry is identified through optical microscopic evaluation and x-ray diffraction analysis which is necessary to determine the appropriateness of the masonry substrate for chemical consolidation treatment.

- Water Solubility: The percent water-soluble contents of untreated masonry samples is determined. Such information is utilized in identifying the vulnerability of the masonry to water-related deterioration.

- Acid Solubility: The percent acid-soluble contents of untreated masonry samples
is determined to identify the masonry's vulnerability to acid-related deterioration when exposed to acidic precipitation.

- Water Absorption: The water absorption capacity and rate are measured for each sample and may be correlated to the masonry's available pore capacity for consolidation treatment. This information is utilized in selection of the most suitable consolidation treatment(s) and application procedures.

- Hygrosopic Moisture Uptake: The hygrosopic characteristics of untreated masonry samples is determined. Such information assists in identifying the kind of natural cements and foreign matter in the masonry samples.

- Anionic Salt Analysis: The percent concentrations of chloride, sulfate and nitrate salts present in each masonry sample are determined. Knowing the nature and distribution of salts in the masonry samples helps to identify the nature and cause of ongoing deterioration.

Once the above testing procedures have been completed, evaluation of the laboratory data in conjunction with the survey of existing conditions of the masonry can assist in identifying the causes of decay, the suitability of the substrate for consolidation and finally in selecting the appropriate consolidant(s) for the masonry conditions present at the job site.

Masonry samples treated with the selected consolidant(s) are then analyzed to determine the performance of the treatment. Consolidating and penetrating abilities of the consolidants, as well as their effect on the appearance and physical properties of the masonry substrate are evaluated. Comparison of treated and untreated samples helps to evaluate the change in the characteristics of the masonry treated with the consolidant. The following tests are suggested for the laboratory evaluation of treated masonry samples:

- Water Solubility
- Acid Solubility
o Water Absorption

The above tests are repeated with treated samples in the same way as described for untreated samples. Treated and untreated samples are then compared to evaluate the change in the characteristics of the masonry caused by the consolidating treatments.

Other tests recommended for the treated samples include:

o Absorption of Treatment: The amount of consolidant deposited in each of the treated masonry samples is determined to evaluate the effectiveness of the treatment and efficiency of the application procedures. An increase in weight after treatment is an indication of new material deposited in the sample by the consolidation treatment.

o Depth of Penetration: The visual evaluation of penetration depth of the proposed consolidant(s) is made by simply splitting the treated samples parallel to the direction of consolidant flow or examining them utilizing a Scanning Electron Microscope. Superficial penetration tends to contribute to further deterioration through the formation of a hardened surface crust.

o Color Change: The visual evaluation of treated and untreated samples are made to determine whether color change and/or surface gloss are created by application of the consolidant.

o Water Vapor Transmission: The water vapor transmission of treated and untreated masonry samples are compared to determine the reduction in water vapor transmission created by the consolidant.

o Compressive Strength / Tensile Strength: The measured compressive strength and tensile strength of treated and untreated masonry samples are compared to estimate the improvement in the mechanical properties of masonry following consolidation and to determine the consolidating abilities of the consolidant.

o Salt Crystallization: The resistance of consolidated samples to the effects of severe weathering and salt crystallization is evaluated by comparing the test results of treated and
untreated samples. Such information is used to assess the long-term effectiveness of the consolidation treatment.

- Accelerated Weathering Tests: The durability and ultraviolet stability of the consolidation treatment is determined by means of chamber accelerated weathering tests. Chamber for Accelerated Decay (CAD) cycles combine chemical attack, water and salt action, thermal effects, and solar radiation which are the causes of stone decay.57

  The consolidants which show the most effective performance for the specific masonry samples may be proposed for evaluation under field conditions.

2.5.2. FIELD TESTING PROGRAM:

Upon the completion of the laboratory tests, it is necessary that a series of field tests be made with each of the prescribed consolidation treatments. Field trials do not provide much information in the short term about the preservative effect of the treatment; nevertheless, they are valuable for the practical experience they provide.

The on-site test area should be representative of the more severely weathered areas and its condition before treatment should be carefully recorded. The size of the test area is suggested as approximately 10 or 20 square feet.58 The test area should be thoroughly cleaned of surface contaminants and allowed to dry prior to application to get adequate penetration of the consolidant. Manufacturer's recommendations are followed for application procedures and rates. After allowing the treatment to cure, core samples are taken from the test area to be submitted for laboratory evaluation which verifies the previous laboratory findings. The comparison of the treated test area to the adjacent untreated area provides an indication of the treatment's effectiveness. Furthermore, on-site testing indicates the rate of application, rate of consumption and exact application procedures to be used under field conditions, such as the number of applications and how the products are applied.
Laboratory and field testing programs are intended to provide some criteria for the evaluation of stone consolidants which will make their selection easier and more precise. However, standard test methods are lacking. Various proposed tests are still in the development stage and it is not yet certain that they will in fact provide realistic assessment of the treatment.

Recently, an ASTM (American Society for Testing and Materials) committee (ASTM Committee E-6 on Buildings) is in the process of establishing a guideline for the selection and use of stone consolidants. There has been some controversy regarding these guidelines. A concern has been voiced by some architectural conservators indicating that these guidelines may mislead some contractors in a way that they may not seek proper professional advice. On the other hand, many conservators favor the development of guidelines which provide basic information about the proper use of consolidants, including the need to seek the specialized service of a conservator in both treatment choice and application.

Laboratory and field tests must also be done for demonstrating effect of combined treatments (e.g. cleaning, consolidation and fills).
END NOTES: CHAPTER 2


31. Ibid.


33. Ibid., p. 832.


40. Ibid., p. 153.

42. A. E. Charola, "Brief Introduction to Silanes, Siloxanes, Silicones and Silicate Esters," p. 315.


CHAPTER 3
REVIEW OF USE OF ALKOXY SILANES IN CONSERVATION

3.1. CONSOLIDATION OF STONE:
3.1.1. HISTORY OF THE USE OF ALKOXY SILANES FOR STONE CONSOLIDATION:

As consolidants, alkoxy silanes, especially ethyl silicate, have found a wide acceptance in present conservation practice. Current literature on consolidation of deteriorated stone contains numerous projects which have utilized ethyl silicates as consolidants with significant success. However, the idea of using ethyl silicate for conservation of stone is not new; it dates back to 1861.

The synthesis of silicon tetrachloride, which was reported by J. J. Berzelius in 1824, stimulated the synthesis of organosilicon compounds, among them tetraethoxysilane and triethoxymethylsilane.¹ In 1846, Von Ebelmen prepared silicic acid ether from silicon tetrachloride and alcohol. In 1874, triethoxymethylsilane was synthesized by A. Ladenberg. Until these substances became available as an industrial chemical, they remained a laboratory curiosity to conservators.

The earliest attempt to use silicic ether or ethyl silicate for stone conservation was made in an 1861 meeting of the Royal Institute of British Architects by A. Hofmann for treatment of the Houses of Parliament in London.² However, it is not clear if this substance was ever utilized on the buildings until the 1920's. In 1923, A. P. Laurie obtained a British patent for the use of silicic ether in stone consolidation. Following this patent, he was granted three similar patents in the United States in 1925 and 1926.³ The liquid he suggested was actually a partially polymerized form of ethyl silicate. Afterwards, to some
extent, silicon esters became available as a commercial product especially in England. During the period from 1927 to 1939, hydrolised derivatives of ethyl silicate, which were broadly studied, interested chemists in a variety of industries, such as the manufacture of paints, coatings, fire-proof textiles, impregnating agents for preservation of stone, brick or woodwork, etc.\(^4\)

In 1932, R. J. Schaffer published a report on the results of weathering behaviour of natural stone treated with silicon esters, sodium silicate, limewash, paraffin wax and other chemicals.\(^5\) None of the preservatives was regarded as effective for the protection of stone. On the other hand in 1934, F. Rathgen and J. Koch mentioned silicic acid esters as effective agents for stone consolidation as a result of extensive experimentation with different stone protection agents.\(^6\) Another British patent obtained by G. King in 1939 claimed the use of fungicides, insecticides, germicides, antiseptic or other substances with silicic esters mainly for masonry preservation.\(^7\)

Around the time of World War II, the improvements relating to the organosilicon industry were rapid. Partially polymerized ethyl silicates, such as ethyl silicate 40, began to be widely marketed. Around 1947, some of the commercial products available from England through Silicon (Organic) Developments Ltd. were: Silester O, apparently ethyl silicate 40; Silester 1 and Silester 2, more highly polymerized ethyl silicate; Kexcement, a mixture of sillimanite and Silester 2.\(^8\) Treatment of stone with ethyl silicate had its start in England, but as early as 1947, experimental studies with various chemical formulations of ethyl silicates, such as condensed ethyl silicate, ethyl silicate 40, were carried out at various historic sites in the United States: Chapel at Valley Forge, PA., the Eternal Light Peace Monument at Gettysburg, PA., adobe huts in Wyoming National Parks, etc.\(^9\) In the early 1950's, the influence of catalysts on the hydrolysis of ethyl silicate was studied in detail.\(^10\) The first publication describing the use of ethyl silicate/methyl(trialkoxy)silane mixtures for stone preservation by J. Blasej et al. in 1959 opened a new era in stone consolidation.\(^11\)
3.1.2. RECENT EXPERIMENTS WITH ALKOXY SILANES IN STONE CONSOLIDATION:

Development of alkoxy silane mixtures stimulated laboratory research and marketing of such products in Europe, particularly in Germany. During the 1960's, laboratory research and experimental field work with silicic acid esters as stone conservation agents were carried out extensively in Germany. Promising results of these tests led to the development of one and two-component stone consolidants based on pure silicic acid esters or a combination of silicic acid esters and organosilicon hydrophobic agents.\textsuperscript{12} Around 1970, German manufacturers such as Wacker-Chemie, Goldschmith AG, Bau-and Silikat Chemie began to market stone consolidants containing chemicals of these types. Two of the most frequently used products are Stone Strengthener H and Stone Strengthener OH which are marketed by Wacker-Chemie. These products are in the form of one-pack materials. In contrast to the Stone Strengthener OH, H product provides water repellency as well as consolidation.

German literature contains numerous enthusiastic reports about the successful application of silicic acid based products to consolidate deteriorated German sandstones. Some of the historic structures treated with alkoxy silanes are Bamberg Cathedral (1973), Cologne Cathedral (1975), and the Alte Pinakotheek in Munich (1975-1976). A partial list of historically important structures and/or statuary which have been consolidated with alkoxy silanes over the years is presented in Appendix C. It includes both European and United States applications.

Josef Riederer reported that during the early 1970's, progress was made not only in the field of research, but also in the techniques applied in Germany.\textsuperscript{13} He emphasized that between 1972 and 1975 the use of ethyl silicates for stone consolidation increased to 38% of all treatments (193 total) in Bavaria, while the use of other polymers and soluble silicates decreased. Riederer claimed that in the case of porous stones, ethyl silicate has
proved to be superior to all other stone consolidants. In his report, the depth of penetration in an ordinary sandstone with ethyl silicate is said to be about 4 cm.

On the other hand, as of 1964 the overall British experience with ethyl silicates were reported disappointing by Bailey and Schaffer. In 1972, John Ashurst and Brian Clarke also reported that any of the stone preservatives, among them ethyl silicate, field tested since 1961 by the Building Research Station and the Ancient Monuments Branch of the Ministry of Works (now Department of the Environment) showed no overall beneficial effects. In spite of these negative results, the use of alkoxy silanes were reexamined by many researchers. Clifford Price, who was a Senior Scientific Officer at the Building Research Station in England, stated that alkoxy silanes were considered to be suitable materials for stone preservation, although they were listed as the most expensive stone preservatives in England.

In 1976, a new consolidant, called Brethane, was developed by C. Price and his team at the Building Research Establishment. Brethane is identified as a three-component product which is mixed immediately before use. The components of Brethane are trimethoxymethylsilane, ethanol, and water. It was reported by Price that, in addition to laboratory testing, field trials were carried out with Brethane involving the treatment of a wide variety of stonework in situ at twenty four sites between 1976 and 1979 to assess the effectiveness of the product. The product was reported to reduce the rate of stone decay very substantially.

Price also pointed out the limitations of Brethane. Treatment was said to be irreversible, but reapplication is possible. Some short term sponginess and darkening in the stone were reported. Brethane was said to be unsuitable for stonework which is heavily contaminated with sodium chloride, since this salt interferes with the setting of Brethane. The product was not recommended for use where there is rising damp. Additionally, high cost and consumption of the material to achieve deep impregnation was noted as a
drawback. It was estimated that 5 litres of Brethane per square metre is required to have a penetration of 25 mm. in a stone with 20% porosity. Additionally, it was suggested that labor costs can be very high, because an operator may only be able to treat an area of 1 m² per day.

Further laboratory studies and field trials were suggested to make a decision about licencing the production and use of Brethane. Since Brethane was a newly developed consolidant, its use was recommended only for cases where decay was advanced. In 1983, Brethane began being marketed by Colebrand Ltd. and it is still on the market.

The Victoria and Albert Museum in London has been actively involved in the problems of stone deterioration and its treatment since 1965. In his 1982 report, Larson outlined the Museum's approach to the techniques of stone conservation, particularly stressing the use of alkoxy silanes for consolidation of stone and marble. Experiments with alkoxy silanes for stone consolidation began in the early 1970's at the Victoria and Albert Museum. Between 1970 and 1982, a variety of commercially available silanes, which included X54-802 (trimethoxymethylsilane), ICI EP 5850 (triethoxymethylsilane), Wacker VP 1301 (ethyl silicate and triethoxyethyl silane), and Tegovakon (a material similar to the Wacker VP 1301), were tested on a range of stones including Carrara marble, several English limestones and some English sandstones.

The author noted that although they all provided some consolidation, gave good penetration and produced little color change on the treated surface, it was X54-802 that gave consistently good results. Anne Moncrieff, a Senior Scientific Officer at the Victoria and Albert Museum, reported that penetration of 5 cm. was achieved with this material on moderately weathered marble. However, the use of X54-802 was discontinued at the Museum in 1977 due to the several problems encountered during its use. Experimental work with another product, Dow-Corning T.40149 (trimethoxymethylsilane), was initiated in 1976 at the Museum. As of 1982, J. H. Larson reported that excellent results were
obtained with this material over a period of six years.\textsuperscript{21}

The penetration of the consolidant in depth is necessary to obtain a lasting effect of the treatment. Not only consolidant itself, but also the method of application has an influence on the effectiveness of a consolidation treatment. Several conservators have expressed their opinions regarding the improvements of application methods to attain deeper penetration with consolidants.

R. Rossi-Manaresi suggested in her paper (1975) that deep penetration is obtained by keeping large quantities of consolidant in close and very long contact with the stone by dabbing with a brush or by a direct, slow percolation process on the surface.\textsuperscript{22} She added that application by spraying can not provide such a close contact.

On the other hand, Rolf Wihr advocated the use of a spray system providing a continuous rain of consolidant and recirculating run off material in order to obtain a deeper penetration, based on observation that stone gradually becomes fully soaked in rain.\textsuperscript{23} Although the high consumption of material and cost of spray apparatus were admitted as disadvantages, the author noted that this method is suitable for large scale building surfaces and provides a greater penetration depth than any other method. It was said that 800 liters of Wacker Stone Strengthener OH was applied by this method to the facade of the fortress of Wurzburg measuring 80 m\textsuperscript{2} in two and a half hours. A penetration depth of up to 25 cm. was achieved. The method was said to be under patent in most European countries.

According to Helmut Weber, repeat application after one or two weeks is an effective method of consolidation treatment, as well as continuous spray applications.\textsuperscript{24} The repeat application has been extensively used on deteriorated sandstones in Germany. The restoration of the Alte Pinakothek, which is a historically important art gallery building in Munich, is worth mentioning because of the conservation approach which was applied.\textsuperscript{25} In 1975, the conservation program was initiated through laboratory and field testing. During the following years, larger on-site test areas were treated and regularly monitored to
evaluate the effectiveness of a variety of consolidation treatments by comparing treated and untreated areas. These tests revealed that a combination of silicic acid esters (Wacker Stone Strengthener OH) followed by silicic acid esters with water repellent additives (Wacker Stone Strengthener H) provided the most satisfactory results. After 10 years of evaluation, previous test results were confirmed and the overall conservation began in 1984.

A vacuum system, named the Balvac system, was developed at the Victoria and Albert Museum for consolidation of decayed stone objects in 1975.\textsuperscript{26} It was reported that with this method, the penetration of the consolidant was greater than that which could be achieved by brush application. However, based on the experiments with vacuum consolidation at the Museum, J. H. Larson pointed out his objections to the system by saying that there are many deficiencies in the use of vacuum impregnation techniques. He claimed that in some cases in England, severe cracking of stone sculpture occurred as a result of the vacuum method. In addition, he reported that, in six years time, two of the sculptures treated with vacuum consolidation at the Museum in 1976 deteriorated more rapidly than the objects treated with brush. He argued that the vacuum method does not seem to encapsulate salts more than brush applied systems. Another drawback reported was that after the vacuum is released, the consolidant tends to migrate inwards resulting in lesser consolidation of the surface than of the inside of the stone. Also, this method is of no use on buildings.

Increasing research into the development of alkoxysilanes as stone consolidants led to development of mixtures of acrylics and alkoxysilanes as an alternative. It is believed that combining the qualities of both products might create a more effective range of consolidants.

Acrylic/silane mixtures have been used extensively in the restoration of several monuments in Italy. Between 1973 and 1974, the Centro per la Conservazione delle Sculture All'aperto carried out a series of experimental testing of ten commercially available
stone consolidants applied to a calcitic Bologna sandstone. The main concern of the study was to find efficient methods of consolidation for the sandstone monuments in Bologna which were in an advanced state of deterioration. Each consolidant was applied both in situ, on different monuments, and in the laboratory on samples of the same sandstone.

As part of this study, O. Nonfarmale carried out the treatment of the Francisco Coriolani tomb (1555) and the Joannes Brand tomb (15th century) in the cloister of St. Domenico's church in Bologna. Exfoliating and crumbling sandstone of these tombs were consolidated by a mixture of acrylic resin (Paraloid B-72) and silane (Dri-Film 104, prepolymerized methylalkoxysilane) in organic solvent, based on the thought that the adhesive properties of the acrylic resin and the consolidating, water repellent properties of the silane could be combined. The surface was impregnated with the mixture, first by spraying then by brushing (total 5 applications) to prevent the breaking away of raised crusts. The restoration was completed with a mechanical cleaning process. Overall, the treatment was reported as successful and long lasting. After treatment, all the raised crusts were reattached to the surface.

However, in a later report R. Rossi-Manaresi and A. Tucci pointed out that the mixture Paraloid B-72/Dri-Film 104 has a disadvantage in that it causes a slight darkening of the treated stone. In addition, preconsolidation of exfoliating sandstone with this mixture was said to prevent subsequent cleaning by pack techniques, such as poultices. Because reattached crusts may be loosened and detached through the application of pack techniques, it seems that only mechanical cleaning is applicable in this case, which is time consuming and not feasible for large surfaces. The water repellent nature of the mixture also prevents cleaning with water.

The authors proposed that a preconsolidation of similar calcite-cemented sandstone with an acrylic/siliconate/lime water mixture (Primal AC33/ Silirain-Water/ Lime water) appears to reattach loose flakes, does not produce any darkening effect and allows an easy,
safe cleaning utilizing pack techniques. They investigated the possibility of using this mixture, instead of Paraloid B-72/Dri-Film 104, for final impregnation, too. It was concluded that the more concentrated formulation of acrylic/siliconate/limewater mixture is adequate for final repeated impregnation, since it proved to provide a consolidative and protective effect similar to that of Paraloid B-72/Dri-Film 104. However, this treatment was reported to produce a whitening effect, if not properly applied.

The Victoria and Albert Museum in London started experimental testing with acrylic/silane mixtures in 1978. J. H. Larson claimed that silanes make very good deep consolidants, but poor surface consolidants, whereas acrylics are known as good surface consolidants, but are not effective for consolidation in depth. Thus, the combination of two might exhibit better performance.

One of the mixtures tested was Raccanello E.0057 (acrylic) diluted with Dow-Corning T.40149 (trimethoxymethylsilane) forming solutions varying from 5%-20% (by volume). This treatment is mentioned as the main consolidation treatment used at the Museum at the time (1982). The author indicated that although this combination produces only a mixture rather than a chemical bonding, it has several advantages over the majority of silane treatments.

For one thing, extremely good penetration into stone and marble was achieved with this mixture simply by brush application. The penetration of 5 cm. was achieved on a French limestone sample with this treatment in the Museum. Retreatment with the above mixture was also said to be possible. It was said that preconsolidation carried out with the same mixture can allow subsequent cleaning by using solvents, such as acetone and toluene. Furthermore, the ease of bonding the pieces treated with acrylic/silane mixture by using a range of acrylic, polyester and epoxy adhesives and long-term durability of acrylic fillers for acrylic/silane consolidated stones were mentioned as advantages.

Larson reported that two sculptures in the Museum (Bernini's 'Neptune and Triton'
Sculpture, Carrara marble; 12th century English Sculpture, Caen stone) were consolidated successfully with T.40149/E.0057 around 1982.

In 1980, experimental testing with another acrylic/silane mixture, Dow-Corning T.40149 and Paraloid B-72, started in the Victoria and Albert Museum. Paraloid B-72 was said to be dissolved in T.40149 without the addition of any solvent, so that the acrylic content of the solution could be quantified. The effectiveness of the treatment was reported to be very promising based on trials on English sandstones, limestones and Carrara marble with solutions containing between 2% and 5% of acrylic to silane.

As a result of extensive practical experience at the British Museum, S. B. Hanna reported that highly successful results were obtained by using silane systems in the treatment of badly deteriorated limestones. The British Museum adopted two different silanes for further evaluation for the treatment of salt-contaminated, extensively deteriorated limestones in the early 1980's. Wacker Stone Strengthener OH and uncatalyzed acrylic/silane mixture (Dow-Corning T.40149/Raccanello E.55050) were chosen based on successful experiences elsewhere.

Hanna indicated that although Wacker OH restores physical strength to the stone, it is more difficult to clean the surface after consolidation than when using the acrylic/silane mixture. After treatment with the Wacker system, the reattachment of detached flakes were said to be possible by using an acrylic resin. Retreatment is also claimed to be possible with this consolidant.

According to Hanna, solutions of Raccanello E.55050 in Dow-Corning T.40149 with varying strengths (5, 10, 15 and 20%-by volume) also yielded effective results. Initial darkening as a drawback of this treatment was reported. However, it was said to fade away during the following 12 months. The author advised not to apply more than 20% concentrations of acrylic, since percentages above this point can cause residual darkening and disruption within the stone if applied in more than 100 ml. quantities at any one time. It
appears that T.40149 and E.55050 do not form copolymers within the stone. It is assumed that the silane acts as a solvent carrying the acrylic to a greater depth of penetration than it would achieve on its own.

In 1984, the badly degraded Egyptian limestone head of Amenophis III (1417-1379 B.C.) was treated with both alkoxysilane and acrylic/silane mixture at the British Museum. Initial application of uncatalyzed silane (Dow-Corning T.40149, trimethoxymethylsilane) was said to aid the subsequent applications of the acrylic/silane mixture and increase the capacity of the stone to absorb more viscous acrylic/silane solution. During the subsequent applications the acrylic content of the solution was increased from 5% to 20%. Acetone was applied on cotton wool swabs to clean the surface after consolidation.

Another report by S. M. Bradley regarding an investigation of the effectiveness of organo silanes on deteriorated limestone at the British Museum concluded that Wacker stone Strengthener H, Wacker Stone Strengthener OH and a solution of Raccanello acrylic in trimethoxymethylsilane are suitable materials for consolidation of deteriorated limestone sculpture displayed indoors. A study of a variety of commercial stone consolidants on three different limestones by E. D. Witte et al. came to the conclusion that ethyl silicates are the most promising consolidants.

It is apparent from the experiences reported above that alkoxysilanes are still promising materials for stone consolidation. A certain optimism has resulted from increased research on the development of different techniques and the materials themselves. However, a lot more research needs to be done on the evaluation of the long-term effectiveness of past treatments as well as new materials, new combinations of materials and new techniques.
3.2. CONSOLIDATION OF EARTHEN BUILDING MATERIALS:

Adobe, also called mudbrick or sun-dried brick, and related earthen building materials and techniques are among the oldest and most common building materials on earth. Construction with rammed earth dates back to the Neolithic period (10,000 to 3,000 B.C.). Adobe is still widely used with various traditional techniques in many countries. Today, by various estimates, between 30 and 40 percent of the world's population lives in earthen buildings.

Adobe building materials are made by mixing sand, silt and clay with water to an adequate plasticity so that it can be formed in wooden molds or used as mortar or plaster. Often, fibrous organic materials, such as straw and animal hair are added to reduce the cracking when the adobe dries. Adobe, by its composition, is less durable than stone and obviously more susceptible to weathering. Generally, the deterioration of adobe structures is attributable to excessive moisture, either rainwater or ground water. When the moisture content reaches an extreme level, the mechanical strength of the adobe is reduced beyond the loads placed on it. As a result, the structure can collapse partially or completely. The consolidation of vertical surfaces and the capping of the top part of earth walls play an important role among the various preservation techniques of earthen architecture, especially earthen archaeological sites. Mainly, synthetic resins, usually thermoplastics, and ethyl silicates are used as consolidants on adobe. Since 1969, ethyl silicate has been applied to the consolidation of adobe with satisfactory results.

As early as 1942, John B. Stone and Abraham J. Teplitz obtained a patent for the use of "alkyl silicate" in earth consolidation, with particular application to oil wells. Partially polymerized ethyl silicates were considered preferable in order to create high strength and hardness. It was not until 26 years later that a strong interest began at an international level in the preservation problems associated with earth structures and a critical need for the preservation of earthen architecture has been acknowledged by many countries.
where the tradition of using earth as a building material exists.

In 1968, research regarding the conservation of archaeological sites in unbaked earth was carried out in Iraq. After studying the actual causes of the mud-brick deterioration, laboratory tests were performed for surface protection. Among the various products available at the time, ethyl silicate seemed to give the best preliminary results. In 1969, large scale field tests with partially polymerized ethyl silicate were done in the Seleucia area and in Hatra. Ethyl silicate was sprayed onto the vertical surfaces of the mudbrick walls.

There are several publications on the evaluation of this work. Giorgio Torraca reported in 1970 that the penetration of the partially polymerized ethyl silicate [Silester OS (Monsanto)] was poor (10-15 mm). A later report by Gilbert Bultinck in the same year indicated that partially polymerized ethyl silicate formed a hard surface layer without adhesion to the mudbrick, based on examination during the previous field tests in Iraq. According to Giacomo Chiari, approximately in two years time, ethyl silicate treated walls were still in perfect condition compared to untreated walls, in the spring of 1971. Twenty years after the field applications, he evaluated the performance of the field treatments with ethyl silicate. Ethyl silicate treatment was not effective on the surfaces of walls severely affected by salt water, especially at the Seleucia Archives. On the other hand, ethyl silicate treatment seemed to be sufficient to provide the necessary water resistance in Hatra where the water table was much lower. It was reported that even very fine details were perfectly preserved. It should be stressed, however, that the site was simply abandoned and no maintenance work has been done since 1971. It is apparent that the lack of maintenance over such a long period played a significant role in the failure related to the various conservation measures undertaken in this site. Without constant maintenance and repair, there is little hope in preserving mudbrick structures, regardless of the treatment performed.
While this research was being carried out in Iraq, two international symposia on mudbrick conservation were held in Yazd, in 1971 and 1976, by the Iranian National Committee of ICOMOS. In following years, many other meetings on the conservation of mudbrick and other raw earth materials were held for the purpose of establishing a methodology for the study of earthen structures and archaeological ruins, exchange of ideas and experience, and expanding current knowledge of appropriate techniques for the conservation of earthen architecture. These meetings are listed in Appendix D.

Ethyl silicate based consolidants have been applied with success in many other sites and countries, as well. The treatment of some painted and unpainted adobe friezes with ethyl silicate in two archaeological sites in Peru, Garagay and Chan Chan, were sponsored by UNESCO (1975-1977). The mud friezes in Chan Chan exhibited hygroscopic salt deposition. These salts are deposited by winds carrying small droplets of sea water. Small holes in the friezes were filled with mud before the application of ethyl silicate. Treatment of adobe friezes in Chan Chan was particularly successful, even though they were exposed to sea aerosol for 10 years and subjected to a severe flood in 1983.

In the case of Garagay, problems were different, because the friezes have painted figures. Several applications of ethyl silicate were performed by spraying to consolidate the mudbrick support of the painting even before attempting to clean the surface. Applications were a few days apart. In addition, a series of injections of an acrylic emulsion were made through the preexisting cracks to strengthen the inner part of the wall. Finally, an acrylic resin (Paraloid) was applied to fix the superficial layers of painting. Chiari indicated in his 1980 report that the results of the adobe frieze treatment in Peru were very encouraging. He also pointed out that the use of mixed techniques has an advantage of overlapping the best properties of each product, for instance ethyl silicate performs well on the surface as a consolidant, while acrylic or polyvinylic resins work well as binding agents, when injected inside the wall.
The mudbrick support of an ancient wall painting (3500-3000 B.C.) from the site of Teleilat Ghassul, Jordan was treated with an ethyl silicate consolidant [Stone Strengthener H (Wacker)] in 1978 and 1979. The painting was broken into many pieces and fragments. After strengthening the paint layer and gluing the small fragments, the major pieces were completely impregnated from the rear face through capillary absorption by placing the mudbrick surface in a shallow pool of a 50 % solution of Wacker Stone Strengthener H in toluene. It was reported that the requisite degree of strengthening effect was produced for the previously very friable mudbrick and this eased the handling and prevented the damage which could have occurred during reassembling and mounting the pieces to reconstitute the total mural. After the completion of treatment, the painting was installed in the Amman Museum.

There are several studies related to the long-term effectiveness of an ethyl silicate based consolidant on mudbrick. Lewin and Schwartzbaum studied the untreated and treated specimens of the Teleilat Ghassul mural painting, which remained for future study, to determine the effect of four years of normal indoor aging on the composition of the consolidant and on the impregnated material. They concluded that the hydrolysis continues to occur very slowly during long-term aging, because reactive ethoxy groups were still present in the treated material. Whether this slow increase in the degree of hydrolysis during aging can result in a loss of consolidating and strengthening effect is open to debate. If so, a retreatment with ethyl silicate to regain the required degree of consolidation might be a possibility, but only if the material has regained its original porosity. In addition, it is known that as the hydrolysis reactions continue toward completion, a decrease in volume is produced, However, it is not yet known whether or not this shrinking can generate stress in the material in the long-term.

More recently, in 1987, Chiari studied the samples from an adobe brick coming from the Huaca de la Luna in Trujillo, Peru for the purpose of obtaining more data on the
long-term behavior of ethyl silicate treatment. The samples were treated by complete impregnation with partially polymerized ethyl silicate [Silester ZNS (Monsanto)] dispersed in alcohol. Following treatment, the samples were photographed under a Scanning Electron Microscope (SEM) at different time intervals, from one day to sixteen months, to observe the chemical interaction of ethyl silicate based consolidant with adobe at the microscopic level. These observations also confirmed the slowness of the hydrolysis reaction, although the results of this study are considered preliminary due to the short time range. In addition, it was observed that the material regained its porosity and general appearance, but kept the desired property of water resistance. Based on the fact that the structure of the material undergoes so little modification with ethyl silicate based treatment, Chiari suggests that reapplication of other consolidants can be considered, if needed. He does not recommend the ethyl silicate based consolidants blended with water repellent organosilicon components (such as Wacker H, a mixture of methyltriethoxysilane and tetraethoxysilane in toluene solvent and catalyst) for an adobe treatment. This is because water repellency, both at vapor and liquid level, is not a desirable property for adobe conservation.

In 1985, the Museum of New Mexico started an adobe test wall program at Fort Selden State Monument, in Southern New Mexico, USA. Test walls were constructed to monitor the erosional rates of selected adobe preservation techniques in the hope that the experiments will provide information regarding the long-term preservation requirements of the historic walls at Fort Selden, as well as other earth buildings. This phase of the test wall project is scheduled for completion in 1995. Experiments included assessing the efficacy of chemically amended mud plaster, observing capillary rise in relation to the different wall bases, and evaluation of various capping techniques to protect the top part of the walls. The chemical substances were either sprayed on the wall surface, applied with a paint roller, or mixed in with the mud plaster. It was reported by Taylor that preservation techniques employed on these test walls showed a varied range of erosional patterns after

---

69
three and a half years of exposure.\textsuperscript{50} Overall, it was observed that the chemically amended mixes have eroded much less than the spray and roll-on applications. Spalling occurred in the plastered surfaces of the sprayed panels.

A collaborative program was established at Fort Selden by the Getty Conservation Institute (GCI) and the Museum of New Mexico State Monument early in 1988.\textsuperscript{51} More test walls were built in order to evaluate various preservation materials and techniques that do not change the wall’s physical appearance, such as plastering, capping, etc. The experiments included: the application of consolidants, consolidant application techniques, drainage, shelter designs and materials, reburial techniques for archaeological sites, and some structural reinforcing material and methods.

The consolidants used for the treatment of the adobe test walls were alkoxy silanes [Stone Strengthener H (ProSoCo) and Stone Strengthener OH (ProSoCo)] and isocyanates which exhibited most satisfactory results against deterioration by water and salts during the preliminary laboratory testing performed by the Getty Conservation Institute at the end of 1986.\textsuperscript{52} Alkoxy silanes were applied in different amounts and solvent mixtures (ketone and mineral spirits) by spraying, brushing, multiple coating, and bulk infiltration. Bulk infiltration is a technique whereby holes are drilled into the wall and funnels are used to deliver consolidant to a substantial depth where impregnation is obtained. Bulk infiltration was used in combination with surface application of consolidant by brushing. After one month’s curing, test walls were subjected to an accelerated weathering water spray system in order to evaluate materials and procedures in a short time period. Two water spray cycles per day were applied for two months, and later on walls were allowed to weather naturally.

After two and a half years of weathering, an evaluation of this experiment by Charles Selwitz et al. indicated that, in general, a mixture of methyltriethoxysilane and ethyl silicate was found to be effective while ethyl silicate was not.\textsuperscript{53} The test walls treated with Stone Strengthener H showed good consolidation without discoloration. However, the
same walls exhibited surface erosion. The better result was obtained with Stone Strengthener H in a mineral spirits solvent rather than the ketone solvent. The authors suggested that it was the presence of heavier hydrocarbons in the solvent which provided additional water barrier and repellency properties.

Trials with alkoxy silanes on the historic adobe from the 19th century adobe remains at Fort Selden were also carried out. Although the aged adobe took up the consolidants, it was not mechanically strengthened. Authors theorize that a slow dehydration takes place which takes the clay to a form that prevents the water-based curing mechanism from occurring. They suggest a rehydration of aged adobe before consolidation may be required.

Different findings were reported by Helmi who studied mudbrick samples from two archaeological sites in Egypt to determine the deterioration factors of adobe and to find out the suitable consolidants for their conservation. Samples were treated with tetraethoxysilane, trimethylmethoxysilane, and methylmethacrylate-buthylacrylate copolymer. Two applications were performed, a month apart, then samples were allowed to cure for one month before scanning electron microscope examination. Deterioration of this particular mudbrick was due to ground water infiltration, temperature fluctuation between day and night and wind abrasion. In addition, the author claims that the adobe's texture, which is formed of ill-sorted and loosely packed constituent grains of different sizes, accelerated the deterioration. It was concluded from the obtained data that ethyl silicate is the most suitable consolidant for the studied Egyptian adobe. Ethyl silicate succeeded in forming the network links of the polymer, whereas trimethylmethoxysilane formed a less continuous layer on the grains.

The composition and grain size distribution of adobe are important factors when choosing the right type of consolidant. Neville Agnew et al, studied the interaction of chemical consolidants with adobe and adobe constituents and came to the conclusion that adobes containing kaolinite are effectively consolidated with silanes. On the other hand,
silanes do not develop a strong enough bond to bridge quartz and montmorillonite particles, which is why they do not perform well on adobes containing montmorillonite, and/or mixed-layer clays.

As is obvious from the preceding discussion, controversial results have been obtained from different research and experiments regarding the use of alkoxysilanes for the conservation of earthen building materials. For instance, according to Chiari,56 a suitable consolidant for adobe should provide water resistance but not water repellency in order to allow water migration both in liquid and vapor phase while the research project at Fort Selden confirms the effectiveness of alkoxysilanes which also provide water repellency. Although alkoxysilanes seem to be most promising consolidation materials for adobe, as in the case of stone consolidation, there is still a need for more research both on the materials and the application techniques. It is also crucial that past treatments continue to be monitored since this will yield very valuable information for researchers.
END NOTES: CHAPTER 3


2. Ibid., pp. 155-156.


4. Ibid., pp. 157-162.

5. Ibid., pp. 162.


8. Ibid., p. 166.

9. Ibid., p. 165.

10. Ibid., p. 151.

11. Ibid., p. 171.


16. Ibid., p.184.


32. Ibid., pp. 174-176.


44. Ibid., pp. 77-81.


CHAPTER 4
CONCLUSIONS AND RECOMMENDATIONS

Off all products applied over the years, alkoxysilanes and related compounds are still the most promising consolidants. After more than twenty years of experience, alkoxysilanes have so far proved to be effective for the consolidation of sandstones, limestones and earthen building materials. Considering the chemical structure, their big advantage is that they polymerize to produce a chemically stable end-product similar to the minerals composing the stone (e.g. sandstone and earth) itself. Their ability to penetrate deeply into porous stone, which derives at least in part from the extremely low viscosity of the monomers, also makes alkoxysilanes attractive consolidants.

While these properties favor the choice of alkoxysilanes as consolidants where such treatment is necessary, there are various factors which have not been fully explored. The mechanism of polymerization and the effect which the rates of hydrolysis and condensation reactions have on the structure and stability of the resulting polymer are some of the aspects that are still open to debate. Similarly, the effects of factors such as temperature, relative humidity and the presence of salts on the consolidation process are not completely understood. It is apparent that a lot more research needs to be done before a complete understanding of the functioning of silane systems is achieved. Not only the materials themselves and the conditions that affect the behavior of the materials, but also the application techniques utilized require further study. Controversy in the publications over the use of alkoxysilanes on stone and adobe conservation might partially result from the lack of research and an incomplete understanding of the complexity of alkoxysilane chemistry.
Other factors also need to be considered. For example, alkoxysilanes are rather expensive materials. The labor costs of application may also be very high. It would, therefore, be unreasonable to treat large areas with alkoxysilanes. Spray application also limits their use, making them more suited to small objects or architectural details rather than large building surfaces.

There is no doubt that alkoxysilanes have extended the life of decaying stonework in many cases. However, alkoxysilanes, like other conservation materials, can provide a consolidative and protective effect only for a limited time period. Thereafter, reapplication of the same consolidant or a different one will become an issue. Although it has been claimed by many authors that alkoxysilane treated stone would be capable of absorbing a further treatment, very little has been published about the retreatment of alkoxysilane treated stone or adobe. Many questions can be raised such as: Can alkoxysilane treated stone be retreated with the same or another consolidant? What will be the effect of retreatment on the first treatment? What will be the cumulative effects of repeated treatment on the original historic material? There is clearly a need for more research on the retreatment of consolidated masonry and earthen materials in order to provide answers to these and related questions.

Current literature includes an increasing number of case studies where alkoxysilanes have been used as consolidants. However, information concerning the long-term effectiveness of these reported applications are rarely documented. Well-documented, detailed descriptions of the treatments and records of subsequent inspections including regular monitoring of the consolidated area should become part of the conservation program. This information will assist conservators in evaluating the effectiveness of various treatments. In this regard, documentation of unsuccessful consolidation is as valuable as successful work, because it too, provides important feedback. Documentation methods, which best record before and after treatment conditions, need to be further
investigated and standardized.

However, although the long-term performance of a consolidant can only be proved with time, it is not always possible to wait for years in order to evaluate a particular treatment. In addition, lack of performance data for the newly developed materials creates a need for laboratory and field tests to provide a reliable indication of a treatment's effectiveness. Unfortunately, the development of such tests is still in a very early stage and it is not certain that they provide a realistic basis for the evaluation of a treatment. More work is needed to develop truly indicative laboratory and field tests for the evaluation of consolidation treatments.

In conclusion, it is evident that there have been radical changes in the conservation of stone and earthen building materials in the past twenty years and these developments will undoubtedly be subject to further changes in the future. There will never be an 'ideal' material in the field of stone and adobe consolidation, because one can not expect to formulate one single system for a wide range of problems. Different projects will require different approaches and methods of treatment. Basic principles like minimum intervention and reversibility, or at least retreatability, must still be considered. Though research into new conservation materials has its place, it is only through a complete understanding of traditional materials and technologies and mechanisms of decay that suitable approaches can be developed for a wide variety of issues in conservation.
This information is obtained from a variety of sources. The name of the products and the addresses of the manufacturers included in this list thus may be out-of-date.

<table>
<thead>
<tr>
<th>PRODUCT NAME</th>
<th>COMPONENTS</th>
<th>MANUFACTURER</th>
</tr>
</thead>
<tbody>
<tr>
<td>MONUMENTIQUE</td>
<td>One-component Silicon Ester (without water repellent)</td>
<td>Bau-Chemie Prochaska und Pucher KG</td>
</tr>
<tr>
<td>Sandstone Consolidant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brethane</td>
<td>Three-compound product Trimethoxymethylsilane, Ethanol, Water, and Manosec Lead-36 catalyst</td>
<td>Bau-Chemie Prochaska und Pucher KG</td>
</tr>
<tr>
<td>T4-0149</td>
<td>Trimethoxymethylsilane</td>
<td>Dow Corning Ltd.</td>
</tr>
<tr>
<td>Z-6070</td>
<td>Trimethoxymethylsilane (same chemical compound as T4-0149, but with different marketing purposes)</td>
<td>Dow Corning Ltd.</td>
</tr>
<tr>
<td>X1-9010</td>
<td>Triethoxysilane</td>
<td>Dow Corning Ltd.</td>
</tr>
<tr>
<td>Dynasil A</td>
<td>Ethyl Silicate</td>
<td>Dynamit Nobel AG</td>
</tr>
<tr>
<td>Dynasil 51</td>
<td>Partially Polymerized Methyl Silicate</td>
<td>Dynamit Nobel AG</td>
</tr>
<tr>
<td>Dynasil 40</td>
<td>Partially Polymerized Ethyl Silicate</td>
<td>Dynamit Nobel AG</td>
</tr>
<tr>
<td>DRI FILM 104</td>
<td>Prepolymerized Methylalkoxysilane</td>
<td>General Electric</td>
</tr>
<tr>
<td>PRODUCT NAME</td>
<td>COMPONENTS</td>
<td>MANUFACTURER</td>
</tr>
<tr>
<td>---------------------</td>
<td>---------------------------------------------------------------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>TEGOVAKON H</td>
<td>Two-component mixture of Silicon Esters with Water-Repellent</td>
<td>Th. Goldschmidt AG</td>
</tr>
<tr>
<td>TEGOVAKON GS</td>
<td>One-component product similar to TEGOVAKON H</td>
<td>Th. Goldschmidt AG</td>
</tr>
<tr>
<td>TEGOVAKON V</td>
<td>Ethyl Silicate</td>
<td>Th. Goldschmidt AG</td>
</tr>
<tr>
<td>TEGOVAKON T</td>
<td>Ethyl Silicate and Triethoxymethylsilane</td>
<td>Th. Goldschmidt AG</td>
</tr>
<tr>
<td>Aqua-Trete</td>
<td>Alkylalkoxysilane(97%) Methanol</td>
<td>Hüls America, Inc.</td>
</tr>
<tr>
<td>EP 5850</td>
<td>Triethoxysilane</td>
<td>ICI Organic Division</td>
</tr>
<tr>
<td>Silester OS</td>
<td>Partially Polymerized Ethyl Silicate with 40% available silica</td>
<td>Monsanto Company</td>
</tr>
<tr>
<td>Silester ZNS</td>
<td>Partially Polymerized Ethyl Silicate with 40% available silica</td>
<td>Monsanto Company</td>
</tr>
<tr>
<td>BR 74</td>
<td>Partially Polymerized</td>
<td>Montecatini, Società</td>
</tr>
<tr>
<td>Raccanello E55050</td>
<td>Acrylic-silane</td>
<td>Raccanello</td>
</tr>
<tr>
<td>Raccanello E0057</td>
<td>Acrylic-silane</td>
<td>Raccanello</td>
</tr>
<tr>
<td>Wykester</td>
<td>Silicon Ester</td>
<td>Richardson and Starling, Ltd.</td>
</tr>
<tr>
<td>Rhodorsil X54-802</td>
<td>Trimethoxymethylsilane</td>
<td>Rhône-Poulenc</td>
</tr>
<tr>
<td>Silester O</td>
<td>Partially Polymerized Ethyl Silicate with 40% available silica</td>
<td>Silicon (Organic) Developments Ltd.</td>
</tr>
<tr>
<td>Silester 1</td>
<td>Partially Polymerized Ethyl Silicate with a condensing agent</td>
<td>Silicon (Organic) Developments Ltd.</td>
</tr>
<tr>
<td>Silester 2</td>
<td>Partially Polymerized Ethyl Silicate with a condensing agent</td>
<td>Silicon (Organic) Developments Ltd.</td>
</tr>
<tr>
<td>Tetra(ethyl)orthosilicate (TEOS)</td>
<td>Ethyl Silicate</td>
<td>Union Carbide and Carbon Chemicals Corporation</td>
</tr>
<tr>
<td>PRODUCT NAME</td>
<td>COMPONENTS</td>
<td>MANUFACTURER</td>
</tr>
<tr>
<td>----------------------</td>
<td>-------------------------------------------------------</td>
<td>---------------------------------------------------</td>
</tr>
<tr>
<td>Ethyl Silicate 40</td>
<td>Partially Polymerized Ethyl Silicate with 40% available silica</td>
<td>Union Carbide and Carbon Chemicals Corporation</td>
</tr>
<tr>
<td>A-174</td>
<td>Methyl Acrylopropyl Trimethoxysilane</td>
<td>Union Carbide and Carbon Chemicals Corporation</td>
</tr>
<tr>
<td>A-1100</td>
<td>Aminopropyl Trimethoxysilane</td>
<td>Union Carbide and Carbon Chemicals Corporation</td>
</tr>
<tr>
<td>Strengthener H (Conservare H)</td>
<td>One-component product Ethyl Silicate and Triethoxymethylsilane</td>
<td>Wacker-Chemie GmbH Germany ProSoCo, Inc./USA</td>
</tr>
<tr>
<td>Strengthener OH (Conservare OH)</td>
<td>One-component product Ethyl Silicate</td>
<td>Wacker-Chemie GmbH Germany ProSoCo, Inc.</td>
</tr>
<tr>
<td>Conservare H40 Water Repellent</td>
<td>Ethyl Silicate</td>
<td>ProSoCo, Inc.</td>
</tr>
</tbody>
</table>

**MANUFACTURERS LIST:**

- Bau-Chemie Prochaska und Pucher KG 81 Garmisch-Partenkirchen Austria
- Ciba-Geigy AC CH-4002 Basel Switzerland
- Colebrand Ltd. 20 Warwick St., Regent St. London, W1R 6BE England
- Dow Corning, Ltd. Midland Michigan, 48640, USA/ Barry, Glamorgam CF 677L England
- Dynamit Nobel AG Troisdorf Germany
- Th. Goldschmidt AG Essen Germany
- ICI Organic Division Penart Research Center Penart House, Otterbourne Hill Winchester, Hampshire, England
### MANUFACTURERS LIST:

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Address/Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monsanto Company</td>
<td>800 North Lindberg Blvd. St. Louis, MO 63166 USA</td>
</tr>
<tr>
<td>Montecatini, Società</td>
<td>Via F. Turati 18, Milan, Italy</td>
</tr>
<tr>
<td>ProSoCo, Inc.</td>
<td>P.O.Box 1578 Kansas City, KS 66117 USA</td>
</tr>
<tr>
<td>Raccanello</td>
<td>Ard.F.lli. Raccanello S.p.A. Industria Vernice e Smalti, Padua Italy</td>
</tr>
<tr>
<td>Rhône-Poulenc Industries</td>
<td>22 Avenue Montaigne F 75008 Paris France</td>
</tr>
<tr>
<td>Richardson and Starling, Ltd.</td>
<td>Winchester England</td>
</tr>
<tr>
<td>Rohm GmbH</td>
<td>Postfach 4242, Kirschenallee D6100 Darmstadt 1 Germany</td>
</tr>
<tr>
<td>Silicon(Organic) Developments, Ltd.</td>
<td>11 Cavendish Place London W1 England</td>
</tr>
<tr>
<td>Union Carbide Corp.</td>
<td>30 E. 42nd Street, New York USA</td>
</tr>
<tr>
<td>Wacker-Chemie GmbH</td>
<td>Sparte E, Postfach D800 Munchen 22 Germany</td>
</tr>
</tbody>
</table>
APPENDIX B

TEST METHODS FOR THE LABORATORY EVALUATION OF STONE

The test methods regarding natural stone listed below are taken from tests published by the American Society for Testing and Materials (ASTM) and the Deutsche Industrie Norms (German Industrial Standards - DIN).

AMERICAN SOCIETY FOR TESTING AND MATERIALS STANDARD TEST METHODS REGARDING STONE:

<table>
<thead>
<tr>
<th>ASTM TEST METHOD</th>
<th>PROPERTY</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-117-64</td>
<td>Standard Method of Salt Spray (Fog) Testing.</td>
</tr>
<tr>
<td>C-20</td>
<td>Apparent Porosity.</td>
</tr>
<tr>
<td>C-88-69</td>
<td>Sodium Sulfate Crystallization.</td>
</tr>
<tr>
<td>C-97-47</td>
<td>Absorption and Bulk Specific Gravity of Natural Building Stone.</td>
</tr>
<tr>
<td>C-99-52</td>
<td>Modulus of Rupture.</td>
</tr>
<tr>
<td>C-170-50</td>
<td>Compressive Strength of Natural Building Stone.</td>
</tr>
<tr>
<td>C-241-51</td>
<td>Abrasion Resistance.</td>
</tr>
<tr>
<td>C-355-64</td>
<td>Standard Methods of Test for Water Vapor Transmission of Thick Materials (It can be used for stone).</td>
</tr>
<tr>
<td>ASTM TEST METHOD</td>
<td>PROPERTY</td>
</tr>
<tr>
<td>------------------</td>
<td>----------</td>
</tr>
<tr>
<td>D-119-71</td>
<td>Standard Definitions Relating to Natural Building Stones.</td>
</tr>
<tr>
<td>D-2247-68</td>
<td>Standard Test Method of Testing Coated Metal Specimens at 100 Percent Relative Humidity (Water Condensation / Evaporation). It can be used for stone.</td>
</tr>
<tr>
<td>D-822</td>
<td>Recommended Practice for Operating Light- and Water- Exposure Apparatus (Carbon Arc Type).</td>
</tr>
</tbody>
</table>

**DEUTSCHE INDUSTRIE NORMS (GERMAN INDUSTRIAL STANDARDS-DIN)**

**REGARDING STONE:**

<table>
<thead>
<tr>
<th>DIN TEST METHOD</th>
<th>PROPERTY</th>
</tr>
</thead>
<tbody>
<tr>
<td>50017</td>
<td>Testing of Materials, Structural Components and Equipment, Method of Test in Damp Heat Alternating Atmosphere Containing Sulfur Dioxide</td>
</tr>
<tr>
<td>DIN TEST METHOD</td>
<td>PROPERTY</td>
</tr>
<tr>
<td>-----------------</td>
<td>----------</td>
</tr>
<tr>
<td>50018</td>
<td>Sulfurous Acid Fog.</td>
</tr>
<tr>
<td>52100</td>
<td>Guidelines for the Testing of Natural Stone.</td>
</tr>
<tr>
<td>52101</td>
<td>Sampling.</td>
</tr>
<tr>
<td>52102</td>
<td>Determination of Density, Bulk Density, True Density, Density Grade, True Porosity.</td>
</tr>
<tr>
<td>52103</td>
<td>Determination of Water Absorption.</td>
</tr>
<tr>
<td>52105</td>
<td>Compression Test.</td>
</tr>
<tr>
<td>52106</td>
<td>Principles for the Assessment of the Weathering Resistance.</td>
</tr>
<tr>
<td>52107</td>
<td>Resistance to Impact (cubes).</td>
</tr>
<tr>
<td>52108</td>
<td>Wear Test with Grinding Wheel.</td>
</tr>
<tr>
<td>52111</td>
<td>Sodium Sulfate Crystallization Test.</td>
</tr>
<tr>
<td>52112</td>
<td>Flexure Test.</td>
</tr>
<tr>
<td>52113</td>
<td>Determination of Saturation Value.</td>
</tr>
<tr>
<td>52615</td>
<td>Water Vapor Transmission.</td>
</tr>
</tbody>
</table>

ASTM Standards can be obtained from:

American Society for Testing and Materials (ASTM)
1916 Race Street
Philadelphia, PA. 19103-1187
USA
(215) 299-5585

DIN Test Methods can be obtained from:

Beuth-Vertrieb Gmbh
1 Berlin 30
Burggrafenstrasse 4-7
GERMANY

Information about RILEM was not available.
APPENDIX C
SELECTED PROJECTS TREATED WITH ALKOXYSILANES

The following is a partial list of selected buildings and/or statuary on which alkoxy silanes have been applied. The list includes both European and United States applications. This information is obtained from a variety of sources, including ProSoCo's "Conservare Stone Strengtheners Reference List."

EUROPEAN APPLICATIONS:

<table>
<thead>
<tr>
<th>Building</th>
<th>Location</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Church of St. Francis</td>
<td>Alghero, Sardina, Italy, 1973</td>
<td></td>
</tr>
<tr>
<td>Bamberg Cathedral</td>
<td>Bamberg, Germany, 1973</td>
<td></td>
</tr>
<tr>
<td>Catholic Church</td>
<td>Seeburg, Germany, 1973</td>
<td></td>
</tr>
<tr>
<td>Church St. Aegidien</td>
<td>Braunschewig, Germany, 1974</td>
<td></td>
</tr>
<tr>
<td>Friedensangel (Angel of Peace)</td>
<td>Munich, Germany, 1978</td>
<td></td>
</tr>
<tr>
<td>Cologne Cathedral</td>
<td>Cologne, Germany, 1975</td>
<td></td>
</tr>
<tr>
<td>Apollo Temple</td>
<td>Munich, Germany, 1975</td>
<td></td>
</tr>
<tr>
<td>Town Hall</td>
<td>Titmoning, Bavaria, Germany, 1975</td>
<td></td>
</tr>
<tr>
<td>City Hall</td>
<td>Zurich, Switzerland, 1975</td>
<td></td>
</tr>
<tr>
<td>Location</td>
<td>Description</td>
<td>Year(s)</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>------------------------------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>Town Hall</td>
<td>Paderborn, Germany, 1975</td>
<td></td>
</tr>
<tr>
<td>Old Picture Gallery</td>
<td>Munich, Germany, 1975/1976</td>
<td></td>
</tr>
<tr>
<td>Bavarian Portal</td>
<td>Group of Statues, Landsberg, Germany, 1976</td>
<td></td>
</tr>
<tr>
<td>Castle &quot;Friedrichstein&quot;</td>
<td>Bad Wildungen, Germany, 1976</td>
<td></td>
</tr>
<tr>
<td>Cathedral</td>
<td>Statue &quot;Man of Sorrow&quot;, Ulm, Germany, 1976</td>
<td></td>
</tr>
<tr>
<td>Rathausen (Town Hall)</td>
<td>Zurich, Switzerland, 1976</td>
<td></td>
</tr>
<tr>
<td>&quot;Bankgesellschaft&quot;</td>
<td>Zurich, Switzerland, Appx. 1976</td>
<td></td>
</tr>
<tr>
<td>Tintern Abbey</td>
<td>Nave column, England, 1976</td>
<td></td>
</tr>
<tr>
<td>Audley End</td>
<td>George III temple column, England, 1976</td>
<td></td>
</tr>
<tr>
<td>Furness Abbey</td>
<td>Chapter House roundel, England, 1976</td>
<td></td>
</tr>
<tr>
<td>Windsor Castle</td>
<td>Norman Gate boss, England, 1976</td>
<td></td>
</tr>
<tr>
<td>Ministry of Finance</td>
<td>Hanover, Germany, 1976/1977</td>
<td></td>
</tr>
<tr>
<td>Overseas Museum</td>
<td>Bremen, Germany, 1977</td>
<td></td>
</tr>
<tr>
<td>Post Office</td>
<td>Verden, Germany, 1977</td>
<td></td>
</tr>
<tr>
<td>St. Martin's Church</td>
<td>Kaiserslautern, Germany, 1977</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wacker Stone Strengthener OH Sandstone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wacker Stone Strengthener OH Sandstone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wacker Stone Strengthener OH Sandstone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wacker Stone Strengthener OH Sandstone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wacker Stone Strengthener OH Sandstone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wacker Stone Strengthener OH Sandstone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wacker Stone Strengthener OH Sandstone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Brethane Sandstone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Brethane Sandstone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Brethane Sandstone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Brethane Sandstone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Brethane Sandstone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Brethane Sandstone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Brethane Calcareous sandstone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wacker Stone Strengthener OH Sandstone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wacker Stone Strengthener OH Sandstone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wacker Stone Strengthener OH Sandstone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wacker Stone Strengthener OH Sandstone</td>
<td></td>
</tr>
</tbody>
</table>
Town Hall
Illertissen, Germany, 1977

Tower of London
Wakefield Tower (single block)
England, 1977

Goodrich Castle, Solar column
England, 1977

Wells Cathedral, Statue 117
England, 1977

King's Manor, Doorway
York, England, 1977

St. Laurenzen Church
St. Gallen, Switzerland, 1978

St. Thomas Church
Augsburg, Germany, 1978

Roman Aqueduct
Mainz, Germany, 1978

St. Severins Cathedral
Cologne, Germany

Hercules Monument
Kassel, Germany

Beverly Minster
Corbel head
England, 1978

God's House Tower voussoirs
Southampton, England, 1978

Hampton Court
Tracery
England, 1979

Dorchester Abbey
Capstones
England, 1979

Stratton Methodist Church
North Devon, England

Lloyds Bank
South Molton, England

Wacker Stone Strengthener H
Brethane
Calcareous sandstone

Brethane
Sandstone

Brethane
Limestone

Brethane
Magnesian limestone

Wacker Stone Strengthener H and OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH Sandstone

Wacker Stone Strengthener OH

Brethane
Magnesian limestone

Brethane
Limestone

Brethane
Siliceous limestone

Brethane
Limestone

Wacker Stone Strengthener Sandstone

Wacker Stone Strengthener Sandstone/Brick
Ramsburg Building Society
Sherbourne, Dorfset, England

Devon Bank
Devon, England

St. Paul's Church
Munich, Germany, 1980

Municipal Theatre
Bern, Switzerland, 1980

Youth Center
Hamburgh, Germany, 1980-1981

Town Hall
Brugge, Belgium, 1981

Queen Square House
Bristol, England, 1981

St. Michael's Church
Stuggart, Germany, 1981

New Castle
Meersburg, Germany, 1982

Landesmuseum
Darmstadt, Germany, 1980-1982

Neustaedter Church
Eschwege, Germany, 1982

Old People's Home
Effnerpltz, Munich, Germany, 1983

Orangery
Weibersheim, Germany, 1983

Church St. Apostein
Viernhelm, Germany, 1983

Kaiser Wilhelm Memorial
"Gedachtnis Kirche"
West Berlin, Germany, 1983

Justice Palace
Munich, Germany, 1983

Church "Klosterkirche"
Ochsenhausen, Obergallgaeu, Germany, 1983

Wacker Stone Strengthener

Wacker Stone Strengthener Sandstone

Wacker Stone Strengthener H

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH

Wacker Stone Strengthener OH
Hoechst AG Headquarters Building
Frankfort, Germany, 1983

Steeple of Lutherkirche
Frankfort, Germany, 1983

Tower of City Hall
Charlottenberg, Berlin, Germany, 1983

Bayer, Vereinsbank
Augsburg, Germany, 1984

Alte Pinakothek (Art Gallery)
Munich, Germany, 1984

Franciscan Church
Salzburg, Austria, 1984

Wacker Stone Strengthener H
and OH
Wacker Stone Strengthener OH
Wacker Stone Strengthener OH
Wacker Stone Strengthener OH
Wacker Stone Strengthener OH
Wacker Stone Strengthener OH
Wacker Stone Strengthener OH

UNITED STATES APPLICATIONS:

United States Capitol
West Central Front
Washington, D.C., 1987

Indiana State Capitol
Indianapolis, Indiana

Conservare H Stone Strengthener
Sandstone/Limestone
Conservare H Stone Strengthener
Limestone
Conservare OH Stone Strengthener
Sandstone
Conservare OH Stone Strengthener
Sandstone
Conservare H Stone Strengthener
Limestone
Conservare OH Stone Strengthener
Conservare H40 Water Repellent
Sandstone
Conservare OH Stone Strengthener
Sandstone
Conservare H Stone Strengthener
Conservare H40 Water Repellent
Marble
Memorial Hall
Harvard University
Boston, Massachusetts

Harvard Medical Quadrangle
Boston, Massachusetts

First and Second Church
Boston, Massachusetts

First Baptist Church
St. Joseph, Missouri

New York City Landmark Structure
956 East 156th St.
Bronx, New York

555 Washington Avenue
St. Louis, Missouri

New York City Landmark Structure
770-772 Dawson Street
South Bronx, New York

St. Francis Church
St. Louis, Missouri

St. Peter-in-Chains Cathedral
Cincinnati, Ohio

City Hall
Walla Walla, Washington

Coachman Project
Clearwater, Florida

St. Paul's Cathedral Diocesan
Building and Rectory Building
National Register and Pittsburgh
Landmarks Buildings, 1904 and 1926
Pittsburgh, Pennsylvania

Roman Temple and Colonnades
Hearst Castle
Simeon, California

Limestone Statuary
Hearst Castle
San Simeon, California

Conservare OH and H Stone
Strengthener
Sandstone

Conservare H Stone Strengthener
Conservare H40 Water Repellent
Marble/Limestone

Conservare H Stone Strengthener
Sandstone/Brownstone/
Puddingstone

Conservare OH Stone Strengthener
Sandstone

Conservare OH Stone Strengthener
Brownstone

Conservare OH Stone Strengthener
Brownstone

Conservare H Stone Strengthener
Limestone

Conservare OH Stone Strengthener
Limestone

Conservare OH Stone Strengthener
Sandstone

Conservare OH Stone Strengthener
Brick

Conservare H40 Water Repellent
Limestone

Conservare H Stone Strengthener
Conservare H40 Water Repellent
Marble/Cast Stone

Conservare OH and H Stone
Strengthener
Limestone
IOOF Tomb
Lafayette I Cemetery
New Orleans, LA, 1985-86

Statue of Religious Liberty
5th & Market St.
Philadelphia, Pennsylvania, mid 1986

Easton Cemetery
Main Gate
Easton, Pennsylvania, 1988

Ohio State Capitol
Selected Cornice Areas
Columbus, Ohio

Trinity Church
New York, NY, 1990-92

Conservare H Stone Strengthener

Conservare OH Stone Strengthener
Marble

Conservare H and OH Stone Strengthener
Conservare H40 Water Repellent
Sandstone

Conservare OH Stone Strengthener

Conservare H Stone Strengthener
APPENDIX D

MEETINGS ON THE CONSERVATION OF EARTHEN ARCHITECTURE

- The First International Conference on the Conservation of Mudbrick Monuments (Iran/ICOMOS), Yazd, Iran, 25-30 November 1972;
- The Second International Symposium on the Conservation of Monuments in Mudbrick (Iran/ICOMOS), Yazd, Iran, 6-11 March 1976;
- The Adobe Preservation Working Session (US/ICOMOS-ICCROM), Santa Fe, New Mexico, USA, 3-7 October 1977;
- The Third International Symposium of Mudbrick Preservation (Turkey/ICOMOS/ICOMICCROM), Ankara, Turkey, 29 September-4 October 1980;
- Fifth International Meetings of Experts on the Conservation of Earthen Architecture (ICCROM/CRATerre-EAG/ICOMOS) Rome, Italy, 22-23 October 1987;
- Sixth International Conference on the Conservation of Earthen Architecture (ICCROM/The Getty Conservation Institute, Museum of New Mexico State Monuments/US/ICOMOS), Las Cruces, New Mexico, USA, 14-19 October 1990;
- The Forthcoming Meeting: Seventh International Conference on the Study and Conservation of Earthen Architecture (General Directorate for Buildings and National Monuments/ICCROM/CRATerre-EAG) will be held in Portugal, 24-29 October 1993.
BIBLIOGRAPHY


Anne & Jerome Fisher

FINE ARTS LIBRARY

University of Pennsylvania

Please return this book as soon as you have finished with it. It must be returned by the latest date stamped below.