PROTECTIVE MATERIAL COATINGS FOR PRESERVING CULTURAL HERITAGE MONUMENTS AND ARTWORK

Amir Ershad Langroudi

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Preface

Historical and cultural monuments are a bridge between past and present generations. These works have irreplaceable material and spiritual value, which indicates the need to preserve and maintain them in the best way for transmission to future generations. However, in many cases, the aging deterioration of these artworks can not be completely prevented, but appropriate methods of maintenance and protection can significantly reduce the rate of their decline and erosion. However, in many cases, monuments and artworks are in open spaces without care and protection guards, exposed to vandalism and weathering degradation, or air pollution sources.

Another challenge with historical artifacts is that many of them have been made by unknown individuals, artists, and artisans over decades and even centuries.

In many cases, in addition to proper maintenance, serious interventions are required to use appropriate coatings to maintain these works with long-term efficiency. Various processes are used to produce nanocomposite coatings, one of which is the wet chemical process by the sol-gel way.

Given that historical and cultural works are made of different materials, it isn't easy to address them in one book. Hence, the protective coatings for some of the most influential ones in human civilization, such as leather, parchment, paper, metals, historical artworks, and monuments made of brick, and stone are addressed in the form of 5 chapters in this book. In the first chapter, various analysis techniques are used to describe the materials used in historical monuments or the coatings used to preserve them. The second chapter introduces the properties of metals, alloys, and their common corrosion and proposes protection strategies for metal monuments. Also, various protective coatings, emphasizing nanocomposite coatings to prevent corrosion, especially electrochemical corrosion, are examined.

Chapter 3 is devoted to studying natural leather and parchments, which, as natural polymers, must be protected from damage by environmental factors such as UV, temperature, and humidity. There are various coatings for surface treatment of leather and parchment, each of which has advantages and disadvantages that are discussed in this chapter.

The fourth chapter deals with stone works, which contain many historical sources. Having sufficient knowledge about erosion processes and the mechanisms governing these processes, and the impact of environmental factors can improve the preservation of these works in the open space. In recent years, nanocomposite coatings have been considered for their protection. In addition, it is possible to add antimicrobial agents and nanoparticles to the base composition of the coating to create additional functions such as self-cleaning properties and resistance of microorganisms.

Chapter 5 deals with nanotechnology. It creates more effective materials and innovative methods to protect historical monuments and cultural heritage. This technology can be used in various fields of conservation and restoration of historical and cultural monuments, production of transparent coatings with the suitable application for protecting historical monuments, removal, cleaning of improper repairs of the past, and new techniques and methods for protection and restoration.

It is hoped that this book will be a positive step towards promoting scientific research and its application in protecting and preserving cultural and historical heritage. By better preserving, these works will create a better perspective for the future.

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CHAPTER 1

Instrumental Techniques for Characterization of Historical Materials: Conservation and Protection

Abstract: Conservation methods and intervention materials should be compatible with preserving historical and artistic monuments. Therefore, it is necessary to characterize the chemical compositions, microstructures, thermal and mechanical properties, the corrosion and weathering conditions of historical and cultural monuments, and the proposed coating to protect them. The environmental impacts and mechanisms of change due to their natural aging or artificial aging processes should be investigated. Various chemical methods have been developed because of the incredible variety of materials used to prepare historical and cultural monuments and artifacts. A variety of ways for analyzing elements, including atomic absorption spectroscopy, X-ray fluorescence, proton emission X-rays (PIXE), and μ-PIXE, and X-ray energy spectroscopy in scanning electron microscopy, are presented with a few practical examples. Infrared and Raman spectroscopy are the conventional methods used to characterize mineral and organic compounds. X-ray diffraction (XRD) is also a fast and inexpensive technique for distinguishing amorphous and crystalline materials and characterizing natural and synthetic crystals. Among the imaging techniques, the optical microscope is used for obtaining necessary information about various specimens in relatively small magnifications up to about 2,000 times. Scanning and transmitting electron microscopes (SEM-TEM) provide images at high resolution. The Atomic Force Microscopy (AFM) represents the three-dimensional topography of the surface. Thermal analysis is a quick and accurate method for measuring the percent of mass changes in material with temperatures such as water evaporation, solvents and volatile materials, and organic compounds decomposition. Mechanical-thermal analysis can provide practical information such as glass transition temperature and elastic modulus. A variety of methods for determining weathering resistance, corrosion resistance, and surface hydrophobicity are introduced. This review describes some of the typical applications of laboratory techniques and provides scientific information for right choice of materials and valuable coatings for their protection.

Keywords: Chemical and Mechanical Properties, Conservation, Corrosion, Heritage and Artifacts, Materials, Physical, Weathering.

INTRODUCTION

There are several ways to determine the elements that make up a material, its crystal structure, chemical composition, and physical and mechanical properties.

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One of the most practical methods can be based on the nature of identification. In most detection methods, a focused photon, electron, or ion beam is emitted into the material. The collision of this beam with a matter or its reflections provides different information about the case. Special equipment records and analyzes the amount and manner of changes such as energy, intensity, or radiation distribution. Finally, by analyzing the data, the type and amount of constituent elements, chemical compounds in the material, variety of phases, and crystal structure can be determined [1].

Fig. (**1**) indicates the spectrum of electromagnetic radiation in terms of wavelength. According to Planck's formula (Eqn. **1**), the relationship between energy and wavelength for photons can be obtained from the following equation:

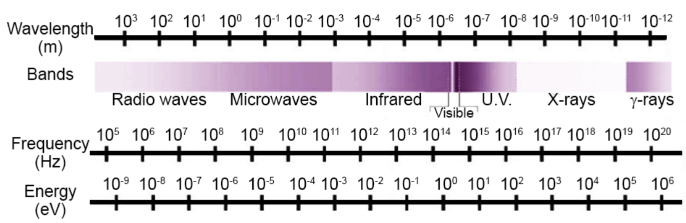

Fig. (1). Electromagnetic spectrum, with wavelength, frequency, and energy scale [2].

$$E=h\nu=hc/\lambda \quad \textbf{(1)}$$

In this formula, E is the energy, λ is the frequency, n is the wavelength, h is the Planck constant, and c is the light speed. According to this formula, low wavelength rays (*i.e.*, γ-rays and X-rays) have high energy. They interact with a small level of atoms with relatively high energy, such as the nucleus of an atom or electrons in orbits close to the nucleus (core electrons). Medium energy bands (*e.g.*, U.V. and Visible) interact mostly with electrons located in the outermost orbits of atoms (valance electrons). Microwave and radio waves have long wavelengths and low frequencies. They interact with shallow energy levels, such as electrons located between the atoms that make up chemical bonds or stimulate atomic and molecular motions.

Table **1** shows several types of techniques designed based on the physical process for detection and measurement. They include the nature of the incident beam and the type of radiation or particle detected. It should be noted that each instrument uses a specific type of electromagnetic or particle beam to investigate the subject. Therefore, their applications are limited to particular experiments.

Table 1. Some of the techniques are based on the nature of the radiation [2, 3].

Analysis Method	Incident Beam	Detected Beam
X-ray diffraction, XRD	X-rays	X-rays
X-ray fluorescence, XRF	X-rays	X-rays
Proton induced X-ray fluorescence PIXE	protons	X-rays
Scanning electron microscopy (SEM) Energy dispersive spectroscopy (EDS)	electrons	X-rays
Atomic absorption spectroscopy, AAS	visible	visible
Ultraviolet spectroscopy, U.V.	ultraviolet	ultraviolet
Infrared spectroscopy, IR	infrared	infrared
Raman spectroscopy, RS	infrared	infrared

The radiation will be scattered and elastic in the absence of energy exchange between the probe beam and the material. The process will be considered as scattering (*e.g*., wave interference). Considering the interaction involves exchanging energy between the incident radiation and the atom in the material, the process is anelastic and is treated as spectroscopy. When particles are irradiated with atoms in the sample, the absorbed energy can stimulate specific energy levels, ranging from much energy to stimulate the nucleus to an electronic and molecular search for lower-energy molecules. Therefore, spectrometry techniques can also be classified based on energy levels. In general, any small measurement of the relationship between intensity and energy in any part of the electromagnetic spectrum is called spectroscopy. These measurements are called colorimeters in the visible part of the spectrum.

Both scattering and spectroscopy processes can involve imaging techniques by a visual image or a distribution map. Scanning tunneling microscopy or atomic force microscope deal with the altitude distribution of matter at the atomic level work based on direct measurement of interatomic forces or tunneling energy.

In general, the classification of characterization methods can be as following (see Scheme **1**):

1. The chemical nature of materials includes analyzing chemical elements in the sample and the chemical composition and structural nature of crystalline materials in amorphous and crystalline.

2. Studying texture and morphology of the material with a microscope in different magnifications (*i.e*., imaging techniques).

CHAPTER 2

Conservation and Protection Coatings for Historical Metallic Artworks

Abstract: In this chapter, the characteristic of metals, alloys, and their typical corrosion are introduced. Then, the protection strategies are proposed for the conservation and protection of historical metallic artifacts. The protective coatings are also investigated to prevent electrochemical corrosion in metal artworks from traditional materials and methods to new nanocomposite coatings. The characteristics of protective coatings in terms of composition, yellowing, and degradation are evaluated. Besides chemical stability and protective properties, which are crucial factors in choosing protective coatings for ancient metal artworks, the principles and theoretical foundations of protecting and restoring historical monuments sometimes limit the use of these materials. Therefore, it is necessary to review and evaluate the materials and methods of coating metal artifacts connected with the theoretical frameworks of restoration.

Keywords: Corrosion, Historical metal objects, Nanocomposite, Polymer, Protective coatings.

INTRODUCTION

Metals are essential both artistically and industrially. The spread of metals and their alloys throughout history and the realization of metal properties and their application in various fields such as sculpture, jewelry, tools and weapons of war, medals, utensils indicate the unique value of these materials [1, 2].

Metallic elements are in different forms as pure metals, metallic oxide, and sulfides in nature. Apart from mercury, metals are solid at room temperature. In the beginning, humans used metals that were found pure, such as copper, gold, and silver. Purification was generally made by heating the metal oxide with a reduction agent as carbon-based material as charcoal, coke [3].

Although the fabrication of objects made of precious metals progressed significantly, it has reached a high level in ancient Iran in the Sassanid era [4]. The methods of making metalworking techniques during the Sassanid era are fascinating and, at the same time, complex. Most of the metal parts obtained indi-

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cate that the parts must have been cast or hammered, and in some cases, must have been carefully formed or shaped. From this period, pieces have been found in which two different metals have been fabricated together. These objects show that a part of the first metal was melted and molded, and after machining and polishing, they were put back in the mold, and the second metallic melt was poured on it. In the post-Islamic period, during the Seljuk period to the Safavid period, metals and their formation have made tremendous progress in ancient Iran [5].

This chapter reviews some historical metals and alloys such as copper, brass and bronze, silver, iron, and protective coatings.

Regarding their importance in the industry, metallic materials are classified into two groups: the first group is ferrous, and the second is non-ferrous metals. Iron-based alloys such as steel and cast iron are in the first class, while the non-ferrous metals include other metals except iron-based alloy such as copper, gold, bronze.

General Characteristic of Metals

The characteristic of metals depends on the type of atomic arrangement in the crystal and its structure. Atoms in metals have metal bonds that share their electrons. Metals can replace acidic hydrogen in chemical reactions. The placement of atoms in metals creates a regular crystal lattice. The typical crystal lattice in metals includes hexagonal, body-centered cubic (BCC), and face-centered cubic (FCC) [6]. These crystal lattices give metals unique properties such as different formability. The strength of metals depends on the type of crystal structure. The slip of the dislocation plates in the crystal structure, the degree of adhesion and bonding of the crystals determine formability. In the metal bond model, electrons in the outermost metal atomic circuit interacting with their nucleus interact with the atoms' nuclei and share them. Therefore, this factor causes the good mechanical properties of metals. Corrosion is the destruction and spoilage or change in the properties and characteristics of materials (usually metals and alloys) due to their reaction to the environment. A metallic alloy is a material with metallic properties composed of two or more chemical elements, provided that it is at least one of the metal elements. An alloy system consists of several components with all possible ratios. If the system consists of two elements, it is called a dual or bimetallic alloy system, and if it consists of three components, it is called a triple alloy system. Alloy systems are generally classified based on a phase diagram on equilibrium conditions [6].

Some purposes of preparing the alloy are: change in physical properties such as melting temperature, color, change in mechanical properties like tensile strength, abrasion, changes in chemical properties such as increased corrosion resistance, changes in technological and functional properties such as casting and rolling.

Copper Metal and Alloys

The initially manufactured copper objects were small hammered objects dating back to the first half of the fourth millennium B.C., the end of the Stone Age. Human beings encountered a substance that did not break when hit but deformed due to its softness during this period [7, 8].

This was probably the metal making of copper. Of course, at that time, humanity had not yet realized the melting properties of metals. This was perhaps discovered by potters while baking their pottery in the kiln. They noticed that some of the stones melted in the heat and turned into something else. This resistant material was also precious for artisans. Examples of such ancient sites are the Arisman Archaeological Site, one of the largest industrial-metalworking centers in Iran, and excavations at the site have uncovered traces of melting furnaces. This ancient site, which is considered a kind of industrial town, has valuable works from the fourth millennium B.C., which has made it one of the wealthiest ancient sites in Iran and the world.

The copper metal is bright red. Copper and its alloys are a good conductor of heat, which have been used in the construction of kitchen utensils. Copper can solder and harden. Naturally, copper metal is very soft, so copper alloys were prepared by adding arsenic, zinc, tin, and silver [9].

Copper is one of the purest metals in nature and is found in most of the world's mines. In the old days, they reduced it into copper metal by heating copper oxide with carbon-based material like coal and coke. Copper minerals such as azurite $2CuCO_3Cu(OH)_2$ (blue), malachite $CuCO_3Cu(OH)_2$ (green), and its sulfide minerals such as chalcopyrite ($CuFeS_2$), covelline (CuS), chalcocite (Cu_2S), or copper oxides such as Cuprite (Cu_2O) are familiar sources of copper compounds in ores. The copper metal can be weathering and creates a green patina on the stone and plaster that is not easily removed [10].

Since pure copper does not have enough mechanical strength, ancient metalworkers smelted it with other materials to increase its strength. About 2500 to 1500 B.C., with the discovery of tin, the Bronze Age began, and artisans combined these two metals to create a stronger metal alloy. Thus, in the second millennium B.C., bronze became one of the most prominent industries. In the Hasanlu area in northwestern Iran, many examples of bronze objects of this period have been found [11]. The Kurdistan Region is Iran's vital bronze production center and the ancient world during the Bronze Age. Artists in the area were able

CHAPTER 3

A Survey on Appearance Changes of Historical Parchment and Leather by the Surface Coatings

Abstract: As a natural polymer, skin and its products, such as leather, have long been a human interest. The handwritten book and its manuscripts made of parchment and different leather products are among the most valuable heritages of humanity and human civilization. Many of these artworks are at risk of erosion and extinction due to natural damaging environmental factors or improper protection and maintenance. Natural or artificial factors may influence the color change in these works. Photochemical reactions in the degradation of these effects are intensified by natural factors such as humidity, temperature, or light. They can break the chain of collagen molecules in the skin and leather and disrupt these objects' cohesive structures. These reactions damage the molecular chains of collagen and consequently alter its physical and mechanical properties. In this regard, evaluating the appearance of leather in defensive operations or selecting appropriate coatings may measure the proper performance of protective polymer materials. Therefore, color change operations must be considered for any conservation treatment. The options available for preserving and finishing leather and skin artwork techniques are currently limited, and all have drawbacks. In this study, the structure of the skin and its various erosion processes are first discussed. The effect of aging on the discoloration of some conventional protective coatings is then investigated. This article also emphasizes nanotechnology-based solutions to maintain and preserve artistic and cultural artifacts to their original features.

Keywords: Aging, Color, Leather, Parchment, Protective materials.

INTRODUCTION

Written parchments and leather have long been used to make books and other necessities of life. Leather products are among the oldest human technologies, and the conversion of raw skin into leather or usable skin should be one of the first human technologies [1 - 3]. Among the most prominent remnants of the early centuries of Islam are the Kofi-written Qurans on deerskin, which are of great importance and status among Muslims and other religions. Sometimes this same sanctity and blessing have caused improper maintenance, and in some cases, it has caused their destruction [4 - 6].

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Fig. (**1**) shows an example of Qur'anic pamphlet No. 6 in Kufic script attributed to the first Shiite Muslim Imam and the fourth Muslim caliph (Ali ibn Abi Talib) in Astan Quds Razavi, which is written on deerskin [4, 7].

Fig. (1). An example of the Quran in Kufic script written on deerskin attributed to Imam Ali in Astan Quds Razavi Museum [7].

As mentioned, valuable leather and parchment artifacts from ancient times have been less studied due to the limited number of these artifacts and their vulnerable structure [8]. From this perspective, studying and preserving these works is very important and requires more effort to protect and maintain them properly. Significant efforts in protecting artifacts, ornaments, antiquities, and artifacts made of leather and parchment have led to a revision of the traditional approach to protecting these valuable products, the sole purpose of which was to soften them again. One of the essential factors in this category is its comprehensive review before starting any protection operations and adding protective materials. Therefore, a comprehensive study of technology and pathology is necessary and unavoidable [9 - 11]. Because the chemical and classical methods can evaluate historical leather artifacts, some researchers have described the required experiments, including measuring pH, fat, sulfate, and moisture content in leather artworks before any protective treatments [10 - 12].

Another critical issue in studying and protecting these artworks is a structural study to identify the production process and materials used to manufacture them.

For example, studies on a historical Seljuk leather musk specimen from the Qayen Mountain Castle were carried out to identify the skin type and hair follicles' arrangement using a scanning electron microscope. The experiments showed that goatskin was used to make musk leather, which was decontaminated with lime. More chemical tests have proved the presence of plant tannins, sulfate, and aluminum and iron cations. Also, inorganic compounds were examined by elemental analysis with scanning electron microscopy. The results of Raman tests were shown on different layers and the tannins extracted from it, and the free fat in the structure. The results indicated the tanning process had been done using plant tannins, especially the dense group. Comparing the absorption bands of the extracted fat spectrum with the fats and oils used in the finishing of leather indicates the possibility of using animal fats, especially sheep's fat [13]. This research's necessity and objectives include the following: Firstly, manuscripts on animal skins and books with historical leather binding and other leather artifacts with historical and cultural value are available in private and public museums and libraries that need to be maintained. Secondly, natural leather and these kinds of products are produced in handicrafts, which need to be appropriately maintained and treated. Therefore, it is necessary to conduct this research with the following objectives. On the one hand, it examines the types of erosion in products made of leather and parchment, as well as investigates their color change due to aging. On the other hand, this research can better reveal the effect of protective materials on natural leather products and lead to the expansion and development of new products to protect and maintain leather and parchment artworks.

Skin Structure

A brief description of the skin structure is provided here. The skin is made of protein and consists of three essential layers [10]. Fig. (**2**) shows the shape of different layers in the cross-section of the skin.

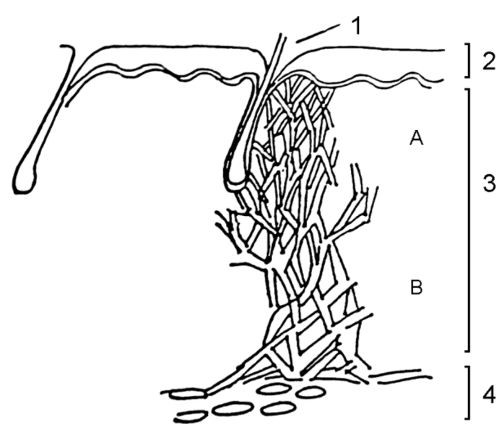

Fig. (2). Skin layers. Hair, 1; Epidermis, 2; Dermis, 3; Hypodermis, 4.

The Epidermis or the Dead Outer Layer

This outer layer is covered by hair and wool and is continuously shed and replaced by its underlying living cells. Skin color is related to melanin pigments made in the lower part of this layer [11, 13]. These tissues are readily soluble in

CHAPTER 4

Challenges of Stone Artifacts Protection and Providing the Solutions using Consolidation and Hydrophobic Coating Treatments

Abstract: Consolidation and hydrophobic treatments of historical carvings and architectural monuments made of stone is a challenging intervention that, in many cases, is considered irreversible due to the chemical bonds that are created between the reinforcing material and the substrate. However, these interventions are often unavoidable, especially when stone structures are at risk of destruction, failure, and collapse due to aging and weathering. Examination of historical monuments and their consolidation and hydrophobicity operations needs to be monitored continuously; otherwise, a deep erosion of layers and loss of cohesion is a risk of complete collapse. Historical monuments, sculptures, and stone inscriptions are fragile and vulnerable due to centuries of exposure to harsh weather and open space. Reinforcement of historical stones requires attention to surface treatments to reduce moisture, prevent biological damage, and increase mechanical properties. In this research, various challenges related to historical and cultural monument protection interventions have been addressed. Several nanoparticles and polymeric materials have been introduced for this purpose. Organic and inorganic materials such as acrylics, silanes, and nanocomposites play an essential role in preparing hydrophobic and reinforcing coatings for use in historical stone artworks. Reinforcement and hydrophobicity operations with silane/siloxane compounds have been proposed as potential polymeric materials for protective coatings and limestone layers' stabilizers. Combined silane and siloxane coatings can improve historical monuments' physical, biological, and mechanical properties against weather conditions. The results showed that the samples coated with silane/siloxane resins have appropriate hydrophobic properties. The reason may be that organic groups of polysiloxanes as hydrophobic agents increase the surface's hydrophobic nature. Besides, Si-OH silane bonding and the integration effect can be caused by covalent bonding by mineral surfaces and filling narrow stone surface gaps. Among other important factors that affect the properties of hydrophobic operations, the presence of fluorinated functional groups on the composition of the coating and the effect of hydrophobic properties of additives on stability and weather resistance in harsh conditions have been discussed. Besides, the use of mineral nanoparticles in the coating composition is a valuable way to improve the combined properties, self-cleaning, and anti-microorganism in conservation and protection treatments. Recent scientific developments also emphasize the need for water-based resins with environmental-friendly characteristics.

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Keywords: Coating, Consolidation, Hydrophobic, Nanoparticle, Polymer, Stone.

INTRODUCTION

Much of the world's cultural heritage is made of stone. These works are slowly but cruelly destroyed. In many cases, the transformation of rocks as building materials is quite evident by examining a historic stone building or a historical monument [1 - 3]. The protection of historical and cultural heritage is essential and has significant economic tourism and national and international value [4 - 6].

Historic buildings have unparalleled splendor, aesthetic, and cultural value and can also be considered an economic resource to attract tourists from other parts of the country or even different countries [4, 7 - 9]. Before any protective measure, the causes of erosion and its complications must be well-identified. In this case, it is possible to prevent further decay and loss of historical effect with appropriate protective measures.

In general, monuments are threatened by the following types of erosion: weathering, chemical, physical and biological aging [10 - 12]. However, these erosion factors can often have a synergistic effect, and it is almost impossible to determine the separate impact of each of these factors. For building materials such as limestone, acidic dissolution of carbonate materials can be the primary chemical weathering mechanism [13 - 15].

Demolition of a stone structure indicates the interaction between the components of the stone and external factors, *i.e.*, environmental conditions under the erosion mechanism's influence [16, 17]. However, in complex cases, determining the cause of erosion cannot be described by these simple models alone. It is necessary to collect more data correctly to determine the exact cause of the decline. The processes of destruction and erosion in the stone materials of historical monuments, on the one hand, depend on the intrinsic factors of the material, such as composition and internal architecture (texture and microstructure), and the other hand, on external factors such as environmental conditions where the building is located, for example, the effect of climate pollution. The chemical composition or mineralogy of the stone largely determines the stone's behavior against physical or chemical invasions, for example, changes in solubility (dissolution) with changes in pH, the existence of complex species, ion change phenomena.

External Factors, such as pressure, the presence of liquid water, pH, oxidation, microorganisms (*e.g., fungi, algae*), and ultimately function humans; these external factors can be considered as factors that cause more damage concerning stone erosion [18, 19].

In its various states or phases (such as liquid, steam, and ice), water is the most crucial cause of rock breakdown. Due to the fuzzy changes of water, which can be a multifunctional factor. Water can also cause the transfer of other substances such as soluble salts, air pollutants, and the environment to develop chemical reactions or physicochemical processes. Water facilitates the growth and expansion of living organisms, which increases its role in degradation processes. Its performance in various chemical reactions with the substrate (dissolution, hydrolysis, reduction, or oxidation) is noted. Of course, the dissolution of carbonates as bicarbonate will occur in the presence of water. The presence of water causes the oxidation of hydrogen sulfide and sulfur oxide to sulfur trioxide, sulfate deposition, oxidation of nitrates, and dissolution of carbonates [20 - 22].

The other sources of damages are:

- temperature changes (thermal fluctuations),
- thermal expansion and contraction,
- internal stress,
- microcracks in heterogeneous materials such as granite cause the rock to be vulnerable to frost.

Crystallization pressures are inversely related to pores and gaps. Therefore, rocks with large pores are less sensitive than rocks with tiny pores. In the past, the effects of air pollution on rocks have received much attention, and most research has focused on pollutants such as sulfur oxides, nitrogen oxides, and carbon dioxide, which can dissolve in water to form an acidic solution [23, 24]. Therefore, they can react with calcareous materials such as limestone or marble. The effects of acidic contaminants depend on the stone's position. For example, if the rock is vertical to be washed regularly with rain, the reaction products are washed away from the rock surface. However, if the stone is in a horizontal position that is somewhat closed and unventilated, the reaction products will accumulate and form a dense black crust. Soluble salts are another reason for the destruction of stone monuments. The growth of salt crystals inside the rock's pores can create stresses that cause the rock to break and turn into powder, which is one reason for the damage to many historical monuments. Many methods can contaminate rock with salt. Air pollution is the primary source of sulfates and nitrates. Other sources include soil, which may penetrate the rock body as moisture rises. Salts in winds blowing from the sea or the desert are another factor that is incompatible with historic buildings' blocks. Salt damage is related to two mechanisms: recrystallization of salts from solution and hydration of salts. In the first case, the damage occurs when the stresses created by the crystal pressure grow inside the pores or micro-cracks exceed the rock's tensile strength. In the

CHAPTER 5

Organic-Inorganic Nanocomposites Coatings in Conservation of Historical Monuments and Artworks

Abstract: Various destruction factors, such as vandalism and weathering, *e.g.*, humidity and light (UV), threaten historical monuments and artworks. It is possible to produce organic and inorganic materials in nanometer dimensions and compose them to produce wide varieties of organic-inorganic nanocomposites with various properties and functionalities such as self-cleaning and anti-bacterial. Besides, the technology of using these materials has also undergone a fundamental change that has created nanotechnologies in the preservation, conservation, and consolidation of historical and cultural monuments. Nanocomposite hybrid coatings can be applied to various substrates of historical and artistic objects such as glass, paper, and stone to improve their performance, such as corrosion resistance or paper deacidification and improving hydrophobicity. The sol-gel method is one of the promising approach to prepare nanocomposite coatings with a variety of functionalities. In addition, sol-gel methods allow preparing nanoparticles with more efficiency. Furthermore, nanotechnology provides the opportunity to conserve and restore artworks like the consolidation of wall paintings and cleaning surfaces from aged polymers and the consolidation of cellulosic papers against fungal growth by monitoring degradation processes such as water destruction and salt contamination.

Keywords: Coating, Hydrophobic, Inorganic nanoparticles, Protection, Sol-gel.

INTRODUCTION

Conservation and protection of historical monuments and cultural heritages are essential for each nation [1 - 4]. Many valuable treasures are endangered or destroyed for different reasons [5 - 7]. In recent years, nanomaterials and nanotechnologies have been suggested to preserve and conserve historical monuments [6 - 13]. The sol-gel process is one of the conventional methods of preparing nanoparticles, and nanocomposite coatings [14 - 22]; some practical examples in this field are mentioned, like consolidation and corrosion resistance improvement [22 - 37]. It also refers to nanomaterials' applications to deacidification from cellulose artworks and removing aging polymeric layers from cultural objects [29 - 36].

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Features of Protective Coatings

Materials, especially organic-based material used to protect historical artifacts, must be tested by multiple and rigorous tests [37 - 40]. Each material's characteristics and operating conditions are determined with these experiments, especially by applying accelerated weathering conditions [41 - 46].

The essential features are considered in this regard include the following:

1. Study properties and stability of materials, specifically chemical structure, physical and mechanical properties, service time, and aging test. Because cultural artifacts should have long-term protection, any treatment must be long-term to minimize intervention and the number of taken actions [47 - 53].
2. Evaluate the interaction between protective materials and historical materials on whether antiquities and preservatives can be placed together without adverse interaction [54 - 56].
3. Evaluation of durability and aging before and after applying protective material [57 - 62].
4. Provide plans to remove the protective material from the monument without severe damage to the work in case of emergency or when a more suitable option is available [63 - 67].
5. Research on maintaining the aesthetic appearance of historical objects after applying the coating [68, 69].
6. Research on color change over time or under light radiation [70 - 74].

In some cases, the above items may conflict. Therefore, it may be necessary to ignore some of them due to their lesser importance and make the best choice with a set of factors.

Polymeric Materials

Various organic and inorganic materials apply to the conservation and restoration of historical artworks [75 - 79]. However, several severe tests must evaluate and approve these materials before using them in practical conditions. These materials' characteristics and performance are considered, especially under critical situations such as artificial aging by accelerating weathering tests. Besides, the probable interactions measure the protective coating materials and the historical materials in the artworks. They should be compatible with each other without any adverse interactions. The conservation and protection coating must preserve the original aesthetic of artworks from any side effects, especially under light irradiation and aging time. Furthermore, eliminating the protective layer from the historical artworks must be done without severe damage if necessary or when better alternative coatings or protective materials are available.

The following categories are more prevalent in protection, conservation, and restoration fields:

1- Silanes and siloxanes [80 - 83]
2- Epoxies and alkoxysilane with a functional group [84 - 89]
3- Acrylics and alkoxysilane with double bond functional groups [90 - 93]

The use of silanes and alkoxysilane compounds can strengthen and stabilize the substrates, such as ancient stones, by deep penetration. Due to the possibility of covalent bonding with the background, it is not easily possible to remove them. The following three sections are devoted to explaining these types of coatings.

Silanes and Siloxanes

Silanes and siloxane-based coatings have been used for many years in various fields to consolidate and protect historical monuments and artworks [94 - 96].

Sol-gel Process

The silanes can be hydrolyzed by water or alcohol and converted to silanols, which are then reacted to by condensation reactions and eventually form polymers called polysiloxanes or silicones [97 - 99]. The absorbing humidity in the historical monument or the moisture in the atmosphere supplies the water required to form silanol. Therefore, hydrolysis and condensation reactions may occur after absorbing the protective coating in the monument and penetrating its cavities [100 - 102]. On the other hand, cosolvents improve homogenizing the reactant mixture and catalysts to accelerate reactions [103 - 105]. Scheme. (**1**) represents the hydrolysis reaction of alkoxysilane to silanol (reaction 1) and the condensation reactions of silanol to siloxanes (reactions 2 and 3). Using various identification methods, hydrolysis and condensation of alkoxysilanes have been studied [105 - 113].

Trimethoxysilane and tetra-ethoxy (or methoxy) silane precursors are widely popular in the conservation and protection field. However, other silane precursors with formula, $R'_nSi(OR)_{4-n}$ also used in which R and R' are organic groups, and n is a number (*i.e.*, $n \leq 4$). Moreover, R' contains a functional group such as vinyl, acrylate, or epoxy for separate polymerization. Scheme. (**2**) shows hydrolysis and condensation of silanes to siloxanes followed by curing reaction of its epoxy functional group with Bisphenol A [114 - 116].

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He is an Associate Professor at the Department of color and Surface coatings (CSC) at the Iran Polymer and Petrochemical Institute (IPPI) with more than 22 years of experience. His main interests are the synthesis and characterization of organic-inorganic nanocomposite materials.

During this period, he taught and directed postgraduate students and also cooperated the research projects with some other research centers, such as the Department of Restoration and Architecture of Islamic Azad University different branches such as; the center of Tehran branch, Science and Research Branch, Abhar branch. He received some funds from the Research Institute of Cultural Heritage & Tourism (RICHT), Iran National Science Foundation (INSF) for his research on conservation and restoration projects, such as the Choghaznabil brick monument, Persepolis, and the protection of leather bookbinding. His scientific activities have been recorded in 3 books, several book chapters, and more than 100 scientific articles.