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Protection of Stone Building Structures Against Corrosion Caused by Moisture

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Abstract

The paper aims to present the most important issues concerning the nature of protection of masonry materials against moisture. The paper describes the parameters which influence the effectiveness of these protection methods such as porosity, salinity, and surface state. Special attention is devoted to the ecological aspect of hydrophobizing preparations available on the market. Also technical criteria and practical advice for the use of these preparations to prevent damage are extensively discussed in the paper.

Introduction

Water is the most common chemical in nature. It plays a significant role both in terms of biology and culture. It constitutes a very crucial component of all living organisms and it creates weather conditions across the globe. Because of its properties, water is widely used in industry, and also in the processes related to the production and use of building materials. However, from the point of view of engineering, water is the major factor which decreases the durability of building structures. In design, construction and maintenance, building structures need to be protected against its detrimental effect.

The basic way to protect building structures against external factors is to provide a suitable type of construction that protects the building structure against rain and wind. The question arises of how to protect the surfaces of building materials used on exposed facades or other building components in a way that would not require any additional protection which in turn could affect the functionality and appearance of the object. Current advanced technologies of building chemicals provide a choice of appropriate solutions.

Water is a very common chemical in nature and thanks to its specific properties it is widely used in construction, both in the processes of manufacturing of building materials and bonding adhesive, in construction and while the buildings are in use. Most of the processes related to degradation of building materials are initiated by water and occur under its influence. The protection of building materials consists in endowing their surfaces with hydrophobic properties and thus the qualities of being waterproof. New technologies allow the preparations to affect the structure of materials at the molecular level. Producers assure us that the hydrophobizing agents that they offer are highly successful, however the actual effectiveness thereof can only be verified based on empirical research and a detailed statistical analysis.

Water creates and intensifies the processes of corrosion. Besides rainwater that directly saturates building materials carrying with it all sorts of impurities described in other sections hereof, in addition snow, hail and fog have a highly adverse effect on building materials as well. Rising ground waters which may contain soluble salts cause damage to building structures both in a mechanical and physical way, and play a significant role as well; due to their hygroscopic properties they may also cause the accumulation of moisture which favours bio-corrosion.

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1. Water properties affecting the corrosion process of building materials

The molecules of water are of a special asymmetric structure in which, apart from two atomic bonds polarized between oxygen and hydrogen O-H, there are also two lone pairs of electrons. They are not arranged linearly but at an angle of approximately 104° which forms a tetrahedron.

This arrangement of atoms determines one of the most important features of the water molecule — polarity. The atoms of hydrogen are connected with oxygen by means of covalent bonds. A large difference in electronegativity between these two chemical elements (oxygen 3,5; hydrogen 2,1) makes the electrons move from the hydrogen atoms in the direction of the oxygen. There is a positive charge on the hydrogen side and a negative charge on the opposite side at the oxygen atom. These asymmetrically distributed electrons in the molecule make it become polarized. As a result, the molecule of water is a dipole, despite the fact that in its entirety it is inert.

The high polarity of H_2O molecules distinguishes them by the capability to dissolve salts — also compounds of polar structure, and they allow the hydration of building mineral binders. The polarization of H_2O molecules results in hydrogen bonds being made by the molecules. Hydrogen bonds have got a fundamental effect on the structure and properties of water. A single molecule can be combined with four others being nearby to form a network of certain durability. The lower the temperature of water the more such net structures occur. However, even at 40° C about 15% of H_2O molecules remain bonded with each other. This special property of water endows it with quite anomalous characteristics such as high surface tension, high heat capacity and a low pour point.

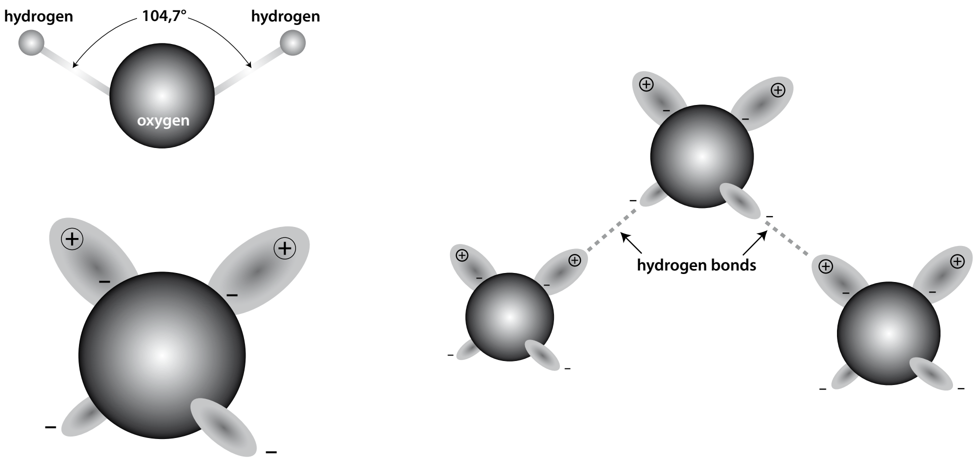

Fig. 1. Models of water molecules

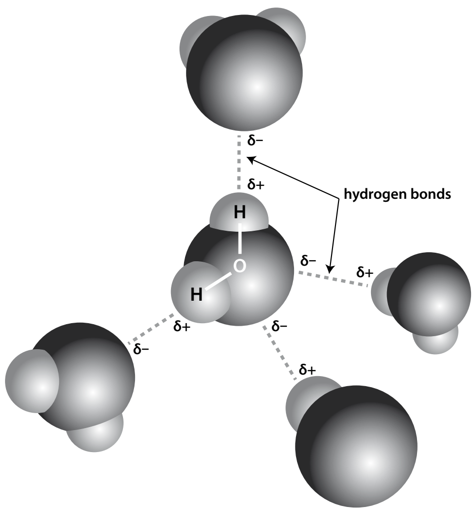

Fig. 2. Hydrogen bonds

These properties are essential for the existence of life — they, among others, make water occur in a liquid state in the conditions that prevail on Earth.

Another characteristic resulting from the polarity of H_2O molecules is the ability to surround ions and other polar molecules (hydratation). This is due to the attraction of dissimilar charges: ions have a specific positive charge (cations) or a negative one (anions), and the polar water molecules have two dissimilar poles. These molecules, which also have features of polarity and thus electrical charges, build into the cross-linked structure of water easily, and are called hydrophilic. They are characterised by good solubility in aqueous solutions.

Non-polar molecules not having a specific charge disturb the three-dimensional structure of water formed by hydrogen bonds. Since such molecules do not bind to H_2O molecules, they are pushed out of the network. They gather in groups and they are arranged in such a way so that the contact surface with water is as small as possible. Such molecules are called hydrophobic; they are poorly soluble in water or insoluble. The existence of such molecules in an aqueous environment results in the formation of “cages” around them — rings made of H_2O molecules connected with hydrogen bonds. They are structures of a higher level of organization that is of lower entropy. Since each system aims at the state of the highest possibly entropy, the formation of “cages” is energetically unfavourable. The best solution is to gather hydrophobic molecules so that they could be surrounded by the “cage” the surface of which is as small as possible. This action towards the energetically optimal state is the force producing hydrophobic effects.

2 Hydrophobization

2.1 Hydrophobization — general information

Hydrophobization is used to protect building structures which are susceptible to the periodic action of water coming from atmospheric precipitation, rainfall and snowfall; against moisture. It does not protect building structures against the influence of water being under hydrostatic pressure such as for instance pressing ground water, water accumulating on horizontal surfaces such as wall crests, cornices, or terraces. Hydrophobization is not a barrier for the diffusion of water vapour which may condensate inside the material. Hydrophobization is also used to protect masonry walls against weathering. Its purpose then is to keep binder solidity in the materials and to preserve its structural consistency.

Hydrophobizing preparations form colourless, non-sticky coatings, showing good adhesion and resistance to aging, on a non-porous stone surface and inside the porous structures of building materials. A thin hydrophobic film should delicately coat the capillary walls and not fill in the entire pore volume. Then the vapour permeability of the base is not significantly changed by hydrophobization. The impregnated material is capable of “breathing” which means that the two-way movement of gases and vapour is not disturbed (Barnat-Hunek 2010).

For wetting the material are responsible among others:

- An extreme wetting angle (fig. 3). It occurs between the material surface and the tangent to the surface of the liquid drawn through the connection point. The hydrophobicity of the surface increases with an increase of the water drop wetting angle. The materials on which the drop of water forms an angle bigger than 90° are considered to be hydrophobic. If the angle is smaller than 90°, the materials are hydrophilic.
- Surface tension of the liquid, which is a characteristic value for specific liquid and depends on the temperature.

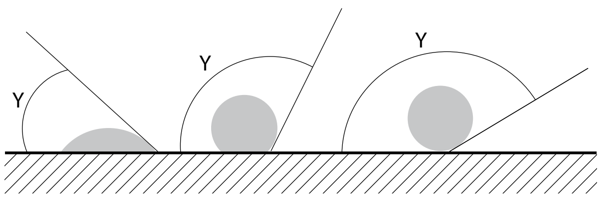

Fig. 3. Extreme angle of water droplets

The nature of hydrophobization is an increase of the limit of the surface tension between water and the impregnated material. The limit surface tension is approximately equal to the difference between the surface tensions of the substances that interface. The smaller the difference the more wettable the material. The surface tension decreases with the increasing temperature.

Silicate materials such as brick, plaster and others are readily wettable by water since the tension surface of water is about 72 mN/m, and silicates about 73–74 mN/m. Therefore the limit value of surface tensions amounts to 1–2 mN/m. As a result of the hydrophobization by means of organic silicon compounds, stone capillaries are coated with a layer of silicone resin, which leads to a decrease in the surface tension up to the value of 20–22 mN/m. The limit tension is then 51–54 mN/m. The surface of the stone becomes non-wettable and a wetting angle of a water drop is increased to about 105° (Barnat-Hunek 2010).

2.2 Hydrophobization — criteria for use

Hydrophobization treatments should be carefully planned, and stone should be free from patina and salinity; it should be relatively dry. Hydrophobization shall bring the desired effects and will not cause accelerated destruction of masonry walls if the following conditions are fulfilled:

- isolating the object from ground water by putting in a horizontal damp-proof course
- protecting the object against the hydrostatic pressure of water (e.g., by constructing roofing, flashings or vertical insulation of foundation walls)
- desalination and cleaning the material designed for hydrophobization
- conducting preliminary tests of hydrophization, which constitute the basis for conservation of the building structure.
- drying or ensuring an optimal, allowable moisture of the base.

Moisture level of building materials is a crucial factor which determines whether there is good adhesion of hydrophobic coatings to the base. When there is too much moisture in the base, the pores are blocked and the penetration of preparations is prevented. This makes it necessary to introduce hydrophobization treatments on dry bases only or upon those of allowable humidity. Unfortunately, the specialist literature does not provide us with a clear answer as to what level of base moisture one can apply hydrophobization. Opinions differ, some authors recommend dry bases only, however to obtain such conditions on masonry walls is practically impossible. Others give 4% as the upper limit of moisture content in the base.

The allowable moisture level is mainly conditioned by the different structure of building materials. The materials with small pores such as, for instance limestone, even at 2–3% of moisture are almost completely filled in with water. However, macropores prevailing in wide-pored materials cover themselves with a thin film of moisture and are not completely filled in. This is important for the end result of hydrophobization. Filling in the pores with water makes it difficult or even impossible to penetrate them with hydrophobizing agents. The macropores, partly filled in, are easily coated with a hydrophobic film.

Considering the above mentioned, before hydrophobization is implemented it is necessary to isolate the building structure from infiltration of water from the ground (e.g., by laying a drainage system), performing hydroinsulation membranes in thick masonry walls, or a damp-proof course if possible. The accumulation of moisture in the masonry which was subjected to hydrophobization makes it more susceptible to damage than it was before impregnation. Firstly, the masonry covered with a hydrophobic layer takes much longer to dry. Secondly, the water evaporation zone is moved into the material. As a result, water-soluble salts are crystallized in the building envelope rather than on the surface. The effects are devastating, the masonry undergoes disintegration.

It should be stressed that saline bases cannot be subjected to hydrophobization, although sometimes totally different opinions are given by sales representatives of hydrophobizing preparations.

When the concentration of salts is by weight over 1% in relation to the sample weight, then in such a case hydrophobization must not be applied. The hydrophobization of saline bases leads to moving the salt crystallization zone into the building materials, the consequence of which is scaling of the base with surface layers falling off. A similar situation is shown in fig. 4.

Fig. 4. Damage to stone surface of the sample caused by salt crystallization

Source: Barnat-Hunek (2010)

Fig. 5. Stone wall which cannot be subjected to hydrophobization (cracks, mortar holes, salinity)

Source: Barnat-Hunek (2010)

It is a common practice to implement the hydrophobization of saline stone, since the desalination of a thick masonry wall is far from being possible. It is necessary to dispose of salts contained in masonry walls by conversion of water-soluble salts into water-insoluble using preparations available on the market. Perfect results are achieved by using silicates. They make salt crystals isolated from water molecules which considerably limits the possibility of transporting salts.

You cannot make a hydrophobic coating on a surface which contains cracks and voids bigger than 0,3 mm (fig. 5).[1] Before the product is applied all cracks need to be repaired since hydrophobization will not provide leak-tightness. It is particularly difficult on masonry walls which were not plastered, since the historic masonry walls are frequently full of holes, joint cracks, etc., and repairing thereof is a challenging and time consuming task.

The use of preparations containing volatile organic solvents applied so far was allowed only to the exteriors of building structures. Nowadays producers of construction chemicals must consider the need to protect the natural environment and changes in regulations which oblige them to reduce emissions of volatile organic solvents. The legal regulations made the chemical concerns develop and manufacture water-based impregnating emulsions.

It should be emphasized that prior to the practical use of preparations there should be preliminary laboratory tests carried out in situ, and the selection of preparations should be compatible with the individual features of the base.

Test hydrophobization conducted under field conditions and implemented on the fragments of masonry walls should include:

- measurement of the consumption of hydrophobizing preparations for 1 m^2 of the masonry surface
- choice of application method (painting, pouring, spraying, etc.)
- defining the colour variation and surface condition of masonry walls after hydrophobization
- defining the effectiveness of hydrophobization by measuring the surface absorbability of brick, stone and mortar by means of the Karsten tube; this measurement is to determine the amount of water absorbed by the masonry in a particular time; the less water is absorbed by the masonry the better hydrophobic effect

It should be noted that the load-bearing components of the masonry (bricks, stones and mortar joining) are characterised by quite different physical-chemical properties. Therefore, the absorbability with hydrophobizing preparations as well the final result of hydrophobization for brick and mortar will be different. This fact needs to be considered while deciding on the method of hydrophobization. Also the consumption of the preparation for brick and joint should be determined.

The principle is assumed that mortar should have higher porosity and absorbability and lower strength than stone or brick. Therefore, to make the masonry, as a solid element, absorb a similar

1. [In the journal (in both Polish and English texts) European practice of number notation is followed — for example, 36 333,33 (European style) = 36 333.33 (Canadian style) = 36,333.33 (US and British style). Furthermore in the International System of Units (SI units), fixed spaces rather than commas are used to mark off groups of three digits, both to the left and to the right of the decimal point. — Ed.]

amount of preparation, the consumption of hydrophobizing preparation in the case of joints should be smaller. This fact makes the hydrophobization of brick and stone walls, which have not been plastered, a very time-consuming task (e.g., it eliminates the use of the hydrophobization method by means of pouring or application with a roller).

If conditions allow, laboratory tests are recommended on the material taken from the masonry, including:

- depth of penetration of hydrophobizing preparations into the structure of bedrock
- surface absorbability of the bedrock at a long-lasting contact with water
- tests for the existence of nitrate, sulphate and chloride ions since the application of hydrophobizing agents selected improperly may cause secondary salinity of masonry walls

Hydrophobic impregnation should be implemented when it is dry and it does not rain, at a temperature from +5 to +25/30°C. At a higher air temperature the agent could evaporate out of the surface too quickly.

Prior to commencing the impregnation of the facade, all surfaces which will not be impregnated (e.g., glass, metal elements, polished stones, wood, etc.), need to be carefully protected. In case of contact, wash them immediately with white rubbing alcohol. Special caution should be taken when there is polystyrene or bituminous material close to the component designated for impregnation. Using the agent with an organic solvent could cause the polystyrene insulation to dissolve and in the case of bitumen its spreading and making the facade dirty. In this case water-dilutable preparations can be used.

The main criteria which can be used for the evaluation of technical suitability of preparations for impregnating stone are:

- maintaining the aesthetics of the natural stone surface (no stains, no colour variations)
- effectiveness and durability of protection
- ease of use
- compliance with the environmental requirements

The most suitable are hydrophobizing preparations with properties of good penetration into the stone and those which do not seal the surface. The structure of pores has got a significant influence on the effectiveness of the hydrophobization of building materials, since the capability of liquids and gasses to penetrate into the material is dependent thereon. It should be noted that waterproofing impregnation is effective only if the critical depth of penetration is obtained and the surface absorbs an appropriate amount of the impregnating agent.

Hydrophobization is not a simple phenomenon and there are quite a number of factors which are responsible for the quality of hydrophobic coatings: chemical composition, structure and absorbability of the base, its moisture, surface contamination level, technique and amount of preparation applied, its properties, concentration, viscosity and the type of solvent.

2.3 Methods of Hydrophobization

Depending on the depth of penetration of preparations into the base one can speak of surface or structural hydrophobization.

2.3.1 Surface hydrophobization

This method consists in introducing the agent into the surface area of the material. The depth of penetration in the case of this method depends on the base type and is a maximum of a few millimetres. Hydrophobization can be performed using a flat, wide brush or a roller by applying the solution several times by means of the "wet-on-wet" method. Depending on the base absorbency these activities are repeated several times. Better results can be obtained by spraying with a low pressure machine or a water pressure pump. It is advised not to let the substance spread since they are toxic agents. The depth of penetration of preparations is bigger than in the case of application with a brush or a roller. Different depths of hydrophobization can be obtained depending on the base. The substance is administered until the base ceases to absorb the preparation and there will be a stream of about 50 cm running along the surface. The stream should run continuously.

Using the method of surface hydrophobization does not always produce the desired effect since the penetration of hydrophobizing agents into the base structure is too weak. Given the inadequacy of such solutions one should pay attention to the methods of structural protection.

2.3.2 Structural hydrophobization

Structural hydrophobization is implemented throughout the whole mass of the component or in the case of large-sized components to a depth of 3–5 cm. The hydrophobizing substance penetrates into the surface pores as well as inside pores which endows the object with homogeneous characteristics. The migration of water inside the material is more difficult, and little salts contained in the material do not cause degradation.

The use of structural hydrophobization for the components of outdoor furniture or sculptures is possible since it is performed by immersion of components in hydrophobizing solutions until the complete saturation takes place. Applying preparations with a brush or by spraying does not bring the expected results. In the case of large-sized components, especially masonry walls which in the basement can be up to 2 m thick, structural hydrophobization is very difficult to implement.

There are numerous opinions according to which it is possible to carry out structural hydrophobization in situ by means of the method of continuous flow of the solution which allows complete saturation of the object. Methods of structural saturation are propagated and often used by scientists from the Nicolaus Copernicus University in Toruń[2], or the Academy of Fine Arts in Cracow[3].

Types of structural hydrophobization methods are:

- Method of continuous flow which consists in pouring the preparation onto the material.
  A plastic bottle with a curved pipe is used for this purpose. Saturation needs to be done without any intervals by means of the "wet on wet" method in order to avoid breaking the column of liquid in the capillaries. The most popular way is the method of continuous flow through the load-bearing layer — lignin. The depth of penetration should range from 3 to 5 cm since the complete saturation of the masonry is not economic and even in fact unfeasible. The depth of penetration can be controlled according to the consumption of the solution per 1 m^2 of the surface. For concrete, whose absorbability is by weight about 6%, 3–4 l/m^2 are needed. In the case of bedrock, which is very popular in the Lublin province, the absorbability of which is by weight 24%, one would need to use as much as 12 l/m^2.
- Method of point saturation according to the Nicolaus Copernicus University in Toruń.
  The application of this method requires a set of tubes, for instance test-tubes, equipped with plastic hoses whose ends are topped with narrow funnels. In the tip end there is a polyurethane sponge which prevents uncontrolled flow of the preparation. Containers with solutions are placed above the impregnated parts and tip ends made of sponge should contact the base. Because of gravity the preparation flows out of the tube and penetrates the pores of the material. The penetration speed depends on the structural properties of the base, especially capillary rising. This method is efficient, however it requires using quite a number of containers, and spacing of saturation points should be done at a distance of about 10 cm. As regards the impregnation of the facade this is a very labour-consuming method.
- Vacuum method by the English company Balvac.
  The object needs to be tightly protected by plastic foil. The air accumulated under the foil needs to be removed with a vacuum pump. When the appropriate amount of vacuum is accumulated at the bottom part of the object, the hydrophobizing solution is introduced by means of a polyurethane hose until the object is saturated. Positive results have been achieved by using this method in conservation works of fence posts at the Extermination Camp Auschwitz-Birkenau. This method was given very positive opinions in England where it has been used for over 25 years, as well as in France. The implementation of vacuum impregnation of the facade is quite complicated as it requires the object to be tightly sealed in order to produce a void. The ground contacting the masonry needs to be impregnated with the solution and subsequently

2. [Polish: Uniwersytet Mikołaj Kopernika w Toruniu — Ed.]
3. [Polish: Akademia Sztuk Pięknych im. Jana Matejki w Krakowie — Ed.]

covered with foil and coated with sand or soil. Components showing considerable signs of damage must not be subjected to vacuum impregnation (Domasłowski et al. 2000).

Summarizing the abovementioned, obtaining the desired effects of structural hydrophobization involves high financial costs as they are costly agents, the consumption of which is considerable in the case of porous materials. Bearing in mind the economic balance and effort, surface hydrophobization is recommended for the conservation of masonry walls or facades of the buildings. By proper selection of preparations based on preliminary tests of hydrophobization effectiveness, satisfactory results can be obtained.

2.4 Hydrophobizing agents

Extensive research on the hydrophobization of stone masonry walls have been conducted at the Nicolaus Copernicus University in Toruń for years as well as at the Institute of Industrial Chemistry in Warsaw, at the Building Research Institute[4] in Warsaw.

In preventive conservation the following hydrophobizing agents have been used:

- **Soaps** are salts of fatty, resin and naphthenic acids. Basic components of soaps are: sodium, potassium, alkaline earth metals, heavy metals. Because of low resistance to dirt and mechanical damage and darkening the base, soaps are not recommended for the conservation of building structures.
- **Waxes** are organic substances of natural origin (e.g., animal — beewax; vegetable waxes; mineral waxes — fossil wax, parafine, microcrystalline wax) or synthetic (macroparafine, polyethylene waxes). Among all the described substances the best hydrophobizing properties were obtained by using microcrystaline waxes which form tight coatings resistant to stains and aging. Waxes are widely used in the conservation of non-porous materials such as marble. They are not recommended for the protection of porous bases such as light limestone. Despite good hydrophobicity, they easily undergo mechanical damage and colour variations (Domasłowski 1993).
- In conservation works, **synthetic resins** were used, including: polyvinyl acetate, polymethacrylates, polyvinylacetals and others. They were not widely used in the hydrophobization of building structures since the coatings formed were characterised by high absorbability, swelling and cracking. The coatings after having been expanded did not have sufficient adhesion to the base.
- Many years' research on the properties of hydrophobic compounds used in preventive conservation have shown that the best results were obtained in the case of **organosilicone** compounds. For the hydrophobization of porous stones only organosilicone compounds are recommended. The use of organosilicone preparations for hydrophobization is very popular not only in Europe but also all over the world, for instance silicone emulsions were applied for the conservation of the Capitol in Washington D.C., and the Cathedral of the Archangel Michael in Kremlin in Moscow. They have been used for over 40 years as a barrier against moisture in building materials. Organosilicone compounds are formed by combining silicon and carbon atoms Si–C, yet silicon constitutes the main component of the compound.
- **Silicones** are intermediate compounds between inorganic silicates and organic hydrocarbons. Silicones are capable of forming long lasting spatial networks. While applying silicones to the surface of the material they bind its non-organic part Si–O–Si with the mineral base which leads to the moving of water-repellent organic groups R to the outside (fig. 6). Consequently, this thin layer of the compound endows the base with hydrophobic properties.

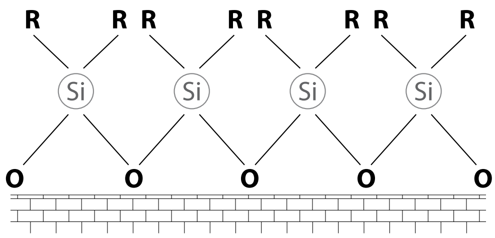

Fig. 6. The principle of organosilicone compounds action

4. [Polish: Instytut Techniki Budowlanej (ITB) — Ed.]

As a result of hydrolytic polycondensation there are thin films, coatings formed on the walls of the material pores which are of high hydrophobic parameters. These coatings are firm, resistant to changes of temperature, light, microorganisms and they have good adhesion to the base. They are characterised by poor viscosity, and low surface tension thanks to which they penetrate deeply into the structure of the porous material.

Silanes, siloxanes and silicone resins do not differ in terms of the effects they have but they do as far as the structure and molecule size are concerned. The molecule size of organosilicon compounds affects the depth and speed of penetration of preparations into the structure of building materials. Silicone microemulsions have the smallest molecules, siloxanes have bigger molecules. Silicone resins have the largest molecules which are about 100 times 100 bigger than the siloxane molecules. The diameters of some compounds such as macromolecular siliconates can be too big to actually penetrate into the fine-pored structure of material such as limestone.

The analysis of literature and the author's own studies show that the hydrophobizing preparations of hydrocarbon solvents protect buildings materials against the action of moisture to a much greater degree than water-dilutable preparations. This results from, among other things, a bigger angle of wetting the coating with the organic solvent.

In conservation practice, condensed solutions of alkyl alkoxysilnes are used for hydrophobization. It is important that their viscosity is poor so that they easily penetrate into the stone. They form firm, water resistant coatings of good adhesion to the base. Preparations in the form of cream have been quite popular over the last few years. Experiments carried out in Poland and abroad, and in practice proved the effectiveness of such creams.

Silicon rubber was used in the conservation of sandstone in the form of 2% solutions of rubber in rubbing alcohol. However, they must not be used for limestone since the acetic acid that is produced, damages calcite (Łukaszewicz 2002).

2.5 Requirements for preparations used for surface hydrophobization of stones

Technical requirements for repair and protective materials which are hydrophobizing agents have been defined by the Building Research Institute. The Recommendations for Granting Technical Approvals[5] (ZUAT) define a set of basic requirements for building materials.

ITB has issued three publications on hydrophobization so far:

- concrete — ZUAT-15/VI.11–1/00:2000
- ceramics — ZUAT-15/VI.11–2/01:2001
- building stones — ZUAT-15/VI.11–3/03:2003

The recommendations for Granting Technical Approvals to hydrophobizing agents of building stones (tab. 1) have been set forth in ZUAT-15/VI.11–3/2003 "Preparations for surface hydrophobization of building materials. Part 3. Building stones" (see: Krzywobłocka-Laurów, 2003).

Hydrophobization should not result in significant colour variants of the material, spots, stains, making the surface darker or glossier or in the occurrence of new salts based on chemical reactions with the material.

The test is carried out with a bare eye by comparing the hydrophobized surface with the one which was not subjected to this treatment. The preliminary evaluation of the effect of hydrobization is also defined based on the modified test of water drop absorption into the hydrophophobized surface of the building material. This consists in measuring the time during which the water droplet of defined volume penetrates into surface that was subjected to hydrophobization. This time needs to be compared with the time of water penetration into the reference surface, not having been impregnated. A characteristic value of the hydrophobization effect is the water drop absorption ratio and the water impermeability ratio.

The most important of the discussed parameters in terms of hydrophobic durability of the coatings is the surface absorbability n_p [kg/m^2]. This is the absorbability of the material determined by capillary rising, but in terms of water penetration from the surface of the sample contacting water, not by submerging the sample.

5. [Polish: Zalecenia Udzielania Aprobat Technicznych – Ed.]

Tab. 1. Technical requirements concerning agents for surface hydrophobization of building stones according to ZUAT-15/VI.11–3/2003ITB (see: Krzywobłocka-Laurów 2003)

Characteristic	Requirement	Test according to
The appearance of the surface compared to that before hydrophobization	No changes	ITB procedure
Water drop absorption rate, %:		ITB procedure and PN-EN 13755:2002
– for stones of water absorbability up to 5,0% by weight	$\leq 5{,}0$	
– for stones of water absorbability above 5,0% by weight	$\leq 10{,}0$	
Non-permeability ratio, %:		ITB procedure
– for stones of water absorbability from 0,5 to 5,0% by weight	$\geq 95{,}0$	
– for stones of water absorbability above 5,0% by weight	$\geq 90{,}0$	
The ratio of surface absorbability of stone after hydrophobization to its absorbability without this treatment after a time t, depending on the absorbability of this stone, %:		ITB procedure and PN-EN 1925:2001
– for stones of water absorbability up to 5% by weigh:		
after 6,0 h	$\leq 5{,}0$	
after 24,0 h	$\leq 8{,}0$	
after 48,0 h	$\leq 10{,}0$	
after 336,0 h	$\leq 12{,}0$	
– for stones of water absorbability above 5% by weigh:		
after 0,5 h	$\leq 8{,}0$	
after 6,0 h	$\leq 10{,}0$	
after 24,0 h	$\leq 15{,}0$	
after 48,0 h	$\leq 20{,}0$	
The relative ratio of water vapour permeability of cement mortar after hydrophobization	$\geq 0{,}8$	ITB procedure LO-4 PN-EN ISO 7783-2:2001

Another important property of impregnated materials is their relative vapour permeability coefficient once hydrophobization has been done. This coefficient shows how many times the vapour permeability of the tested material was decreased once the hydrophybizing preparation has been applied thereto.

2.6 Durability of the masonry's hydrophobization

It should be emphasized that the effectiveness of hyrophobization which is defined under laboratory conditions, differs very often from that applied on actual masonry. Therefore, tests to be conducted in the field on the effectiveness of hydrophobization would be recommended for instance by means of the Karsten tube.

The durability of hydrophobization is rather brief and it is evaluated at approximately 10 years. In situ testing carried out by scientists in 1990 (Krzywobłocka-Laurów, Rościszewski, and Zielecka 1993) in the historic building structures of Cracow, Olsztyn, Słupsk, Szczecin, Warsaw and Zamość have shown the good condition of surfaces protected by means of organosilicone agents in the operation period from 10 to 21 years. A better hydrophobic effect was observed on silicate materials and a worse on the materials with limestone binder. However, experimental studies conducted abroad indicate that a minimum service life of waterproof impregnation for concrete is up to three years. Therefore, hydrophobization treatments should be repeated after their durability period has expired. According to Prof. W. Domasłowski from the Nicolaus Copernicus University in Toruń, diluted solutions are used in the course of hydrophobization and thus this work can be repeated. This work does not have any detrimental effects since it is the silica that is the end product when the preparation undergoes decomposition.

As a result of water penetration and frost corrosion, delamination may be found at the interface between the base and the coating. Therefore it is advised to avoid conditions that favour water vapour diffusion, water accumulating under the hydrophobic coating, especially water containing water soluble salts. The literature on the subject has repeatedly taken up the subject of the insufficient hydrophobization of limestone and sandstone with lime and clay binders. Clay materials can affect the course of hydrophobization, however no detailed research in this respect has been conducted so far.

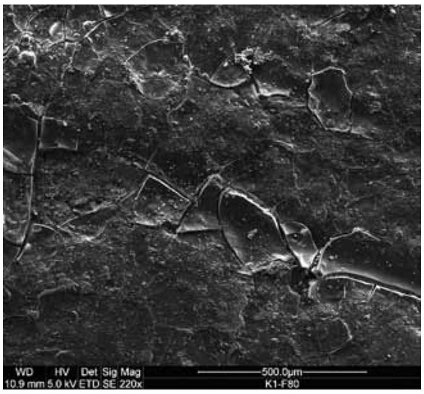

Fig. 7. Damage of hydrophobic layer in the stone structure resulting from long lasting water action. SEM picture taken after 12 months from hydrophobization

Protective capacities can be lost depending on heat-moisture conditions, for instance during strong winds preparations may simply vaporize. Wind causes loosening and scaling of the surface layers of masonry walls including the hydrophobic coating. Over time, adhesion is aging, especially due to changes of temperature, crystallization of salts and other corrosive factors. The loss of hydrophobicity of the coating depends also on the dose of solar radiation it absorbs. The coating can be damaged by sunlight.

Conclusions

Moisture and salts soluble in water are the most detrimental factors that cause damage to historic and modern building structures. Therefore, the major objective of conservation works should be the elimination of the effects and sources of dampness and salinity in the historic substance.

One of the effective ways to protect the stone masonry walls against rainwater is their hydrophobization. The hydrophobizing preparations available on the market have different properties and they are not always suitable for all building materials. The fact that modern construction chemicals are improperly introduced and affect the historic building structures gives rise to a lot of controversy. Producers of hydrophobizing agents frequently do not provide us with any instructions regarding hydrophobization of, for instance, stones little known to conservators and producers of construction chemicals all over Poland. An example is the “Kazimierz rock” which is treated as a “regional” stone.

When deciding on the hydrophobization of masonry walls, not only the technical aspects play a significant role but also ecological and economical issues are more and more important. These are very expensive conservation treatments which very often deal with a historic substance. The effectiveness and objective of the performance thereof should be based on preliminary tests carried out in situ and in the laboratory.

Firstly, one should perform the building diagnostics which consists in checking the amount of salts and moisture in masonry, due to the fact that a high level of salinity and a large amount of water in masonry do not allow hydrophobization. A prerequisite of hydrophobization is to actually remove moisture from masonry e.g. by introducing a damp-poof course in the masonry, drainage around the building, drying masonry walls. The causes of damage to masonry walls are to be determined and eliminated if possible.

Secondly, it is advisable that each particular building structure should always be case-specific thus technologies of proven effectiveness should be applied.

For this purpose it is recommended to carry out test hydrophobization under field conditions on parts of masonry walls and if possible also laboratory tests following the instructions set forth by

ZUAT (The Recommendations for Granting Technical Approvals) issued by the Building Research Institute in Warsaw.

The problem of the disintegration of masonry walls in the context of their hydrophobization should be treated as a whole, and the selection of repair – hydrophobizing agents should be compatible with the individual characteristics of each particular building structure. Only such an approach can guarantee the durability of conservation works.

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