

SUPERHYDROPHOBIC-OLEOPHOBIC SURFACES AND COATINGS
IN ANTI-GRAFFITI APPLICATIONS



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SUPERHYDROPHOBIC-OLEOPHOBIC SURFACES AND COATINGS IN ANTI-
GRAFFITI APPLICATIONS

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ABSTRACT

SUPERHYDROPHOBIC-OLEOPHOBIC SURFACES AND COATINGS IN ANTI-GRAFFITI APPLICATIONS

Graffiti is the arising phenomenon which affects cultural heritage whole around the world from the beginning of the second half of 20th century. There has been many efforts to avoid graffiti application onto these heritage by using law and scientific methods. During the those times, many removing procedure were applied to get rid of graffiti from the heritage. Graffiti should not be confused with street art. Graffiti was defined as illegal way to affect public properties. From the beginning of the 21th century, due to increased amount to remove graffiti from heritage and protect them from these attacks, especially by the EU, many projects have been conducted which lead new products are now on the market. By this time, some implications have also been developed to protect these heritage by coatings. One of these implications are creating superhydrophobic surfaces onto masonry heritage and makes easier to remove graffiti without any effects onto stone surface and avoid penetration of the dye into these structures. For this purpose, four different substrate and eight different dispersion were prepared by using wettability phenomenon which are about lowering surface free energy and creating rough surfaces. Goniometer was used to provide contact angle results to characterize coating with specimen as hydrophobic- superhydrophobic or none of these. Results demonstrate that coatings which were prepared by sol-gel method was able to create hydrophobic surfaces and they made the surface ease to clean due to letting the drops easily slide away.

ÖZET

ANTI-GRAFİTİ UYGULAMALARINDA SÜPERHİDROFOBİK-OLEOFOBİK YÜZEYLER VE KAPLAMALAR

Grafiti, 20. yüzyılın ikinci yarısından itibaren tüm dünyada kültürel mirası etkileyen olgudur. Hukuk ve bilimsel yöntemler kullanılarak bu miraslara grafiti uygulanmasının önüne geçilmeye çalışılmaktadır. Geçmiş dönemlerde kültürel mirasa yapılan grafitiden kurtulmak için birçok temizleme işlemi uygulanmıştır. Grafiti sokak sanatı ile karıştırılmamalıdır. Grafiti, kamu mallarını etkilemenin yasadışı yolu olarak tanımlanır. 21. yüzyılın başlarından itibaren özellikle AB tarafından graffitilerin mirastan kaldırılması ve mirasın bu saldırılardan korunmasına duyulan ihtiyaç nedeniyle, yeni ürünlerin piyasaya sürülmesine öncülük eden birçok proje yürütülmüştür. Bu zamana kadar, bu mirasın kaplamalarla korunması için bazı çıkarımlar da geliştirilmiştir. Bu uygulamalardan biri, duvar mirası üzerinde süper hidrofobik yüzeyler oluşturmak ve taş yüzeyine herhangi bir etki yapmadan grafiti kaldırmayı kolaylaştırmak ve boyanın bu yapılara nüfuz etmesini önlemektir. Bu amaçla, yüzey serbest enerjisini düşürme ve pürüzlü yüzeyler oluşturma ile ilgili ıslanabilirlik olgusu kullanılarak dört farklı altlık ve sekiz farklı dispersiyon hazırlanmıştır. Kaplanmış numuneyi hidrofobik-süperhidrofobik olarak veya bunların hiçbiri olarak karakterize etmek için temas açısı sonuçları sağlamak için gonyometre kullanıldı. Sonuçlara göre sol-jel yöntemiyle hazırlanan kaplamaların hidrofobik yüzeyler oluşturabildiği ve damlaların kolayca kaymasını sağlayarak yüzeyin temizlenmesini kolaylaştırdığı söylenebilir.

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LIST OF SYMBOLS/ABBREVIATIONS

AG	Anti-Graffiti
Ca	Contact angle
EU	European Union
γ	Surface tension
ΔE^*_{ab}	Colour difference
ICr	Relative Capillary Index
PR%	Protection Percentage Ratio
MEK	Methyl ethyl ketone
IPA	Iso-propyl alcohol
NP	Nanoparticle
R-812	Airsoil R812

1. INTRODUCTION

1.1. AIM OF THE STUDY

Main objective and the aim of the study is to develop coatings which have superhydrophobic and oleophobic features to perform as Anti-Graffiti coatings on natural stone, marble, concrete, and glass surfaces. Main objective is offering suitable coating on natural stone and marble which are mostly visible construction material at public places as a cultural heritage.

For this purpose, some well-known chemicals which have already been investigated as the anti-graffiti coatings and employed other parts of stone monuments conservation were selected to develop proper Anti-Graffiti coating on Ahlat Stone, Marmara Marble, Concrete, and commercial soda lime glass. Paraloid B72, a well-established and most used adhesive in conservation applications of cultural heritage, Aerosil R812 silica nano particles and fluorinated silanes were employed for this purpose. By using sol-gel technology, solutions were developed and then applied onto given substrates to investigate their efficacy against graffiti applications.

1.2. GRAFFITI PHENOMENON

Scratching graffiti by using some dye on porous stone monuments which are classified as cultural heritage is a novel problem on the field of conservation. To overcome this soaring phenomenon, there are some efforts to investigate possible coating applications that are currently used to preserve these monuments.

According to legal system, the term graffiti refers marking properties without content of their owners which makes it distinctive from urban art, thus, in this perspective and its today meaning, it is an illegal process classified as one of the most visible public crime [1]. Under these conditions, one of the most observed public crime is considered graffiti applications on building façades which could be both public or private properties and easily accessible [2]. However, graffiti had totally different meaning than its today meaning. The word of graffiti in the Turkish Language Institution dictionary is 'wall writing', and in Oxford

dictionary, it is defined as ‘drawings scribbled, scratched, or sprayed illicitly on a wall or other surfaces in a public place’. The origin of this word is Italian; *graffiare* (scratch, draw, scribble) and now started to be used. Graffiti was also considered as a political resistance phenomenon by taking into account Palestine Intifada example [3] . It is the also way of saying ‘I was here’ or ‘I have been here’ by humankind ever since the ancient times [4] .

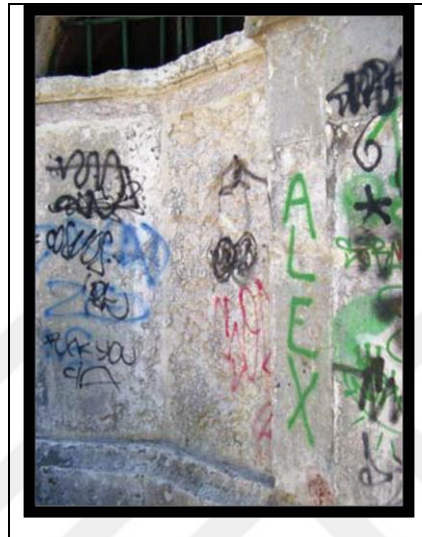


Figure 1.1. Graffiti in the west abutment of the Aqueduct built in limestone. Portugal, Lisbon, Águas Livres Aqueduct, 2005. “Alex” spreads on ca. 1m. LNEC / J. Delgado Rodrigues [5]

In terms of economics, graffiti has also been rising problem. For the public communities, as a result of spending money on cleaning procedures by urban administrations and private citizens, it can be considered as a real burden. There is a report that reffere Tennessee Department of Transportation spent more than 240,000 dollars for cleaning, and Las Vegas administration spent more than three million dollars each year to remove graffiti [6] . There is an estimation that cost of cleaning Milano (Italy) of graffiti would have been 100 million euros, and besides this, evaluated the cost of vandalism, including the graffiti removal to be approximately eight million euros which was evaluated by Trenord (Lombardy Railroad Agency, Ital) [7] . Morelia, where a famous World Heritage city center settled, spent hundreds of thousands pesos every year for graffiti removing as city of San Francisco spent 20 million dollar annually according to a report dated back to 2013 [2] . Istanbul Municipality spent 600.000 Turkish Liras to remove graffiti from public transport so-called ‘Marmaray’ in 2018, and they made a deal in 2020 for removing graffiti from the same

public transport for 55.000 Turkish Liras until the end of the year¹. In the UK, Network-rail reported that they spend more than £3.5m every year, removing graffiti² which can be considered as a huge amount of money even for well-developed country as UK. Another report has been published in Australia showed that almost five million Australian Dollars was spent to remove graffiti [4]. Nevertheless, Network-rail reported that how much they spent graffiti removal; they also stated that Banksy's Birmingham Homelessness art is protected³. Administrative applications and common public opinion are able to distinct graffiti and street or urban art in case of Banksy case in Birmingham. Since there is a distinction between this public opinion on the graffiti and urban art, coatings have been developed from the time the graffiti applications were recognized as a problem.

Open-air museum monuments, which is a significant part of the World Heritages, building, and structures are very open to environmental and humane attacks. These are mostly undergo deterioration due to various factors which can be listed as air pollution, physical and chemical weathering, microbial discoloration, and also the presence of undesirable graffiti [8] . Graffiti is the kind of human contagion on these kinds of monuments. In European Cities, around 3,500,000 protected monuments which are classified as part of cultural heritage are already affected by graffiti [9] . With the intention of overcoming to this recently soaring problem, which is most widely shared by all conservators and restaurateurs whom they are on the field to remove these drawings from surface of monuments and façade of building, between 2005-2008 GRAFFITAGE and in between 2014-2016 GRAFFOLUTION projects were conducted and financed by EU commission to ensure satisfactory extraction of graffiti without any damage to monuments surface and support urban environment policies to both prevent and eliminate graffiti [9] . Apart from these hugely funded EU projects, another remarkable projects can be listed as, The EFFACEUR Project (2011-2012) which was designed and conducted by small and medium-sized businesses with an objective of developing new anti-graffiti materials to the market, The BioRemoGraf (2013-2015) which is known as the pioneering study to develop novel biological removal methods based on using microorganisms by leaving the surface undamaged unless none of the chemical or mechanical (including laser) are able to detract

¹ <https://www.borsagundem.com/haber/temizligin-marmaraya-maliyeti-55-bin-lira/1461099>

² <https://www.networkrail.co.uk/communities/living-by-the-railway/bridge-maintenance/graffiti-removal>

³ <https://www.networkrail.co.uk/news/network-rail-protects-banksys-birmingham-homelessness-art>

graffiti from the surface without affecting the substrate, and the SICH PRIN project (2010–2011) which was focused on the developing new and eco-sustainable methods based on enzymatic cleaning of graffiti from the surface with lipase [10] .

As it can be seen, there is an escalating attention and huge effort for improving graffiti removal or protection procedures and methods. Due to the fact that, when the graffiti is applied onto a stone surface without any anti-graffiti coating protection, it is known that this graffiti chemical mostly cleaned many times later after it was applied and leads graffiti to interact with environmental agents and stone substrate by suffering chemical and physical alterations whose they have another impact on a stone substrates as known cleaning procedures directly affect the stone by consequences that can be listed as chemical contaminations, surface abrasion and mineralogical alterations related to properties of stone, composition of the graffiti dye and also preferred cleaning agents [9] . Especially for the porous and very porous stones, graffiti dye strongly adhere to substrate and solvent of graffiti to be absorbed in particular for these kinds of stones [11] . For dealing with negative impacts of the porous surfaces, there are some coatings which are used to create hydrophobic surfaces [12] . Spaces within the materials which makes the material permeable to outside affects defines as Porosity, which enables fluid motion inside the material by being both the favorable and unfavorable for building material; helps the fulfill conditions which is about inside-outside environmental exchanging for any kind of material unless facilitating additional deteriorations on the material if it is not controlled or prevented[13] . It is known that water is the main underlying driven forces for many alteration process for porous materials [14] . Although documentations and researches of the conservation treatments are scarce from the beginning of 21st century, precursor investigations about the nature and performance of Anti-Graffiti coatings appeared concurrently with the rise of graffiti problems during the 1960s and 1970s in cities such as New York and Philadelphia by using Hydron 300 (an acrylic-based coating) on public transportation in the 70s, which is the one of the earlier documented uses of a product as an AG coating [15] . Anti-Graffiti coatings are known as being responsible for preserving stone monuments by preventing graffiti attacks into the substrate and possible side-effects of cleaning procedures. Researches have been pursued and conducted before they have been gaining more importance at the beginning of the 21st century. After the above-mentioned projects which have been focused onto graffiti problem, many newly designed and improved materials have also been developed to

use in the removing step of graffiti and coating part of the monuments. In addition this, many commercial products have been developing and putting on the market from the 2008 which was the date the first scientific paper could be dated back [9] . Moreover, Sanmartin et al. pointed out that [8] efficacy of anti-graffiti systems have not been deeply discussed yet and also there is no standardized and compromised methods for evaluation of anti-graffiti treatments on porous materials. It is known that anti-graffiti coatings preserve stone substrates from graffiti dye attacks. Thus, ingredients of the graffiti dye should be known and analyzed to be able to develop proper coatings to conserve masonry surfaces. Correlation between graffiti dye and the surface is also important to understand the behavior of the dye when they contact with the stone surface and then, developing the effective coatings can be possible by taking account of this correlation and behavior. Removing methods, which are performed after graffiti dye applied onto monuments surface with or without protective barrier coatings, can be vary and they can show different characteristics and effectiveness regarding to underlying substrate, coating or implemented dye chemicals.

1.3. DECAY EFFECT OF GRAFFITI DYE ON POROUS STONES AND CURRENTLY USED REMOVAL METHODS

1.3.1. Chemistry of graffiti dye currently used

As graffiti, different materials and methods are used and new materials have always been adopted by graffitiists to expand their material and most of them are applied as spray paints due to quick and ease of applying properties [2] .

According to the knowledge that has been already had, paints are made of pigments binder and solvent which those three have different role in the paints. First one, pigments, they provide the color to the paint and second one, binders, they hold the pigments and stick them to the surface that they are applied, and last one, solvent are responsible of flowing of the mixture of former two in the paint. After the wet application of paints with solvent, binders, and pigments, it should be noted that the solvent in the paint evaporates, the binder solidifies. Thus, it is clear that if the solvent amount of the paint gets higher, it gives the paint greater flow rate which makes it easily penetrate [16] . Paints which are employed in the field of

graffiti have two-phase which can be classified as a vehicle (continuous phase) including binder (polymer or resin), solvent or diluent and pigment (discontinuous phase) additives, primary pigments (fine particle organic or inorganic) and extender (coarse particle inorganic matter)[17]. Thus, it clearly shows the importance of the paint which are preferred for graffiti applications on the masonry structures according to their phases by being dominant in continuous or discontinuous. One of the most important parts of the paints is the pigments which can be inorganic and organic, because of their color giving and opacity properties. Organic pigments are mostly made of titanium-based pigments, zinc-based pigments, antimony-based pigments and lead-based pigments as a white or color lighten pigments. In terms of analyzing results, black and red color are the most widely selected colors by graffitist in the graffiti application [2]. Ti (94%), Fe (84%), Ca (80%) and to a lesser extent Cl (64%), Zn (52%) and Si (46%) are listed as the main elements of red dye (18). Rivas et al. [19] identified rutile (TiO_2), Barite (BaSO_4), Sulphur, Copper in the mostly used paint which are red, blue and black in varying amounts. For the black spray paint, the most frequent elements are listed as Mg (29%), Al (18%), Si (82%), K (8%), Ca (63%), Ti (11%), Mn (8%), Fe (89%), Ni (13%), Co (34%), Cu (32%), Zn (32%), Rb (3%), Sr (11%), Zr (18%) [20]. For example, another color that can be used has graffiti paint pigment, yellow organic pigments; they include iron oxide, lead chromate, zinc chromate, and cadmium sulfide [2]. The silver paint contains: aluminum (19.43%) iron and zinc [19]. Unless there are some analyzing results about applied graffiti, the identification process is not simple due to the moisture, air pollution effects on the composition of the paint, several different layers of graffiti on the same place and last, separation of the graffiti from the substrate still not easy [21]. Gomes et al. [22] demonstrated that if the graffiti layer was exposed to artificial SO_2 aging, it was more difficult to clean, and also substrate was suffered by higher color changes. It was also shown that if alkyd graffiti paint is used, it presented the greatest resistance under SO_2 rich environment as a results of chemical modifications of aged polyethylene-based paint which resulted in graffiti losses and neo-formed mineralogical phases in the surface of the paint proving that removing graffiti become more difficult after aging [23].

As it was mentioned above, the second ingredient of the paints is the binder, which can is responsible to bind together the pigment particles and hold them on the surface [24]. There are different kind of binders which can be classified as their molecular weight and they can

be listed as chlorinated rubber, unsaturated polyesters, epoxide resins, phenolic resins, amino resins, oleoresinous binders and alkyds [17]. These different binders have important effect onto given conservation treatments or to particular sets of environmental conditions [25].

The last and the probably most important ingredient in terms of graffiti applications onto porous masonry structures due to the fluidity which directly affects the penetration of the paint into specimen, is the solvent which are known the vehicle for the pigment by being binder-liquid mixture [24].

1.3.2. Correlation of porous stone surface and graffiti

As it can be predicted that, there is a strong relationship between graffiti scratched sample surfaces and graffiti paint. The chemical composition, color, texture, hardness, roughness, and coherence of the substrate determine the impact of graffiti in terms of damage and removing [2]. For such, in terms of laser cleaning, the number of pulses required for the rougher surface is higher than from the smoother surface [26]. Besides, high porosity seems to suppress the effect of surface roughness on the laser cleaning up to a certain level due to the advantageous of the surface roughness over microstructures and moisture. The effect of moisture and porosity on the laser cleaning process is negligible in the rougher surfaces [26]. For the porous substrates, paint can easily penetrate the specimen, and it makes the cleaning procedure difficult (26-27). Porosity, pore size distribution and degree of interconnection of these pores, that are internal structure of the samples determine the respond of the specimens when they are dyed or coated with protective coatings by affecting the absorption, condensation, evaporation and migration of solvent, thus it is known that high porosity creates suitable environment of the absorption of water by substrate which deteriorates the structure as a result of the porosity channels inside the masonry [27]. According to the laboratory study performed by Dionisio and Ribeiro[28], it was possible to establish that alkyd sprays interact with the stone substrate modifying not only the color, bright and morphology of the stone surfaces but also introducing significant changes in water vapor permeability and water repellence. Thus, in short, there is the significant reduction in water vapor permeability of the stone, the significant increment of the water repellency of the stone surface, significant reduction of the roughness of the stone surface by creating a smooth and uniform overcoat and thus modifying surface texture and details intentionally left in the

original work of art by the artist, moreover, they also showed that different color paints affect differently to stone hydrophobicity [28] which can lead further damages on stone sample [12]. Varying in cleaning effectiveness in terms of porosity of the studied samples was also proven by Lettieri and Masieri, and they demonstrated that [29] neither mechanical nor chemical removing methods were effective in cleaning the paint from the stone surface due to its high porosity.

Some methods are currently used today for removing applications of graffiti from stone substrates. Carmona-Quiroga et al. [30] demonstrated that same substrate absorbed various types of coatings varyingly that affects performances of the AG.

Licchelli et al. [31] showed that even if the totally same coatings are applied by using same experimental procedures onto masonry surfaces, despite more amount, porosity of the each specimens possess huge influence on the results of the removing efficiency.

In terms of effect of porosity of the specimen, Cocco et al. [32] used two commercial sacrificial and semi-permanent AG coatings. Even though application procedure of the semi-permanent coatings varies regarding to applied surface characteristic, as being porous or not, they concluded that effectiveness of the AG coatings has been affected from surface properties, the porosity, and the roughness by influencing the adhesion capability of AG coating, thus, these materials exhibited good performances on the non-porous stones.

Pozo-Antonio et al. [33] demonstrated the effectiveness of the AG coating onto different compositional and textural granitic stones and resulted that if the porosity is less higher cleaning effectiveness is obtained in contrast to higher porosity and fissuration system included Alberto stone that exhibited paint penetration. It is also known that if the selected surface is the part of a steel, glass, glazed tile or any kind of non-porous structure, graffiti can be removed much more easily than porous structure specimens due to the impervious character of the sample against graffiti dye [34].

Carmona-Quiroga et al. [35] determined the effectiveness of AG treatments in connection with penetration depth for two commercial products, fluoroalkyl siloxane, protectosil, marketed by Degussa and hybrid organic-inorganic material (Ormosil) on different types of

stone. Inverse proportion between cleaning efficiency and porosity amount, that is, when the porosity is less coatings provides more effective cleaning for smooth surfaces. In case of granite, it was recorded that CF_3 terminals in the fluorinated coating were able to hinder spray paint bonding when it was compared Ormosil unless it was not able to ensure complete removing of graffiti from granite samples.

Roveri et al. [36] developed semi-empirical method to determine absorption of the water for porous stone and coating efficiency. Varying amount of Alkylalkoxysilane oligomers (15% w/w – 40% w/w) and TiO_2 nanoparticles (0.96% w/w – 0.12 % w/w)) in water and 2-propanol were applied onto stone to determine behavior for model construction. They concluded that this model was able to determine water absorption reduction after stone was coated [36]. They also represented behavior of pores according to their size as it can be seen in Fig.1.2

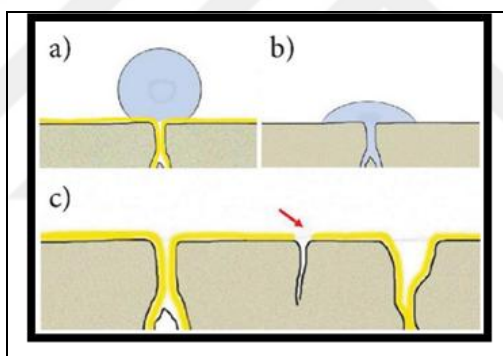


Figure 1.2. Assumptions made for the modelling of pore hydrophobization: (a–b) [36]

In this part, some properties of the graffiti dyes mostly used by graffitiist have been defined, the relationship between those paints and the substrates and relationship between coatings-substrate have been examined. At the end of this part, currently used graffiti removal methods which are classified as physical, and chemical will be discussed.

1.3.3. Currently used physical, chemical graffiti removal methods

There are various methods that have been used to remove graffiti without damaging to the surface of historic masonry, and these techniques are chosen taking account of the fact that what kind of graffiti paint is used and what is the main characteristics of the masonry [16].

Gomes et al. [37] listed nine strict questions which must be answered before starting on-site trials to take them the basis for the main design of the on-site cleaning procedure as listed;

- 1) What was the graffiti tool/medium?
- 2) What is the substrate? What condition is it in? What are the characteristics of its joints?
- 3) What is the risk of damage to the substrate? Are the removal system and the substrate compatible?
- 4) What is the likely effectiveness of the removal system selected?
- 5) Are the necessary materials, equipment, and skills available?
- 6) What are the details of the application of the removal system? Are the removal steps set out in a clear sequence? Is the system easy to use? Does it have a significant margin of error?
- 7) Is the removal procedure likely to have any adverse effect on surface appearance?
- 8) What is the cost of the removal system and what is its cost effectiveness in relation to the historical significance of the building or monument involved?
- 9) What health and safety consideration need to be considered?

By considering of these questions and remarks there have been both traditional, which have been used, and innovative methods that are still under development. Also, these methods can be divided into chemical removal methods, physical removal methods, and biological removal methods which is classified as the brand new and most promising technology in this field [2]. In terms of all representative types of substrates, they must be tested and then if it is necessary fragile surfaces must be consolidated before graffiti removing and those testing procedure should fully assess the liability of graffiti removal chemicals to transport stain further into the substrate in the face of evaluating all possible chemical incompatibilities and physical damage [37].

Pozo-Antonio et al. [38] performed a set of study to determine efficacy and understand which is the good way to remove graffiti by selecting mechanical and chemical, and laser ablation of the cleaning effectiveness for four colors of graffiti applied on granite and demonstrated that none of the procedures achieved satisfactory removing [38].

There is another comparative analysis for chemical and physical removal methods. Ortiz et al. [39] performed mechanical and chemical and laser method to identify cleaning effectiveness and economical evaluation of these methods on marble surfaces and they demonstrated that the satisfactory results of chemical agents and unsatisfactory results of other methods were obtained. Careddu and Akkoyun [40] used water jet technology to remove graffiti from marble substrates and resulted that it is an effective method for Carrara Veined marble. Gomes et al. [22] revealed that Hydrogommage® and IBIX® methods were not influenced by the graffiti composition because of their abrasive system. It was concluded that *Hydro Si* induced lowest color alterations and placing between *IBIX Si* (highest morphological alterations) and *IBIX Ca* (lowest morphological alteration) according to morphologic alterations. However, they also evaluated Nd:YVO₄ laser ablation, and they showed that this method left colored veils of blue and black on the granite surface.

Pozo-Antonio et al. [41] used hyperspectral non-destructive method to analyze and evaluate the effectiveness of chemical (Wenrox), physical (Hydrogommage) and Nd:YVO₄ laser methods to demonstrate the removing red spray paint on granite and they showed that surfaces cleaned with Hydrogommage and Nd:YVO₄ laser are able to create reflectance values close to the reference granite substrate classified the study success. Varying in cleaning effectiveness in terms of porosity of the studied samples was also proven by Lettieri and Masieri, and they demonstrated that [29] neither mechanical nor chemical removing methods were effective in cleaning the paint from the stone surface due to its high porosity. As a result of considering the graffiti removing methods generally as chemical removal methods and physical (mechanical) methods [37], there have been experimental efforts in both methods to figure out proper way to remove graffiti from the substrate.

It is known and already demonstrated above, those graffiti paints are made out by using different chemicals and chemical formulations to achieve required paints. Therefore, there are solvents and paint strippers are currently known and have always been testing on different researches to see their effectiveness on different specimens, which are capable of dissolving and breaking down these sprays paint [2]. There are various compositions, such as sprays or aerosols, both water-soluble and water-insoluble, and consistencies (gels and poultices) chemical removing agents are on the market to use based on solvent-based paint removers, other organic solvents and alkali-based removers [37]. Weaver [16] claimed that

using the poultices, or cellulose products, such as fluff pulp cellulose or shredded paper-mixed with a cleaning solution to form a paste or slurry, is the most effective graffiti removing method. On the vertical porous substrates or brickworks, these poultices exhibit better performances due to their thicker consistency [37].

For the freshly painted graffiti (1-2 days) consists of water-soluble chemical composition, can be removed via low-pressure water-washing, which is considered as most delicate process with neutral or non-ionic detergent which are tested before using due to their un-neutral characteristic which may leave undesirable residues on stone substances. Ammonia is also considered effective in these removal procedures since it should be noted that most of the commercial graffiti paints made of water-in-soluble materials, which makes them impossible to remove by using water [16].

Isopropyl alcohol, acetone or white spirit may be applied onto fairly new graffiti paints and alkaline compound application with compulsory weak acid wash and water rinse for neutralization or removing all the alkaline onto specimen, can be used to remove oils/grasses and waxes from non-alkali surfaces [2].

Strong alkalis (pH13-14), such as sodium hydroxide-based paint removers (caustic soda or lye), generally should not be used as they can cause efflorescence and staining on masonry surfaces if not properly neutralized[16]. It is known that potassium and other hydroxide paint removers may react with iron compounds in some masonry if it contains in some cases and create residues which makes difficult to clean the surface [16].

Alkaline removers can break down oil-based filmy by means of saponification, and they should be applied with hot water. In contrast, organic solvent removers which dissolve soluble dyes of felt-tip markers since only partly soften, swell and dissolve the binding media, and they generally applied to dry surfaces as the presence of water restricts their effectiveness [37].

In a US patent application, Perlman and Black [42] described a promising composition for chemical removing graffiti.

Pozo- Antonio et al. [38] studied the effectiveness of the commercial removing agents Wendrox[®], Eligraf[®], QuitaGraffi 200[®] + QuitaSombras 60[®] and demonstrated that last solution performed most satisfactory results. Ortiz et al. [39] studied Elephant Snot[®] and Graffipaste[®] to demonstrate the effectiveness of these removing products and they exhibited that the cleaning with surfactant solutions and with specific chemical agents leads to satisfactory results for most of the samples in their study.

Musolino et al. [43] suggested a novel removing approach on Istrian stones (low porosity and high compactness) providing two-components systems by combining silica sol-gel chemistry and dimethyl carbonate. They concluded that wet gels exhibited favorable results to remove graffiti on highly porous structures.

Most recently, physical methods were evaluated in three subcategories, which were classified as traditional cleaning techniques, novel cleaning techniques, and laser removing methods [2]. Weaver [16] listed some of currently used traditional physical methods which have to be tested before applying them onto masonry and these applications are abrasive grits, wet or dry blasting, high pressurized water applying, sanding or grinding and micro abrasive techniques with fine abrasives between 35-40 psi. Beyond these, according to Weaver, these methods should not be considered as a main method of removing graffiti due to resulting the damage into stone and special situations of some masonry which can be easily affected from pressurized washing if they are performed by unprofessional or inexperienced conservators or restorers. Abrasive methods generally not allow to remove a deeply penetrating graffiti medium completely and the damage is usually observed onto masonry as a result of softness of the material beneath or variations in the thickness of the paint thus it is recommended to use only for robust surfaces to prevent localized textural differences [37]. Ortiz et al. [39] performed hydro-cleaning at working pressures of 0.27, 1.09, and 7.67 kg/cm² and demonstrated that pressurized water only removed surface deposits and oxide with surface damage. Pozo-Antonio et al. [38] used the mechanical method Hydrogommage[®] and demonstrated that, although it did not achieve complete graffiti removal, it performed satisfactory cleaning performance besides the damage considered more intense, which was so-called mineral grain extraction.

As it was mentioned above, there are also some novel techniques which are still studied to develop them for graffiti removal applications with their merits and limitations, for instance, ultrasonic action has the potential to damage the substrate when the inappropriate frequency and amplitude are selected; mega-sonic agitation reaches a critical effective limit at 0.1 μm particle size; plasma spraying requires reduced operating pressures that may not be easily implemented, and dry ice blasting or cryogenic (CO_2 -based) cleaning is limited by the problem of thermal shock to the substrate [2]. Based on the US patent belongs to Hara who developed a nozzle design for industrial application, and an experiment was conducted to remove graffiti on a concrete wall by using sodium bicarbonate particles as a powder material which resulted in applicable observations [44]. Dry ice, which is solid form of carbon dioxide, in the form of small pellets of ice are pressure-blasted onto surfaces and after hitting the graffitied structure; the dry ice turns into a gas and returns into the atmosphere as carbon dioxide without leaving no residue behind. Soy-oil cleaning procedures which contains methyl ester, a compound in vegetable oils that are mixed with rubbing alcohol to remove certain types of paint are recommended for removing [2]. Sanmartin et al. [2] also suggest an Openair[®] plasma technology for removing graffiti as a result of hitting the graffiti painted specimens at ultrasonic speed and causing the evaporation of the paint.

Laser ablation removing methods has gaining importance during the past few years in the graffiti cleaning area, and there are many researchers focusing on its effectiveness. Pozo-Antonio et al. [38] performed an experiment by using Nd:YVO₄ laser at 355 nm to demonstrate efficacy of laser cleaning, which showed different effectiveness and unsatisfactory results regarding to paint color and melting of biotite of the granite specimen, over other mechanical and chemical methods. Ortiz et al. [39] evaluated the effectiveness of the 266 nm and 1064 nm laser pulses which display good cleaning performances by varying effectiveness regarding to pulses related to cleaning black sprays (1064 nm) and other spray colors (266 nm), both of them represented good performance to remove surface deposits-Gomes et al. [22] applied red, blue, black, and silver paints onto granite specimens and exposed them SO_2 by placing them into SO_2 rich environment during two months before testing the mechanical removing methods such as Hydrogammage[®], IBIX[®] and Nd:YVO₄ laser cleaning. They concluded that laser left colored veils of blue and black paints on the surfaces, and a more evident trans-lucid film was detected by eye on the surface cleaned which had silver paint as other test methods represent reflectance variation being highest for

silver paint. They also reported that the melting of the biotite grain for the laser cleaning method.

There are also novel methods which are called as biological removal methods. One of the most recent removing methods is labeled as a biological method, bioremediation, which is performed by using a sulfate-reducing bacterium, *Desulfovibrio desulfuricans* ATCC 13541, which is able to transform nitrocellulose based paint binders [2]. Germinario et al. [45] proposed a sustainable and green approach for effective graffiti removing (marker pen) by using the catalytic activity of the enzyme lipase. Sanmartin and Bosch-Roig [10] selected *Pseudomonas stutzeri* 5190, *Aerobacter aerogenes* 13,048 and *Comamonas sp.* 700,440 to observe bio-removal properties against graffiti dye on granite and concrete surfaces. They concluded that it is possible to consider the former one as a candidate for use in the bio-removal of graffiti by using powdered graffiti as an energy source to grow. It was also demonstrated regarding to FTIR-spectra that *Aerobacter aerogenes* 13,048 and *Comamonas sp.* 700,440 were able to induce chemical changes in both graffiti paints.

It should be reminded that, there is a strict recommendation about removing the graffiti as soon as possible to avoid future attacks onto surface, migrating depth into stone before drying inside due to the very fluidic character of the markers and guarantee that the paint do not overlap and combine chemical air pollution which makes it more struggle to clean [34].

1.4. CURRENTLY USED AG COATINGS FOR PRESERVATION OF STONES FROM GRAFFITI

Coatings have been using to avoid water and moisture containment mostly for porous structures that could generate and facilitate fatal problems for the building material which can be listed as microbial growth, material loss, and besides those, formerly, coatings has also been employed for aesthetic purposes and hygiene concerns [13]. When graffiti have been burst as a problem for cultural heritage conservation in third quarter of 20th century, coating materials have been developed to overcome this problem. As it was shown above, in recent years, EU conducted and assisted projects, for instance, GRAFFITAGE (2005-

2008) and in between 2014-2016 GRAFFOLUTION projects were conducted and financed by EU commission to ensure satisfactory extraction of graffiti coatings.

Even these topics will be detailed following parts, it should be noted that before explaining the coatings are employed for stone preservation against graffiti, anti-graffiti materials aim to generate low surface energy conditions to facilitate the removal of paint dyes from masonry surfaces by hindering adherence of low surface tension paints. For this purpose, its achievement and effectiveness can be evaluated in mathematically by determining the static or dynamic contact angle values which were defined by Young's equation for ideal, smooth, even surfaces ($\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos\theta$, γ = surface tension; SG, solid-gas; SL, solid-liquid; LG=Liquid-gas), representing the minimum free energy in the system [46]. Today, instead of calculating the contact angle values by using accepted formulation, goniometers are widely used to determine these values (Figure 1.2). It is also known that a coatings create a barrier or shield onto materials which they are applied by decreasing the some surface properties of substrate such as porosity and surface roughness which changes the permeability of the specimen [13]. In a similar manner, anti-graffiti treatments can reduce the average moisture content within the substrate, which may reduce its eventual deterioration [47].

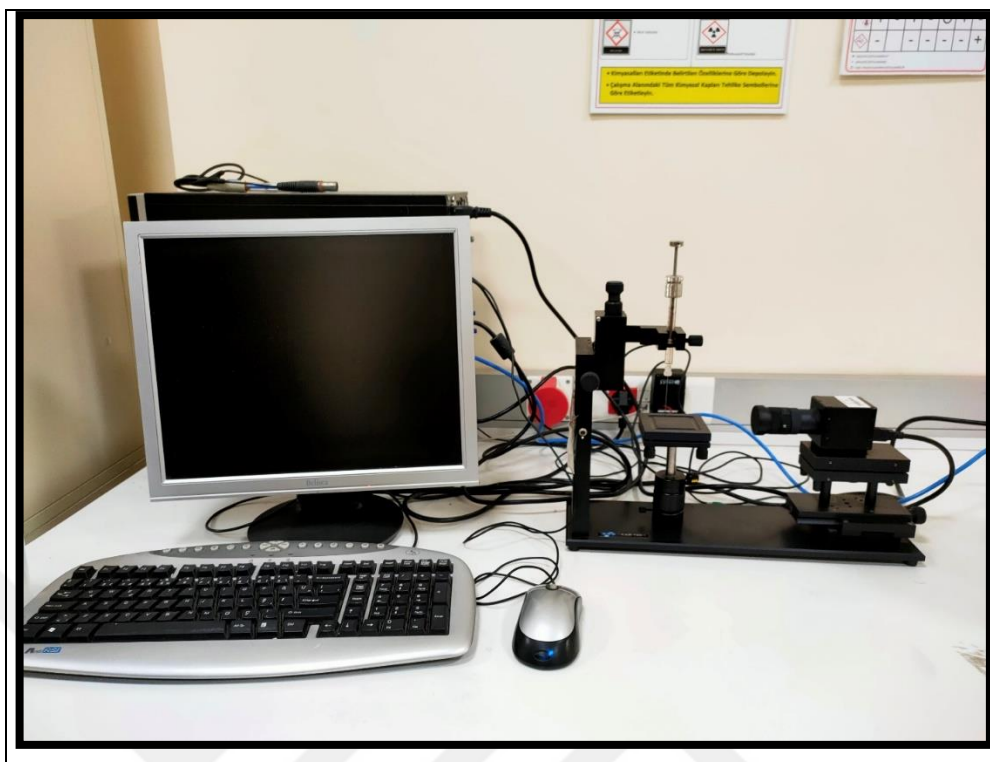


Figure 1.3. Goniometer

Carmona-Quiroga et al. [46] determined the dispersive component of surface energy for anti-graffiti (water-based fluoroalkylsiloxane and Zr Ormosil) coated materials. It demonstrated that both products reduce the surface energy in spite of CH_3 terminals of water-based fluoroalkylsiloxane reduced surface energy more than the CH_3 terminal of ormosil. Anti-graffiti coatings are considered in two main types; sacrificial (temporary coatings) and permanent coatings [9] as a transparent coating system [16]. These coating aims to create barrier onto surface against paint and facilitate graffiti removing by generating a water-and oil-repellent surface that prevent intrusion of dye on roughened surface of coating materials [34].

The permanent anti-graffiti coating can resist many cleaning cycles and usually consists of a coating, and a cleaning agent, unlike sacrificial coatings, is removed with the graffiti while it is cleaning; thus, it should be applied again [48]. Due to reapplying and cleaning procedure (e.g., high pressured water system) sacrificial method is expensive and lean on damaging masonry monuments, further, the durability of these kinds of coatings can be limited under undesirable environment conditions thence uncovered surfaces can be faced to graffiti again [49]. Sacrificial anti-graffiti coatings are mainly produced by organic compounds such as

waxes and carbohydrates likewise the microcrystalline waxes (non-toxic and environmental friendly), which are produced from crude petroleum or synthetically from ethylene gas, are physically permeable to water vapor due to their branched and non-linear carbon chains by showing durability for about 5 years on a vertical surface [47]. Limitations of sacrificial anti-graffiti coatings can be listed as; there are some detectable light colored changes during wet weather, they are not fully reversible due to graffiti residues tending to be left within coating residues and masonry surface, there is no fully protection due to some graffiti migration inside the coating barrier, the selection of universal barrier for all marker types is still not possible, some pore blocking effect avoiding them to applied to the substrates that has salt dissociation problem, its effectiveness decreases after repeated applications of cleaning/staining cycles, carbohydrates and waxes coating inducing fast soiling by holding dust, and they can damage the sustainability for removal and reapplying [37].

Otherwise, the permanent type is a durable coating with low surface energy that weakens the adhesion of the graffiti on the surface [49]. Permanent coatings avoid the penetration of inks and dyes into the coating and prevent masonry surfaces and also provides ease of clean environment for the above explained currently used removing agents [37]. Permanent coatings are not easy to apply on highly porous materials, because the coatings impede the moisture transport from the substrate through the atmosphere, in case of high salt contents in the substrate (as in many historical or ancient monuments) the adhesion of the agent is insufficient and treatments with permanent coatings are irreversible which is contradictory for the protection of historical monuments, thus, permanent systems were not allowed to use all around the world [49]. Weaver [16] suggested kind of a transparent coating by combining different coatings in terms of being permanent or temporary, based including a water based acrylic sealer application firstly on the masonry surface and after this polyethylene emulsion or dispersion should be coated over the underlying sealer.

Due to the fact that there some limitations, application problems and discussion that are assisted by law in countries such as Belgium, Garcia and Malaga designated a procedure which listed the minimum acceptable conditions including hydric and durability properties, color-gloss changes as well as cleaning effectiveness to get satisfactory results under varying test conditions to obtain suitable and durable coatings on the field of cultural heritage porous stones [50]. Weaver [16] offered 5 criteria for coatings by being water-vapor permeable,

invisible, no detectable color changes distinguishable from uncoated parts in wet environment, no discoloring and weathers evenly.

With all that, Lubelli et al. [51] strongly and persistently suggested that drying behavior which vary regarding to kind of applied AG coatings are very important to determine rather AG coatings suitable or not. They draw attention that AG coatings reduce moisture transport by hindering the liquid water transport that makes drying longer even if the product does not have any effect on the water vapor transport leading to enhancing salt decay, frost damage and biological attacks. Moura et al. [52] demonstrated the relationship between drying rate and water vapor permeability, that is, lowest drying index is registered for the product that has the lowest resistance to water vapor diffusion coefficient. These criteria are important due to the fact that Gerdei et al. [49] performed the experiment with permanent type copolymer, polyurethane, methacrylate, 2-C-polymer, and sacrificial wax/paraffin and demonstrated that these agents on a porous substrate reduces the water vapor permeability (breathing) which can cause even damage of the substrates if it is high reduction. This new material (2-C-Polymer) was defined as a silicon-based polymeric charge complex in a formulation of a polyampholyte with a latex core structure and a temporary polycation by adhering of polyampholyte onto the negatively charged natural stone surface and leading hydrogel-forming of polycation in-between latex cores and on the surface forming a film which is employing the low surface energy and water repellence achieving by incorporation of silicon-based methacrylate monomers into the polycation [48]. Meng et al. [48] demonstrated that polyester/polyurethane resin performed best cleaning efficacy unless it reduced water vapor permeability the most of all agent due to its formation of dense water vapor tight surface layer which avoids penetrating of paints the pore network with the porous substrate as same as Copolymer methyl acrylate – ethyl methacrylate which has much lower cleaning efficacy than polyurethane coating. The research group also showed that this newly developed 2-C-Polymer performed satisfactory results in terms of water transport properties, cleaning effectiveness, and changes in visual appearance. This is also important that unlike many silanes, this coating did not impregnate even porous materials.

Malaga and Bengtsson [47] conducted series of the experiment including artificial weathering with wax-based sacrificial coating by implementing them onto paving unit, brick, concrete light, concrete dark, marble white, marble pink, granite white, granite pink,

sandstone, and limestone. In this experiment, acceptable gloss differences and changes were proposed by researchers, and results were evaluated by using these criteria. They showed that gloss did not change for matt samples (0-2 units), except for brick and limestone whereas a slight gloss is increasing, for semi-matt samples (4-7 units) dark concrete show no change while granite showed a slight increase in gloss, for low gloss samples (18 units) no visible change and for high gloss sample (99 unit) a high decrease in gloss.

On today market, there are several AG coatings have been found unless these coatings are not tested to determine real long-term working conditions that is about safety on cultural heritage structures without deterioration of substrate and coating itself [53].

Today, there are novel coatings which are still under testing and developing. Striani et al. [54] synthesized a coating known as *HYBRID_{SUN}* to obtain a coating system on Lecce stone samples. Produced coating was exposed artificial and natural weathering conditions before monitoring hydrophobicity change and color variations. They observed excellent resistance in terms of salt crystallization and there is no mass loss for the stone which was coated by product. Hydrophobicity of the coating was also confirmed before and after abrasion tests [54]. Unless there was no evidence on AG properties of the coating, that is important to see effectiveness on removing and these cycles can be maintained for further durability. Its durability and well hydrophobic character could shed to further investigation to obtain possible AG coating applications.

Apart from stone protection, Rossi et al. [55] conducted an experimental research by using polyorganosilazanes (PSZs) as an innovative material in the coating filed to develop thin coating aiming to ensure corrosion protection, AG and ease to clean character on AA1050 (99.50% min of Al) aluminum alloy observing effects of both curing temperature and curing time. They concluded that this approach exhibited promising results for corrosion protection and AG property by increasing curing time and temperature to activate Si-H and Si-N hydrolysis especially in terms of corrosion protection. If the coatings cured at a temperature equal or higher than 180⁰, better results can be obtained in terms of AG properties unless hydrophobic properties are mainly independent from curing time/temperature.

Barthwall et al. [56] studied novel method to fabricate hydrophobic surfaces on aluminum plate and copper mesh, coated using simple dip-coating by modifying multi-walled carbon

nanotubes (MWCNTs)/ZnO composite with polydimethylsiloxane (PDMS). They resulted that 2.5 wt. % of MWCNTs in the PDMS modified MWCNTs/ZnO composite displayed excellent super-hydrophobic property with a water contact angle of 156° and a sliding angle of 4° . They also observed different properties on long-term such as flame-retardant behavior in the ambient environment. However, this method was not tested onto stone specimens and its AG properties were not evaluated.

Before defining technical information and mathematical models about the coatings such as hydrophobicity which makes ease of clean application by changing surface energy with varying ways and sol-gel methods which is employed to produce coatings straightforwardly, type of coatings and their practices will be covered in detail to gain knowledge about commonly used coatings and experimental coatings which can be offered ahead.

1.4.1. Wax AG coatings

These coatings are classified as sacrificial coating just as micro-waxes, acrylates and polysaccharides are and most sold type of AG coatings due to their neutrality on water vapor permeability and minimal changes in color and brightness in contrast to polyurethane which is the another most common type of the coatings on the market [34]. Except that, wax coating, as acrylics and not as much as polyurethane based coatings, able to hinder liquid moisture transport which reduce the drying rate significantly as a drawback [51]. Cocco et al. [32] used commercial paraffin wax which can be easily removable by hot water and two layers AG coatings which consists of amino-functionalized polysiloxane water emulsion as primer, seconder, as a base, alkyl fluoride functionalized silane monomer + a lyophobic polymer (semi-permanent) in their experiments and concluded that this compound does not perform good removing performance on porous stone unless they show strong modification onto surface in respect to water contact angle measurement by developing water repellence properties which is responsible to decrease wettability. It should also be noted that these coatings fulfill the colorimetric measurements for porous and non-porous surfaces (ΔE value between treated and untreated sample should be < 5) yet this was not suitable for porous surfaces in contrast to its data sheet, semi-permanent one loss its cleaning effectiveness after first staining/cleaning cycle. Similar results for paraffin wax were also confirmed in another experiment which was performed by Gerdei et al. [49]. These results prove that, as it was

said above, unless there are varying option on the market for Anti-graffiti products, their real-time results should be examined before the genuine applications on the substrates if conservators do not want to face any abrupt outputs. Torrisi [57] advised that artificial weathering should be evaluated delicately by comparison to real time weathering. Carmona-Quiroga et al. [53] tested the durability of the commercial sacrificial water based crystalline and polyurethane with a perfluoropolyether backbone against natural and accelerated weathering on Portland limestone and Woodkirk sandstone. Experiments demonstrated that wax coating undergo deterioration under weathering conditions which causes decreasing in the yellow content and increasing in lightness of the surface and reduction of contact angle on sandstone to below 90^0 , as a result, there is cleaning effectiveness loss after weathering.

Lettieri et al. [29] used commercial polymer wax in a study on the effects of a staining action and cleaning outcomes with coating system based on acrylic fluorinated copolymer in water emulsion (primer layer) and polymer waxes added to acrylic fluorinated resins in water emulsion (protective layer) onto highly porous Lecce stone specimen (porosity above 30%). As a result, they concluded that wax-based coating exhibits water repellency otherwise limitation of wettability does not result in a good AG performance and stain mainly remained onto surface with visible color observations, for the second coating system, it was almost completely removed after cleaning and dye penetrated through coating system which evaluated as a positive effect since dye can be removed with coating. On the further study with wax based commercial product which has been conducted by Lettieri et al. [58], they aimed to observe analyzing the distribution of a spray paint inside a highly porous natural stone material (Lecce Stone) with and without anti-graffiti protection in terms of penetration into the protective coating, accumulation as a superficial layer and staining of the internal parts of the stone. They reported that, X-ray spectroscopy (EDS) spectra results confirmed the presence of the thick wax-based coating regarding to reduction calcium, this water emulsion of polymer wax coating exhibits some crack onto stone surface according to ESEM images. Color variation was given as 1.08 before coating applied onto stone unless this value equals to 23.98 that is not acceptable color variation after removing procedure. Malaga and Bengtsson [47] observed that there is no variation on color, gloss and hydrophobic properties of the wax AG coatings after artificial weathering, and with that, coatings perform good performance by resisting graffiti penetration inside coating except leather dyes. Pozo-Antonio et al. [33] evaluated performance of the sacrificial water based crystalline micro

wax and permanent water based fluoralkyl siloxane on Rosa Porrino (less porous) and Alberto (highly porous) granitic specimens. Despite varying performance regarding to stone porosity for both coatings, chemical removal method was applied for permanent coating and mechanical removal applied for sacrificial coating whose they exhibit equally well performance and better performance in terms of color and gloss change on both granites. They also reported that results are more satisfactory if the removing applied after 30 days of graffiti application than those performed 3 days after, on the other hand it should be keep in mind that, according to authors, experimental procedure was carried out in laboratory conditions which are not as same as natural outdoor conditions. Wax coating performed hydrophobic character only on Alberto stone after ten weeks.

Masieri et al. [58] prepared AG coating system and they demonstrated that by using ΔE^*_{ab} results, 5.92, this system exhibits satisfactory removing efficiency due to primer coating (copolymer) avoided penetration of the stain within the porous structures of the stone. This result promotes the idea that has been given about using two-in-one coating systems to obtain fulfilling outcomes.

1.4.2. Polyurethane AG coatings for preservation

Adhesives, sealant and elastomers, polyurethane which can be synthesized by diisocyanate, diol and dispersing agent (dimethylol propionic acid [DMPA]) and can be used to develop coatings to provide hygiene, self-healing and AG properties especially adding fluorine content in it for hydrophobicity, have been evaluated that they can be used, as a result, in terms of fluorinated polyurethanes, there are two types of species, one is hydrophilic which is due to quaternary carboxylate salt and other is hydrophobic which is due to fluorine content [59]. It has been found oligourethane or polyurethane polymer with the fluorinated side groups have very low surface energies even with very low fluorine contents [60]. Polyurethanes draw attention in the critical aspect of their resistance in external environments, particularly resistance to solar radiation and UV [61]. However, polyurethane coatings decreases water vapor permeability as a drawback and Carmona-Quiroga et al. [53] used polyurethane with a perfluoropolyether backbone to demonstrate that after natural and accelerated weathering, 2000 hours in the QUC under UVB, coated surfaces yellowed and

darkened unless it did not loss its water-repellent characteristic. Fluorinated polyurethane coating were evaluated as good candidates in the field of AG coatings [60].

Manvi et al. [59] synthesized fluorinated polyurethane dispersion and evaluated its surface, mechanical, thermal properties [60]. Results indicated by Manvi et al. [59] clarified that increment in the fluorine content (blank, 3, 6, 9 wt%) decreased surface energy that gives high stain resistant to coating and increased roughness. Coating also became more elastic after fluorine added into polyurethane dispersion and provides low hardness due to the migration on the surface of the coatings. It was also shown that increment in the fluorine content increases the particle size that reduced hydrophilicity of the polymer. They concluded that thermal stability improved with increase in fluorine content, since as fluorine content increases cohesive energies of C-F covalent bond in polymer backbone increases, resulting in the improvement of thermal stability. Due the cost of Fluorine and the above result, it is concluded that 6 wt% fluorine gives best result whereas with 9 wt% fluorine develops little cissing and pinholes which spoil the esthetic value of coating [59].

Licchelli et al. [31] aimed to study on selecting suitable perfluoropolyether (PFPE) containing polymer and its effectiveness on the field of AG coating by water-based (avoiding hazardous effects) and requiring less amounts application onto stone on very porous stone. Fluorolink[®] P56 (Solvay-Solexis), an aqueous dispersion of anionic polyurethane containing PFPE blocks and carboxylate side groups, was known its oil- and water- repellence and stain release properties on different materials. As it was shown above, crosslinking is important to obtain satisfactory AG properties thus tris-aziridine was employed to provide polymer crosslinking. They observed the AG properties of both plain and crosslinked coatings. They resulted that although both plain and cured coating obtain high water contact angle values which is related to hydrophobicity, this barrier effect toward water penetration was not considered effective due to the capillary water absorption test that only resulted well at the shortest times unless cured coating exhibit slightly better performance. However, in terms of AG property, it was observed that cured coating (Fluorolink[®] P56/polyaziridine) avoid absorbing the ink stains onto stone leading to complete removal by standard removing procedure without losing coating that allows further staining/cleaning cycles. Therefore, as a result, the fluorinated urethane copolymer is a good candidate as non-sacrificial AG treatment [31].

Adapala et al. [62] modified polyurethane by OH- functional silicone polyacrylate with nanoparticles. They demonstrated that contact angle values in plain polyurethane and polyurethane-5 wt% silicone polyacrylate for water and spray paint increase from 72° and 71.3° to 103° and 102.8° respectively. Adding silica particles also improved mechanical properties of the coating unless its AG properties and mechanical properties decreased beyond 5 wt% polyacrylate and nano-silica addition, respectively, due to accumulation of siliconated component on the surface which resulted in saturation and agglomeration [62]. Last of all, surface hardness, elastic modulus and coefficient of friction was improved in the presence of NPs [62].

Rossi et al. [61] investigated UV radiation behavior of different monomers, in all formulations, a polyester resin with a high number of OH groups was used to have the lowest free volume as possible after curing in order to obtain a high chemical resistance. The formulation IPA was selected since isophthalic acid is suggested to originate with a more compact structure than terephthalic acid (TPA) thus, they resulted that terephthalic-based sample undergo high surface degradation after 200 h, while isophthalic based one resist reach up to 250h to exhibit same degradation that leads to whitening of the surface and water uptake amount remained less when aging cycles increased.

Rabea et al.[63], due to the fact that polysiloxanes exhibit desired properties such as thermal stability, biological resistance, hydrophobicity and undesired optical resistance property that can be surpassed by modifying it with polyurethane (Si-PU) having properties including good thermal stability, freeze resistance, surface property and hydrophobicity, conducted an experiment by using a series of silicone containing polyurethane coatings. They observed that in the presence of additive up to 10 mol% lower the surface free energy can be obtained which led to decrease in the wetting of the surface by graffiti and more satisfactory contact angle values for water and Formamide. Colorimetric measurement also gave the worst results for the coating without any additive which decreases penetration of the dye to the coatings. Therefore, they concluded that low surface free energy should be considered as the critical parameter to produce satisfactory AG coatings [63] in line with the theories. On the further study, Rabea et al. [64] investigated the mechanism of polysiloxane additive and the longevity of the resultant coatings against an accelerated weathering test thus, mechanical,

chemical, and surface properties of the aged samples were evaluated. In this study, they demonstrated that replacement of polyol with the additive up to 5 mol% decreases the surface free energy that is important for AG property. It was also proven that by increasing UV exposure cycles and additive concentration, samples showed unsatisfactory results. Moreover, this result was also confirmed by mechanical and surface evaluation of aged samples that the decrease in anti-graffiti properties during UV cycles was most likely related to degradation of silicone additive. Therefore, they claimed that coating including UV absorbing particles such as silica Nanoparticles or fluorinated containing additives can surpass the limitation resulted by UV exposure.

Liu et al. [65] synthesized polymethylsiloxane grafted by fluorocarbon side chains (PSF) [65]. In the Figure 1.4, their results can be seen.



Figure 1.4. Comparison of anti-graffiti properties between RPU (left) coating and AGPU (right) coating [65]

1.4.3. Polysaccharides AG coatings

Polysaccharide coatings, that are classified as sacrificial coatings, are able to coat surface without any change of natural appearance of the surfaces and exhibit water vapor permeability performance [34]. Polysaccharide coatings are well known to be easily reversible, clear, non-toxic, biodegradable, environmentally friendly, and compatible with most surfaces, including painted surfaces; however, the lack of experimental research for their use on outdoor contemporary murals provides an interesting topic for this subject [66]. Lubelli et al. [51] demonstrated that polysaccharide has no or a very limited effect on the drying behavior and not forming a film onto brick surfaces like waxes. Gagne [66] investigated the potential use of two polysaccharide coatings that are PSS 20 and APP S on outdoor contemporary murals and as a result, it was proposed to be used in the AG coating field due to its satisfactory results such as barrier effect, durability, remaining its transparency. It was observed that PSS 20 and APP S's overall molecular weight significantly decreases during and after aging becoming less effective as a barrier especially after ten years of aging. Another observation is that graffiti removal performed with a pressure washer could achieve a high degree of precision, which means that it is possible to selectively clean graffiti from a surface. Interestingly, due to the pigments of the dye, up to three years of aging, regardless of the type of substrate (brick or cement), Red Krylon Spray Paint is more easily removed from the surface than Black Sharpie Marker. After ten years of aging, the opposite is found, and both coatings perform better against Black Sharpie Marker [66]. This is the fact that, in the graffiti application, the materials which was chosen by painters to perform their graffiti has an impact on removal procedure and coating efficiency. Thus, it should be noted that determination step of the proper coating depends on the analyzing of commonly used graffiti paints on the market and substrate character as well. It gives a rule to conservators who are responsible preserving the masonry monuments to conduct set of experiments for every coating which they can easily find on the market before implementing them onto substrates as an anti-graffiti coating.

1.4.4. Silicon Based Resins

As fluoro-based binders, silicone-based binders or their combinations are employed in the AG coating industry to obtain very low surface free energy that is one of the most effective methods in this field due to its durability, cost problems and environmental advantage about using less extensive removing methods with less aggressive agents [67].

Moura et al. [68] observed the AG properties of permanent aqueous nanostructured coating of silicon-based molecules. They resulted that it showed the unsatisfactory performance on the silicate painted lime-based mortar substrate. It was also demonstrated that this coating can be removed more than 90% of grey paints with high pressure cold water unless yellow traces remained onto surface even after high degree of removing procedure. On the Lime-based mortar substrate without a paint layer surface, this coating allowed to remove more than 30% of blue spray and marker dyes with brushing cold water, on the level 3, it was observed that more than 90% of the blue spray can be removed from the surface unless after level 4 removing blue marker clearly visible onto surface.

On the market, these silicone based coating can be found to use in the AG coating field due to their high hydrophobicity, adhesion, durability with well resistance against weathering [34]. As a result of Si-O bond Silicon resins exhibits better performance than coatings including C-C and C-H bonds. As a result of this, they are thermally and chemically more stable ensuring higher hydrophobicity, water vapor permeability along with a suitable viscosity unless they can be degraded on harsh environmental conditions, thus, they are generally not preferred in presence of a polluted environment [54].

1.4.5. Fluorinated Polymer

Fluorinated compounds ensure super-hydrophobic and oleo-phobic surfaces, which can be obtained by different methods including etching by fluorinated-based gasses (CF_4 , C_2F_6 , SF_6) and sol-gel method [69], that is part of the developing AG coatings. On this issue, coating materials, fluorinated vinyl ethers, urethanes, siloxanes and acrylic units, partially fluorinated polymers and even PTFE (olefin homo-polymer) are employed [70]. Fluorine

atoms in these compounds are employed to ensure water-repellence regarding to their distribution of the fluorinated groups in chains and their orientation on the surface unless it is related to increasing amount of the fluoride that lowers the surface energy even at low concentrations [34]. Sam et al. [71] examined the effect of F-silane content in silica films by forming commercial float glass sample with sol-gel dip coating at room temperature and demonstrated there was not much difference in water contact angle when fluorine content was 0.5 or 0.4 wt%.

Alyamac and Soucek [72] examined the surface modification characters of the series of low, medium, and high molecular weight copolymers by concluding that even higher amount of fluorine throughout the coating could be necessary for dielectric properties and thermal resistance, the incorporation of small amount of fluoroalkyl monomers (5-10 wt%) to copolymerization obtain satisfactory surface properties in terms of contact angle, wettability, oxygen permeability and refractive index.

Malshe and Sangaj [73] performed set of experiment to observe optical, mechanical and protective properties of fluorinated polymers onto mild steel panel with less amount (5-10 wt%) crosslinking agents. They reported that it is possible to achieve desired protection properties addition of fluorine in a range 4-10 wt% in applied polymers. Another conclusion is that the surface exhibited well AG properties as a result of air-drying alkyl coatings cured on these fluorinated coatings could be peeled off from the surface. Fluorinated polymers are well known with their resistance against solar radiation and UV rays, permeability to water vapor and resistance to several staining/cleaning cycles that increases durability making possible to obtain permanent AG coatings [34]. As it was defined above, achieving the permanent coatings reduces the preservation costs. It should be noted that, permanent does not mean that the coatings last forever onto substrate. It only improves the resistance of the coating against more than one cleaning/staining cycles. Scheerder et al. [67] concluded that an increase in the concentration of fluorine could lower the surface free energy of the coatings since the AG properties clearly showed a maximum at lower concentrations of fluorine unless bulk properties play an important role as well. Thus, the reduced mobility, due to the high crosslink density, prevented the graffiti from penetrating the coating while the relative low surface free energy promoted easy removal of the graffiti [67]. This

combined action of surface and bulk properties gave these coatings excellent AG properties (Figure 1.5).

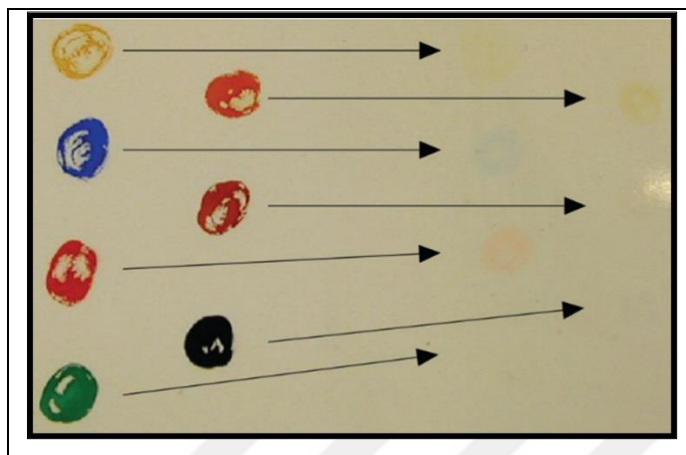


Figure 1.5. “Pearl” effect (left) and the graffiti remaining after cleaning (right) of FP6 [68]

It is due to the fact that synthesizing of the specified polymers are restricted regarding to their costs and complex procedure to produce, thus Kharitonov et al.[74] suggested a method that is based on by using direct fluorination to make possible to modify only thin surface layer several nm to several μm in thickness. They aimed to improve hydrophobicity, adhesion properties and surface conductivity of polymers by using high, low, and ultrahigh molecular weight polyethylene, polypropylene (PP), polyethylene terephthalate (PET) and polyvinylchloride (PVC). They concluded that the hydrophobicity of modified polymers is not changed and is even improved with time contrary to virgin polymers. In terms of the results they showed, improvement of AG coating can be obtained for the case of PP and UHMWPE grafting of styrene and acrylonitrile[74].

Due to the strength of the C-F bond [75], Perfluoroethers have very good stability unless they do not anchor to the limestone surface and thus diffuse throughout the stone which leads Rizzarelli et al.[75] conducted a set of experiment to observe effectiveness the protective agent Zonyl FSP onto calcarenite in Catania. They concluded that this fluorinated product exhibit high degree of water repellence, maintain vapor permeability, show transparency, durable against artificial weathering and able to slow down and hinder to algal colonization onto stone. However, bearing in the mind that other chemicals inside the fluorinated compounds, they can change the behavior of the compound, regarding to algal growth due to nitrogen presence into formula and logical same consideration have been thought for

phosphate presence [57]. Fluorinated polymers have also many disadvantages, such as price, insolubility in common organic solvents and weak mechanical properties, which have to be surpassed by copolymerization of it with low cost monomers, such as acrylates, methacrylates in terms of reducing cost and improving mechanical properties [76].

Commercial product, Fluorolink[®]P56, that is PFPE (perfluoropolyether) based polymeric product, has been applied, by Marzolla [77], to the Carrara Marble in the presence of an epoxy-silane (3-glycidyloxypropyltrimetoxysilane) and of a polyaziridine that are well known curing agents and without these curing agent to evaluate the coatings. In terms of colorimetric measurements, resulted color changes due to the coatings cannot be detected by eye, which is lower than 5 as a chromatic variation value. As colorimetric measurements, contact angle values demonstrated hydrophobicity in varying grade for cured and uncured coatings. After staining/cleaning procedure, cured coatings exhibited better and acceptable performances unless uncured coating was not suitable to use as a coating according to chromatic variation results. Contact angle values of the uncured sample was also decreased after staining/cleaning procedure that was concluded as a loss of coating material with removed ink from the substrate surface [77].

Alessandrini et al. [70] carried out comparative study with acrylic copolymers including fluorine content and without fluorine to define water repellency as coating material onto calcarenite of Noto, that is highly porous limestone, the Candoglia marble, that is highly crystalline and low porosity and highly poly-disperse pore radius. In their experimental procedure, following fluorinated and un-fluorinated monomers were employed: 1H,1H,2H,2H-perfluorodecyl methacrylate (XFDM), 2,2,2-trifluoroethyl methacrylate (TFEM), lauryl methacrylate (LM), methyl acrylate (MA), ethyl methacrylate (EM), and n-butyl vinyl ether (BVE); therefore, copolymers having different fluorine content and distribution along the macro- molecular structure could be prepared. As a result, they concluded that coating efficacy of these acrylic and acrylic vinyl ether copolymers improve with fluorinated side chain, although their performance is never better than that of the alkylalkoxy siloxane product. They also claimed that instantaneous water contact angle measurement must be considered cautious due to capillarity water absorption results which can be observed that XFDM (Poly(1H,1H,2H,2H-perfluorodecyl methacrylate-)) loss its barrier effects in extremely short time unless TFEM (Poly(2,2,2-trifluoroethyl methacrylate))

exhibits better durability for long and short term protection. Even TFEM/BVE (Poly(2,2,2-trifluoroethyl methacrylate-co-butyl vinyl ether) copolymers best coating efficacy among all other coatings in the experiment, its showed insufficient photo-stability results. This experiment also demonstrated that XFDM copolymers resulted darkening on porous stone while colorimetric measurements are negligible on the marble.

Toniolo et al.[78] observed the protective performances of two fluorinated acrylic copolymers by evaluating and comparing with Paraloid B72, a commercial copolymer ethyl methacrylate/methyl acrylate (EM/MA) and its partially fluorinated homologous 2,2,2-trifluoroethyl methacrylate/MA (TFEM/MA) on Candoglia marbles (a very low open porosity stone less than 1% and used in Italian historical architecture, Milan Cathedral). Before and after photo-ageing, they performed the static contact angles, color variations, capillary water absorption and water vapor permeability test to determine effectiveness of this coating. In terms of color variations, they observed that this modified coating induced similar decreases in L^* and after UV exposure, these results turned back to their original ones due to probable degradation of polymeric film that increases visible light dispersion, measured brightness. Another result is that the coating on this marble reduces the water vapor permeability. Fluorine containing ones were evaluated the causing the largest reductions, and among them the tetra- and terpolymers produce the worst results. In regards to contact angle measurements, that is related to hydrophobic character of the surface, XFDM/HFIM/EM/MA tetrapolymer shows the highest contact angle (around 108°), due to the presence of the long perfluorinated side chains from the XFDM units unless TFEM/MA and HFIM/EM/MA display a less efficient water repellent behavior, due to their shorter side chains with terminal CF_3 groups as the only fluorinated moieties, however it was also observed that after aging, XFDM/HFIM/EM/MA tetrapolymer exhibited the highest angle reduction. Paraloid B72 has the poorest water repellency, with a further sharp deterioration of its hydrophobic behavior upon ageing, it completely loss of its hydrophobicity after 1500 h of accelerated ageing. In the case of XFDM/HFIM/EM/MA, capillary absorption tests indicate that its effectiveness totally gone after 24 h as the others display barrier behavior only a few hours. Poor binder property of the Paraloid B72 was also showed when it was mixed with TiO_2 nanoparticles in terms of scarce hydrophobicity and photo-degrading performance of the TiO_2 NPs [14].

Poli et al. [79] investigated protective behavior including capillary water absorption, static contact angles, color variation, water vapor permeability, and SEM morphological analysis of the two new partially fluorinated acrylic copolymers on selected three different marbles such as Candoglia marble, Carrara and S. Giuliano marble. Although samples properties affect coating efficiency, it was shown that increasing amount of fluorine improved the barrier efficiency for Carrara marble. In case of Candoglia marble, results are relatively closer to Carrara marble. Regarding to porosity values, S. Giuliano marble has lowest values which is more decisive rather than coating properties [79].

Lee et al. [80] evaluated the relative adhesive and cohesive strength of fluorinated poly(methyl methacrylate-co-methacrylic acid) and fluorinated phosphate coatings on stone and tile surfaces by pursuing NanoScratch methodology that gives a semi-quantitative information of cohesive and adhesive failures. They resulted that although all coating exhibited binding to the stone and tile surface, polymers show stronger adhesion when it was compared to a small molecule fluorinated phosphate coating. They concluded that adhesion between anionic fluorinated polymers and granite is better than marble [80].

Mazzola et al. [81] aimed to surpass durability and efficacy drawbacks of the protective coating by synthesizing poly-acrylic esters containing variable amounts of fluorine in the α -position of the main chain by obtaining from the copolymerization of ammonium 2-fluoroacrylate and acrylic acid. They reported that best result was provided by reaction catalyzed by BF_3 or TMSCl [81].

Ma et al. [76] prepared and evaluated the hydrophobicity and anti-aging performance of fluorinated poly(ethyl methacrylate-co-butyl acrylate) by adjusting content of the hexafluorobutyl methacrylate (HFMA). They reported that unless in the absence of HFMA, coated sample exhibit 91.9° contact angle value, it is possible to see 129° if the content of HFMA increases up to 50%. It was also exhibited that under UV aging, by increasing HFMA content, weight loss can be reduced. As a conclusion of their work, the maximum compressive strength at 94.5 MPa can be obtained by controlling the amount of the crosslinking agents and monomers. In Figure 1.6, contact angle measurements can be seen. Lazzari et al. [82] claimed that pyrolysis-gas chromatography/mass spectrometry, Py-GC/MS, should be evaluated as outstanding and direct qualitative investigations of

monomers that have been used to produce commercial lattices with either un-fluorinated and partially fluorinated (meth)acrylic units.

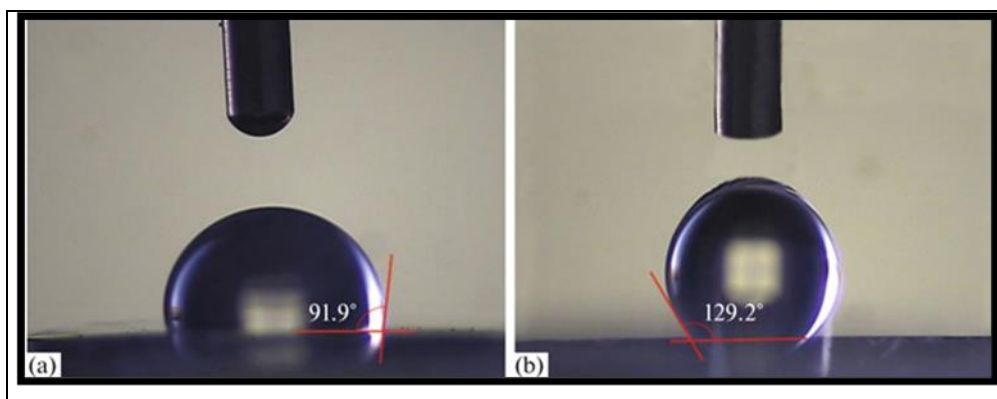


Figure 1.6. The contact angle for the polymer without (a) HFMA and (b) fluorinated poly (EMA-co-BA) [77]

Pozo-Antonio et al. [33] evaluated performance of the permanent water based fluoralkyl siloxane on Rosa Porrino (less porous) and Alberto (highly porous) granitic specimens. They reported that, the permanent water based fluoralkyl siloxane applied on the more porous granite could need more than seventy days to achieve the complete polymerization, which is also related with the amount of active residue of this anti-graffiti material on the stone. Due to the filling of the fissures, the granites coated with the permanent coating showed higher values of static contact angle. However, it was observed that only the application of permanent water based fluoralkyl on Rosa Porriño caused a more intense pinkish color of the K-feldspar grains, with an increase of the value of a^* coordinate (red hue). Also, the surfaces darkened (L^* decreased) and yellowed (b^* coordinate increased). Due to the mobility of the siloxane chain, it provides effective aligned on the surface polymer for fluorocarbonated chains thus, this was tested by Carmona-Quiroga et al [83]. They used commercial fluoralkylsiloxane (Degussa ‘Protectosil Antigraffiti’) onto limestone and granite. As a result, it is concluded that this AG coating provides hydrophobicity onto both limestone and granite unless cleaning efficiency of granite is less due to its rugged surface. Furthermore, water based fluoroalkylsilane materials were suggested due to their resistance against chloride attacks which reduces corrosion of reinforcement [84].

To demonstrate efficacy of the fluorinated compounds, Moura et al. [68] studied the cleaning effectiveness of lime stone, lime-based mortar and lime-based mortar with silicate paint

substrates protected with AG coating which are water based organosiloxane emulsion with special additives (sacrificial), coating with SiO₂ nanoparticles (sacrificial), water based fluoroalkylsiloxane (permanent) and aqueous nanostructured emulsion of silicon-based molecules (permanent). On the removing procedure, they designated levels from 1 to 3 for limestone, high pressure cold water washing, high-pressure hot water washing, commercial based graffiti remover and high-pressure hot water washing, and 1 to 4, brushing with cold water, brushing with hot water, brushing with commercial remover and water washing (1st cycle) and brushing with commercial remover and water washing (2nd cycle) for mortar with or without silicate paint. They employed visual observations, colorimetric measurements and FTIR analysis to identify effectiveness of the applied coating after removing procedures in varying levels. They concluded that first three coating allowed complete removal of the graffiti at the level 3 cleaning procedure for the limestone sample by exhibiting varying effectiveness on different levels. It was observed that, for fluoroalkylsiloxane coating, grey paints was not totally removed after level 1 since, high pressure hot water easily removes all traces and left no paint shadows onto limestone surface. For blue color, only commercial cleaning was able to totally remove color from the coated specimen surfaces disregarding to which coating was used. It is due to the fact that, organosiloxane emulsion with special additives (sacrificial), coating with SiO₂ nanoparticles (sacrificial) and water based fluoroalkylsiloxane (permanent) provided barrier effect onto porous specimen and avoiding the migration the paint into stone pores which makes them ease to clean. For the lime-based mortar substrate without a paint layer, fluoroalkylsiloxane exhibited satisfactory removing performance for grey and blue paint unless none of coatings were able to totally facilitate removal of blue paint. Otherwise, for the silicate painted lime-based mortar substrate, fluoroalkylsiloxane exhibited satisfactory removing performance on level 3 removing process for blue paint. They concluded that fluorinated compound exhibited optimal performances.

Licchelli et al. [85] coated very porous Lecce stone by using commercial fluoroelastomers to observe and investigate its water repellency. In terms of contact angles values, it was observed that sample coated by capillary absorption gave higher contact angle values independent from applied amount unless, by brushing, it was reported that contact angle values are lower than former method even they were still hydrophobic. Water absorption by capillary, that was used to obtain Relative Capillary Absorption Index (ICr) and Protection

Ratio percentage (PR%) data, confirmed that all coating maintained their hydrophobic character less than 10 minutes by only varying rate of the water absorption without effecting final amount of the water that was absorbed. ICr values showed that, in terms of brushing, this data strongly influenced by the amount of the material, lesser amounts gave higher ICr values, contrarily, former method has no influence on the ICr value regarding to applied amount. The most satisfactory PR% results ($\geq 98\%$) are observed when stone specimens are treated by brush with 50 or 75 g/m²[85]. In terms of colorimetric measurements, this was shown that ΔE^* values for brushed samples were more strongly dependent on the applied amount compared to the capillary absorption coated samples. For the all cases, latter one exhibited better colorimetric values in terms of overall chromatic changes. Water vapor permeability values were also affected by the application method of the coatings. It was shown that there was drastic reduction in permeability values for same amount samples regarding to coating method that are, if the coating was applied the brushing method, reduction was more than capillary absorption was able to do. In a conclusion, it was reported that none of this results could be considered as an appreciable for stone protection method [85].

1.4.6. Nanocomposite Materials as Anti-Graffiti Coatings

Nanotechnology enables to obtain specialized compounds/products that represent different and improved properties from their bulk character. Nanocomposites, with enhanced properties, have been evaluated as promising for the surface protection of masonry [86]. However, the production of nanoparticles still has several difficulties [87]. The sol-gel process is a suitable means to synthesize inorganic-organic composite material since the inorganic backbone can be built up by a low temperature process, and organics can survive processing [88]. Nanomaterials based hydrophobic coatings have been widely under investigations and also currently produced [69]. Mainly, from the AG coatings developing point of view, super-hydrophobicity is set as a purpose. This property is described by Wenzel model and Cassie-Baxter model which are mostly about surface roughness by changing liquid-solid and liquid-vapor interfaces (Figure 1.7) [87]. This part will be more detailed above with its own subtitle.

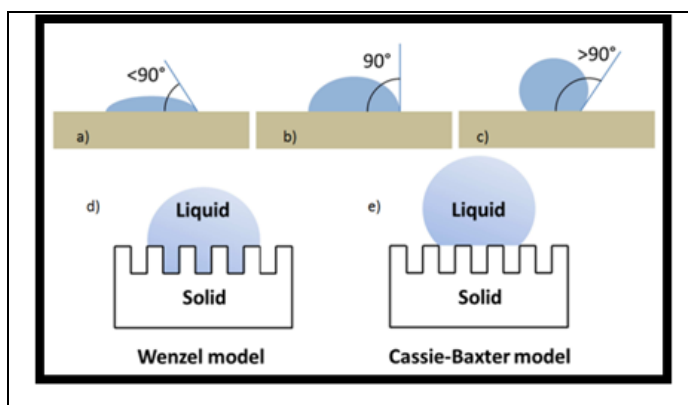


Figure 1.7. a) hydrophilic b) starting point of hydrophobicity c) hydrophobic d) Wenzel Model of hydrophobicity e) Cassie-Baxter Model of hydrophobicity [88]

A project name Horizon 2020 have been currently in progress that aimed to encourage developing nanomaterials based on TiO_2 , ZnO and Ag on the field of conservation of the European Cultural Heritage [89]. In terms of improving mechanical, thermal and weathering performances of organic coating, nano-silica one of the important additives to obtain satisfactory coatings with UV resistance, transparency and high hydrophobicity due to the UV absorber property, low refractive index (1.46) and surface modulus enhance characteristic of the nano-silica [90]. As a results of above mentioned conditions, Rabea et al. [90] developed their previous works, that were mentioned above including the performance of a permanent polyurethane-based anti-graffiti coating containing a silicone additive upon deterioration effect of ageing, to observe UV resistance of these coatings by adding silica nanoparticles in order to enhance UV resistance into the coating formulation. It was observed that silica nanoparticles did not adversely affect to coatings in terms of transparency that is important in the field of cultural heritage. Regarding to contact angle measurement, that was performed for water, diiodomethane and benzyl alcohol, adding silica nanoparticles have no significant effect on surface free energy, despite slight reduction below 90° , due to unchanged results of the contact angle values despite increasing in silica nanoparticles. Mechanical improvements without contact angle improvements were also confirmed by Adapala et al. [62]. In the field of conservation, nanocomposite coatings mainly represented a drawback about reducing the breathability of the stone unless there are many effort have been pursued to overcome this limitation [87].

Far apart from porous stones, Sam et al. [88] prepared inorganic-organic silica based coatings by stirring TEOS (tetraethyl orthosilicate), hydrochloric acid, ethanol and de-ionized water at room temperature, then after adding 0.002 mol GLYMO (3-glycidoxypentyltrimethoxysilane) into solution, it was stirred again for 24 h at the same conditions and SLS glass sample was coated with this nanocomposite coating dip-coated method varying withdrawal rates. As a result, despite slight increase in light transmission, it was not high with very strong adhesion and abrasion resistance even after 1000 cycles. However, it was also observed that under the HCl, coating was not durable if the film thickness reaches 230 nm that was the highest thickness [88].

Kesmez [91] developed nanocomposite coating that is hydrophobic and photocatalytic including Ce doped TiO₂ nanoparticles via sol-gel process and coated glass. In terms of contact angles, this nanocomposite coating that were applied by spraying method onto surface exhibited significant increases for water and hexadecane, hydrophobic and oleophobic, respectively. Coating also did not change the clarity and light transmittance values of the glass sample [91]. Photocatalytic character of the coating was also demonstrated by using decreases in the Rhodamine B concentration with respect to irradiation time of the sample and it was clearly shown that increase amount of nano TiO₂ coating became more photocatalytic. It was also remarked that using the fluorocarbon molecules in the coating during the curing time that led to TiO₂ NPs were able to move to top the surface as physically and this situation may have contributed to the improvement of the photocatalytic property [91]. Although this coating was not applied onto porous or non-porous stone samples, hydrophobic/oleo-phobic and photocatalytic character with high durability of the coating may shed the new studies that focus on observing its AG coating behavior. It is remarkable that self-cleaning properties of the water dispersed TiO₂/poly(carbonate urethane) nanocomposite materials is also well known [92]. TiO₂ NPs were also employed to develop Si-based consolidates [93]. Cappelletti et al. [94] developed a smart hybrid coatings containing home-made TiO₂ nanoparticles mixed with the Alpha[®]SI30 polymer were applied to the three materials (Botticino/ Carrara marbles and Angera stone) in order to obtain super-hydrophobicity. Colorimetric measurements demonstrated that this nanocomposite coating can be applied onto stones due to lower values in terms of total color variation before and after UV aging. It was also showed that by increasing the amount of the TiO₂ into applied coating, contact angle values are rising and closing to the super-

hydrophobic labeling area even it achieved to pass 150⁰ for Carrara marble. Efficiency of TiO₂ NPs adding into fluorinated polymer in terms of photo-degrading effect and good water-repellent character before and after UV aging was also demonstrated [14].

Green chemistry on synthesizing these coating have been gaining importance. Recently, seed oil has been used to produce water based polyurethane dispersions by synthesizing from elastomeric polymers, that is the green way to produce these coatings, and incorporation of these materials with nanomaterials are able to improve mechanical, thermal and anti-bacterial performance of the coatings [95]. Ocak et al. [96] proposed a sustainable bio-nanocomposite coatings composed of biodegradable polymer (poly-L-lactide [PLA]) and montmorillonite clay (MMT) with varying concentrations using dip-coating method and investigated its possible availability for preservation purposes of the marble surfaces by performing the measurements of surface roughness, wettability, water vapor permeability, capillary water absorption, and color changes on the marble surfaces. Montmorillonite clay (MMT) is the well-known nano-clay as halloysite, sepiolite and laponite that are used by incorporating into polymer matrix generated nanocomposite films suitable as coatings for metal and stone substrates, providing surface protection from atmospheric pollutants, corrosive agents, and entomological attacks [86]. MMT, that is the most widely used smectite nanoclay, creates excellent gas barrier properties to the polymer nanocomposites [97]. Furthermore, Cloisite[®]20A was used as the nanobuilding block for the nanocomposite coating preparation that were prepared to protect bread-made museum collections [98]. Ocak et al. [96] demonstrated that contact angle was increased up to 108⁰ by increasing amount of added the MMT into polymeric matrix and decreasing in terms of capillary water absorption. It was also measured that water vapor transmission rate decreases by adding MMT into coating thus it is noteworthy that addition of nano-clay to biodegradable polymer enhanced the water vapor barrier properties of the polymer [96]. Another result recorded that increasing the amount of the MMT into coating results the higher total color difference ΔE^* values. Cozzolino et al. [98] concluded that the including MMT nanocomposite coating has no remarkable change of appearance of the artefacts despite slight color and gloss differences detected. In their study, the entomatic tests revealed that the nanocomposite coating was the most effective for preventing the wheat weevil attack, with no damages detected on the samples and high mortality of the insects [98]. Licchelli et al. [11] used varying amount of MMT nano-clay, that is Dellite[®]HPS a naturally occurring Na-montmorillonite while

Dellite®43B derives from a naturally occurring purified montmorillonite to prepare nanocomposite coating implementing them into Fluorolink® P56 fluorinated polyurethane. GLYMO was employed as a crosslinking agent. Coating efficiency was evaluated as a gel and onto very porous Lecce Stone specimen against acrylic paint and permanent markers removing by using MEK or isopropyl alcohol. It was reported that as a gel fully evaporated gel, Dellite®43B exhibited desired results confirming by the almost spherical shapes of the droplets onto coating and that behavior increases by increasing the amount of MMT into coating unless none of the coatings including MMT or not exhibited desired results against permanent marker. Presence of the surface film was confirmed by SEM results that proved there was no migration into stone due to its very porous character.

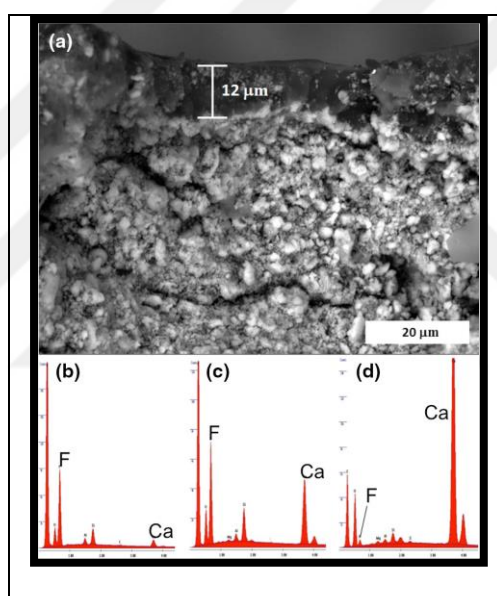


Figure 1.8. a SEM (SE mode) taken on cross section of a LS specimen treated with Dellite® 43B (3 % w/w); b, c, and d EDS spectra taken at 2, 8, and 17 µm from the surface, respectively [11]

Despite contact angle values proved that coatings have hydrophobic properties water absorption profiles demonstrated that Dellite®43B 3 and 5 wt% exhibited decent results in terms of water absorption of the stone in long term operations. Unless Dellite®43B 3 wt% exhibited %43 residual permeability (water vapor permeability test), that is not suitable, none of the coatings allow to use in conserve stone specimens due to their residual permeability values lower than 50%. Colorimetric variations of the coated samples before started staining/cleaning cycles were also acceptable for all coatings. Durability and the efficiency of the coatings were also evaluated after 8 consecutive staining/cleaning cycles by performing colorimetric measurements that were assisted by microscopy images and

contact angle measurements. In terms of contact angle values, it was demonstrated that there were no significant changes on water repellency behavior of the coatings for acrylic spray and permanent marker. Colorimetric measurements indicated that for acrylic sprays, Dellite®43B exhibited best performances after 8 cycles when it was compared other coatings, however, it was also reported that in terms of permanent marker, none of the coatings exhibited desired results except that first cycles. It was also demonstrated that surface character obstructed the removing process thus some residual black spots were examined by microscopic images for acrylic spray paint. In terms of permanent marker, as it was mentioned that none of the coating exhibited desired behavior, results were similar for both coatings and further, SEM and EDS analysis demonstrated that, in some points of the stone, coatings were removed with dye while the removing procedure were applying onto stone surface that is confirmed by fluor, chlorine and calcium peaks of the EDS results. Unless it was known that MEK shows a strong interaction with the hydrogen bonds between the polyurethanes chains due to its strong polarity [61], due to the IPA, the fluorinated polyurethane is partially soluble in IPA, the corresponding cross-linked material could undergo a swelling process during the cleaning procedure. As a consequence, some ink components dissolved in IPA could diffuse into the polymer matrix [11]. In the another study, Corcione et al. [99] prepared organic nano-filled systems based on methacrylate mixture matrix and organically modified boehmite as a nano-filler. In terms of water-repellency, color variations, capillary water absorption, water vapor permeability, penetration into the stone were assessed and compared to the same characteristics displayed by two commercial organic water-borne hydrophobic coatings (concentrated water solution of organically-modified alkyl silanes and milky white emulsion, based on acrylic resins and alkyl silanes) exposing them natural and accelerated weathering conditions before testing to estimate the long-term behavior of the coatings on Gentile and Lecce stones. Contact angle values indicated that it increased when the amount of the nano-filled coating applied on stone surface increases for both stone specimens likewise ΔE^* values. Nano-filled coating exhibited better performance after natural exposure in terms of contact angles unless its un-aged high hardness value could not be detected after aging procedure. High contact angle values make this nano-filler coating a candidate in the AG coatings applications. Moura et al. [68] determined behavior of the sacrificial coating with SiO₂ nanoparticles. It was observed that, this coating allowed complete removing of the graffiti dye from the surface for the limestone case. In the case of lime-based mortar substrate without paint layer, it was

demonstrated that after the last level of removing procedure, small residues and traces were still remain onto surface. On the silicate painted lime-based mortar substrate, this nano-additive coating exhibited best performance to remove blue dye unless it did not achieve to remove grey paint, yellow stain traces were detected. In terms of their physical properties (water repellence, water vapor permeability, drying behavior, open porosity and color), Moura et al.[52] concluded that sacrificial coating with SiO₂ NPs had best performances. However, Rabea et al. [90] demonstrated that increasing the amount of the nanoparticles additive inside the coating may result undesired results in terms of AG property of the coating after more QUV cycles. It was also obtained that the sacrificial coating with SiO₂ nanoparticles product caused the highest color variations [52]. Therefore, it is obvious that amount of NPs must be adjusted to obtain suitable AG coatings. Renda et al. [100] developed protective nanocomposite coatings by using commercial Fluoline HY and Wacker 290 including TiO₂ nanoparticles (particle dimension below 25nm and surface area of 45-55 m²/g) and SiO₂ nanoparticles (particle dimension 7 nm and surface area of 395-420 m²/g) and then demonstrated their effectiveness in terms of water repellent character and availability with respect to color variations on Comiso (highly porous) stone and Noto (less porous) stone samples. In terms of total color variation results, ΔE^* , Wacker 290 included coatings rather adding TiO₂ (that shows slightly better results) or SiO₂ NPs exhibited better results by giving slight variation, less than 5 units that is suitable, for both stone samples unless Fluoline HY showed higher results than units rather adding SiO₂ or TiO₂. In terms of contact angle values, Wacker 290 and its nanocomposite coating exhibited far better results for every case by improving water repellence and resulting higher contact angle values. However, it should be noted that, for Comiso stone that is high porous, Fluoline HY and its nanocomposites were more successful to created hydrophobic surfaces compared to Noto stone coated Fluoline HY included nanocomposite. TiO₂ containing nanocomposite exhibited better performance for Comise stone even its base was chosen as Wacker 290 or Fluoline HY. It was also clear that nanoparticles addition decreases the contact angle values for all cases. All the treatments reduce water absorption of the stones during the first 3 h of contact with water and the capillary absorption coefficient is strongly reduced after the treatment with all the formulations, also in presence of the nanoparticles [100]. Lettieri et al. [101] developed an experimental formulation in the presence of fluorine with SiO₂ NPs and investigated two commercial products fluorine and silicon based which were applied on two calcareous stones. It was reported that newly developed fluorine-based nanocomposite

exhibited required results in terms of total color variation and contact angle, that are almost super-hydrophobic, for both stones. This novel coating also demonstrated improvement of the water vapor permeability. Oleo-phobic behavior was also determined for this nanocomposite coating on both stone specimens. Due to its water vapor permeability and hydro/oleo-phobic behavior and suitable color variations, this coating was recommended to investigate on the AG coating purposes [101]. Two commercially available poly (alkyl siloxane) products in white spirit, Rhodorsil 224 (Rhodia Silicones) 7%wt and Porosil VV plus (AquaBarta) 10% wt, that were used as received with silica (SiO_2) particles (fumed powder, Aldrich) with a 7 nm mean diameter dispersing (2.0% w/v) in the siloxane solutions were investigated on three types of stones, Opuka, Božanovský and Hořický, which have been used for the restoration of the castle of Prague [102]. It was reported that obtaining super-hydrophobic surfaces were possible for both coatings on every stone specimens unless, in terms of color variations, only results from Opuka stones treated nanoparticles coating was acceptable to use. It was also observed that the treatment of the stones with pure (hydrophobic) siloxanes and siloxane- SiO_2 (superhydrophobic) composites resulted in comparable reductions of the water vapor permeability and the water amounts absorbed by capillarity [102]. Roveri et al. [89] conducted an experiment to investigate alkyl alkoxy silane oligomers (15% w/w) with TiO_2 NPs (0.96% w/w), alkyl alkoxy silane monomers (40% w/w) with TiO_2 NPs (0.12% w/w), hydrophobized silica with AgO and ZnO nanoparticles (0.2% w/w) and Silres BS290 (protective treatment based on silanes and siloxanes, Wacker Chemie, dil. 8 wt.% white spirit) behavior on Apuan marble (Carrara region, Italy), Balegem limestone (Ghent region, Belgium) and Schlaitdorf sandstone (Neckar area, Germany) those have varying porosity. Except Silres BS290 and alkoxy silane monomers (40% w/w) with TiO_2 NPs (0.12% w/w) on Schlaitdorf stone, all coatings exhibited suitable color variation. Latter one also led to best improvement in terms of contact angle measurements unless this improvement loses after UV aging inversely to hydrophobized silica with AgO and ZnO nanoparticles (0.2% w/w). Anti-bacterial effectiveness was also verified [89].

1.4.7. Fluorosurfactants

Fluorosurfactants are the short-chained nanometer-sized agents to ensure unchanged water vapor permeability and create hydrophobic samples by penetrating into pore well and

functionalizing as a result of improved diffusion into porous stone matrix [103]. As a result of this diffusion into stone, long-term stability can be achieved unless most of the AG coating loss their AG properties after short time and uptake significant amount of water [104]. Kronlund et al. [103] preferred to use four fluorosurfactants (DuPont, Capstone FS-61, Capstone FS-63, Capstone FS-64 contains additional surfactants less than 2.5%, Capstone FS-65) and two fluorinated polymer (Mafon, Lineplus PDM 210, Lineplus PDM) in the purpose of demonstrating effects on hydrophobization of marble by prolonging the treatment times as well as increasing the concentration.

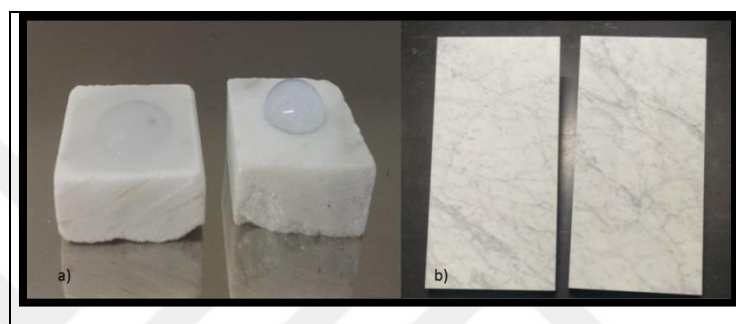


Figure 1.9. The behavior of water droplets placed on an untreated marble stone and a stone treated with 10 vol% Capstone FS-63 for 24 h. The picture is taken after a contact time of ~5 min. b) Untreated (left) marble and marble functionalized with 10 vol% Capstone FS-63 for 24h at 60°C (right) produced for esthetic evaluation [103]

They concluded that, even all treated specimens represent hydrophobic behavior regarding to water contact angle measurements, capillary absorption tests proved that only Capstone FS-63 and Lineplus PDM 210 ensure complete preservation until surface was exposed to strong UV unless Capstone FS-63 exhibited satisfactory and promising results. As a further improvement for large scale cultural heritage protection purpose for low-porosity calcareous stones, Kronlund et al. [105] investigated on a new functionalization method based on the Capstone FS-63 fluorosurfactant system which has been developed to eliminate water contact, to minimize weathering effects and to create a semi-permanent anti-graffiti coating on marble. By taking into consideration of previous drawbacks of this method, that is, requirement of the immersing the marble into functionalized solution at temperature between 60-80°C causing problematic for larger objects (masonry structures), they conducted a new set of experiments by using spray coating to aim reducing the material consumption and operating the method at room temperature. It was demonstrated that applied coatings obtain

AG property by facilitating the surface which the paint easily washed away with a standard pressure washer 3–4 times in a row.

As it is described above, there are many studies which aims to investigate proper and acceptable way to develop Anti-Graffiti coatings. Hydrophobicity is one of the key issues to ensure Anti-Graffiti coating to use on the masonry monuments. These efforts have been focusing on the develop solutions which has hydrophobic properties. This is the first step which the coating should have been provide. Gomes et al. [9] prepared two useful tables, one of them for AG coatings, their applied stone, their response against type of graffiti dyes and removing method, and, second one showed the methods used to evaluate the performance of anti-graffiti effectiveness, harmfulness and durability. Due to importance of the hydrophobicity of the coatings, this phenomenon will be detailed above to understand its basic mechanisms.

1.5. HYDROPHOBICITY AND WETTING ANGLE

In the nature, hydrophobicity phenomenon relies on the Lotus leaf thus this effect is also known as ‘Louts Effect’ and shaped the whole are about self-cleaning and super-hydrophobicity[106]. These kind of coating structures have been fabricated and also some structure as Lotus Leaf have been observed into these coatings which have been employed to make the surface super hydrophobic [107]. This superhydrophobic behavior is obtained from its low surface energy along with rough micro/nanostructure [108]. These micro and nano structure roughness obtain higher contact angle values to water droplet and make its environment improper to adhere the surface thus it can drop off from the surface easily [109]. Especially in the textile industry [110] and other areas besides Anti-graffiti coatings such as solar panels, anti-bio fouling paints, anti-sticking of snow for antennas and windows, dust-free coatings on building glasses, self-cleaning windshields for automobiles, microfluidics, lab-on-a-chip devices and metal refining these coatings have been mainly used and still under developed [108]. This property also refers to self-cleaning [111]. As it was seen above, today, superhydrophobic surfaces can be detected by using goniometer. These devices demonstrate contact angle value which is also known as wettability. Droplets on the surfaces have different phases which are known as solid-liquid, liquid-vapor and solid-vapor phases

and each of them has their own surface tension which can be calculated by using Young's equation below [112].

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad (1.1)$$

It should be noted that, if the interaction between droplet and surface is low, it means surface energy is less which helps to create hydrophobic surface. It is happened when the molecular forces between water molecules is great than the molecular forces between the substrate and water molecules [108]. This theory is related to Young's equation which defines mathematically the cohesion and adhesion forces between solid and liquid and inside the liquid [113].

Wettability or surface hydrophobicity relies on four main characteristics which are classified as Contact angle (CA), sliding angle (SA), contact angle hysteresis, surface roughness and surface energy [114]. Contact angle and sliding angle have also been classified as static and dynamic hydrophobicity [112]. It is important to identify these two parameters to obtain Anti-graffiti coatings as it was described above. Goniometer is the well-known equipment which has been employed to observe contact angle and it is the most practical way to ensure hydrophobicity of the coatings or materials which are tested. To define a surface as superhydrophobic, the sliding angle must be measured to be less than 10° and at the same time contact angle should be higher than 150° [111]. It is possible to obtain these surfaces various kinds of materials [115] and even on the wood, it is possible obtain these surfaces by using simple nano scale dispersion into polymeric materials [116]. Goniometer can also be employed to determine surface tension which is necessary to calculate surface free energy. Hysteresis is also another important phenomenon in terms of hydrophobic coatings. It should be noted that, it is not possible to obtain smooth ideal surfaces where any drop can easily slide thus, angles at the different points of this drop must be different due to the surface of the substrate. The difference at the bottom and upper end of the sliding drop named as contact angle hysteresis and these angles are classified as advancing contact angle and receding contact angle [113].

To achieve hydrophobic surfaces, two different methods have been employed and these fabrication methods are known as top-down, which includes microelectronic process and soft lithography, and, bottom-up, which includes sol-gel, microphase separation and

templating methods, and later one also classified as easier way to fabricate these surfaces [108]. Mainly, there are two ways to fabricate these hydrophobic surfaces by roughening the surfaces or lowering the surface free energy by using silanes or fluoro-containing polymers [117]. However, it should be noted that fluoro-containing chemicals are not good choices for environments thus there are efforts try to achieve nonfluorinated compounds to provide hydrophobic property to applied surfaces by using polyurethanes [118]. Organosilane have also been employed to create environmental friendly low surface free energy surfaces to obtain hydrophobicity [108].

Beside Young's equation, there are two theory which defines hydrophobic behavior of the materials which are classified as Wenzel and Cassie-Baxter theories [114]. These model have been developed since Young's theory is not a proper model for rough surfaces [112]. For Wenzel model (Figure 1.7), a rough surface having a higher surface area than the corresponding smooth surface, the liquid droplet completely penetrates into the cavities on the surface and Cassie-Baxter model (Figure 1.7), the spreading of a liquid droplet on a rough surface destroys the solid-vapor interface and forms solid-liquid and liquid-vapor interfaces, causing the significant reduction in roll-off angle and contact angle hysteresis [87]. In the case of nanomaterials, surface roughness is the way to create micro or nano scale roughness on the surface and makes required arrangements on the surface free energy by lowering it to desired scale to provide hydrophobicity to the surface [111]. Thus, it is clear that coatings developed to protect substrates able to reduce the surface wettability of substrate [14].

1.6. SOL-GEL METHOD

As it can be seen below and mentioned above, sol-gel method has been employed to obtain anti-graffiti coatings. This method is classified as one-step method which provides large scale production for these kinds of coatings and applications economically [117]. In the sol gel process, dispersed solid nano materials undergo reactions known as hydrolysis and condensation to form a gel in a gelation process into liquid phase with continuous oxide chain [119]. At the end of the process, there is a sol of hybrid polymer, containing inorganic structure -Si-O-Si- in an organic matrix [117]. This method allows to develop required thin film coatings, fibers, micro-structure inorganic membranes, aerogels, ceramics, and glass with low process temperature [119]. Sol-gel method mainly have six process steps which are

listed as; hydrolysis of precursor, condensation of sol-gel active species with alcohol or water, gelation, aging, drying and high temperate heat treatment[114].



2. MATERIALS AND METHODS

2.1. MATERIALS

2.1.1. Chemicals

Table 2.1. Chemicals used in the experiments

#	ITEM
1	Hexane
2	Paraloid B72
3	Desmodur N75
4	Aerosil R812
5	BYK Silclean
6	Ethanol
7	Dynasylan (Fluorine Containing Silane)
8	Acetone
9	Toluene
10	HCl
11	Red Dye (Spray)
12	Red Dye

2.1.2. Substrates

Table 2.2. Coated Substrates

#	Substrates
1	Ahlat Stone
2	Marmara Marble
3	Glass
4	Facing Stone (*?)

2.1.3. Equipment

Table 2.3. Equipment

#	ITEMS
1	Goniometer
2	Ultrasonication Bath
3	Laboratory Scale
4	Magnetic Stirrer + Heater
5	Incubator
6	High-Definition Photographic Apparatus

2.2. STUDY DESIGN

In this study, by using the given chemicals (Table 2.1), seven various coatings were prepared in terms of optimal values which were resulted from other studies held with different substrates. Coatings were developed by using magnetic stirrer and ultrasonic bath to achieve homogenous solutions and fully nano dispersion into liquid. Incubator has been employed for the last step of the substrate preparation for curing the coatings onto specimens at least 10 days at 150°C. Four different substrates were selected to observe anti-graffiti properties of the developed coatings. However, it should be noted that, for the glass samples, these all seven dispersions were not tested since main objective of the thesis in observing anti-graffiti behaviour of the coatings on the masonry structures. Hexane based solution was not controlled onto glass because it is not possible for nano particles insert to substrates like marble or for the other substrates and coatings, by using goniometer, contact angle values were determined. After this, dye dropped onto substrates both coated and uncoated sides and picture of these drops have been taken by using high-definition photographic apparatus with different lenses to obtain required images. And finally, dye has been sprayed onto coated and uncoated specimens as a graffiti, then, by only using water and toothbrush removing steps has been conducted. Final situations of the substrates have been observed to understand efficacy of the coatings and how they affect the ease of cleaning procedure.

2.3. PREPARATION OF SUBSTRATES

In the preparation step, as it was reported above, 7 dispersions were made in sol-gel method. These seven solutions can be classified as Acetone-B72, Toluene-B72, Acetone-B72-R812, Toluene-B72-R812, F-Silane Solution, Hexane-R812 solution (w/w %1 & %10), Desmodur-Silclean-R812 solutions. Later, these solutions were applied onto specimens (Table 2.2.) and all substrates were placed into incubator for curing step before characterization with goniometer.



Figure 2.1. Experimental Set-up

2.3.1. Acetone-B72, Toluene-B72, Acetone-B72-R812, Toluene-B72-R812 Preparation

SOL1 and SOL3 are the acetone solvent-based solutions which were prepared with Paraloid. Their only difference is nano silica (Airosil R812) addition into solutions. For the SOL1, there is any nano dispersion into coating unless SOL3 has. In the preparation step, 2.5 grams of acetone was weighted into cotton fabric and then, it was tied up into this cotton fabric. Then, it was hanged into jar by ensuring the contact between fabric and 47.5 grams acetone solution. It is important that this cotton did not place into solution, there was only a connection between below point of the cotton fabric and upper part of acetone. They were stayed 24 hours in the room temperature for full dissolution of the paraloid into acetone. After 24 hours, fully dissolution had taken place. Then, half of the solution was separated from the jar to prepare SOL3 with R812 nano additive. 0.46 grams of R812 nano additive was added into 23 grams of Acetone-Paraloid solution to have 2% w/w SiO₂ additive containing solution. To avoid gelation, 11.5 grams of ethanol was poured into solution. After these, for nano dispersion, solution was placed into ultrasonication for 20 minutes. Same procedure was applied to prepare Toluene based SOL2 and SOL4. Every step was repeated just replacing acetone with toluene.

2.3.2. F-Silane Solution Preparation

SOL5 is the Fluorine based solution which was chosen to fabricate hydrophobic surfaces by using chemical method as it was mentioned above. In this solution, 0.01 mol F-silane solution was mixed with 0.1 mol TEOS and 0.15 mol HCl. In this solution, there was no nano additive.

2.3.3. Hexane-R812 solution (w/w %2 & %10)

SOL6 and SOL7 are the nano additive-based solutions which were prepared by using hexane as their solvent. 2% and 10% percent amount (SOL6 and SOL7) were prepared by adding R812 into Hexane and placing these solutions into ultrasonication for 25 minutes. After ultrasonication, they were both stirring by using magnetic stirrer 1 hours. It should also be noted that magnetic stirrer was never stopped during the experimental procedure.

2.3.4. Desmodur-Silclean-R812 solutions

SOL 8 is the polyurethane based nano coating, which was prepared by using Desmodur, BYK Silclean (surface additive) and R812 nano silica. BYK Silclean is a surface additive which uses to fabricate hydrophobic surfaces. For SOL8, 7 grams of Desmodur was weighted and 43 grams of BYK was poured into polyurethane. Then, they were stirred at 1100 rpm 30 minutes. After this, 0.5 grams of nano additive was added into solution and it was stirred again with same procedure, 1100 rpm 30 minutes. Finally, solution was placed into ultrasonication for 25 minutes.

Table 2.4. Solutions and their contents

Solution #	Content
SOL1	Acetone-B72
SOL2	Toluene-B72
SOL3	Acetone-B72-R812
SOL4	Toluene-B72-R812
SOL5	F-Silane
SOL6	Hexane-R812 (2%)
SOL7	Hexane-R812 (10%)
SOL8	Desmodur-BYK-R812

2.4. CHARACTERIZATION OF THE SUBSTRATES

2.4.1. Contact Angle Measurements

Goniometer was employed for the contact angle measurements. As it was explained, contact angle measurement is the basic step of the hydrophobicity. In this part, by using goniometer, contact angle values of each specimen with coated and uncoated sides have been recorded with water. By means of these recorded values, substrates were classified in terms of their

wettability character as hydrophobic or superhydrophobic. Specimens were placed onto device and results have been recorded.



Figure 2.2. Goniometer measurements with coated Ahlat stone

2.4.2. High-Definition Photograph

In this step, dye containing drops have been placed onto coated and uncoated substrates and their pictures have been taken to see how these drops behave onto coated and uncoated sides of the specimens. With this method, their sliding angles were also observed since it is important that drops should not be stick onto coated surfaces if the coating is classified as anti-graffiti coating.

3. RESULTS

In this study, both way of the fabricating hydrophobic surfaces was utilised. In terms of achieving micro/nano size roughness onto substrate, nano silica dispersions were used. Chemical way of developing hydrophobic surfaces was also employed by using fluorine containing silane solution which was named F-Silane solution. By using these two main and simple approaches, hydrophobic surfaces have been fabricated to create barrier effects onto substrate against dye. There was two characterization part. First one is measuring the contact angle of substrates with coating and without coatings to identify their wettability in mathematically. Second part, most important one due to ease of clean purpose, these coated specimens were stained and removing procedure was applied.

3.1. CHARACTERIZATION OF SUBSTRATES

3.1.1. Contact Angle Measurments

Anti-graffiti coatings must have superhydrophobic or at least hydrophobic character. Most reliable way to identify the hydrophobicity of the coating is measuring the contact angle by using goniometer which was developed for this specific purpose as it was explained above. Four different substrates were coated by using different dispersion which was mentioned above and then their behaviour against water drops have been examined by measuring contact angles or wetting angles.

3.1.1.1. Glass

Acetone-B72-R812, Acetone-B72, Toluene-B72-R812, Toluene-B72, Desmodur-BYK Silclean and F-Silane dispersion coated glass specimen were undergone to contact angle measurement. Results will be given for each specimen with their figures to understand shape of the drop on the coated surfaces to compare them with their own contact angles and each other.

When the glass specimen coated with SOL1, contact angle equals to 103.70° . This result can be defined as hydrophobic. In the figure 3.1, drop on the glass specimen could be seen.

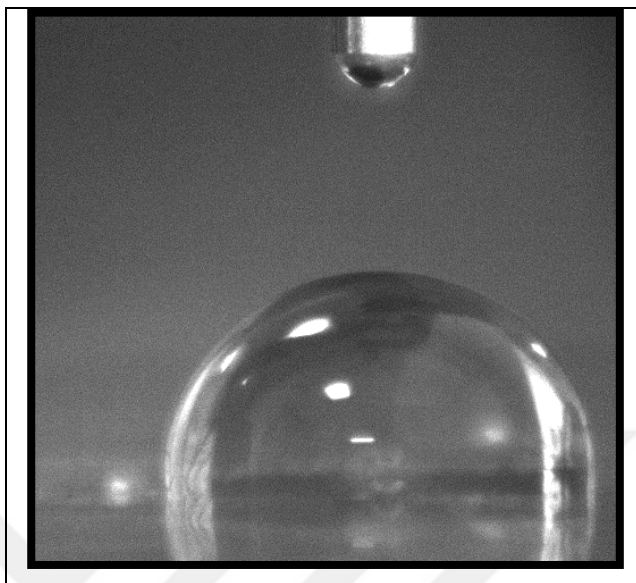


Figure 3.1. SOL1 coated glass substrate with drop

For the Sol 2 which is Toluene-Paraloid B72 solution, contact angle value was recorded from goniometer as 109.29° . It is slightly higher than the same B72 additive added acetone solution when they were compared as it was reported [120] before. In the figure 3.2, shape of the drop onto coated glass substrate is given.

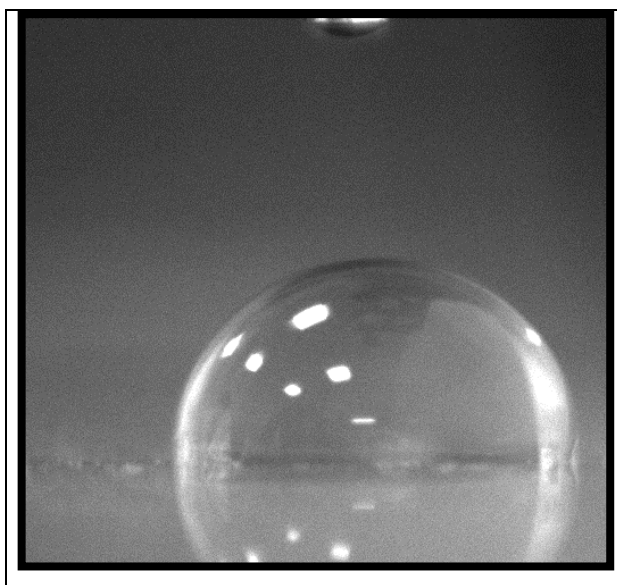


Figure 3.2. SOL2 coated glass substrate with drop

Contact angle value of the SOL3 coated glass specimen was recorded as 94.95° . This result also classified as hydrophobic and in the Figure 3.3, shape of the drop is shown.

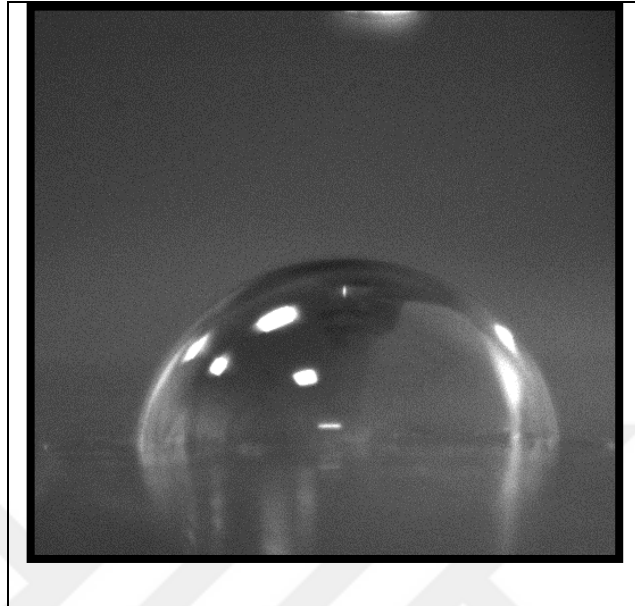


Figure 3.3.SOL3 coated glass specimen with drop

SOL4, which is Toluene solution with paraloid additive and nano dispersion, changes the contact angle values of glass substrate and it is 142.36° . This contact angle value is certain to be identified as superhydrophobic. It was mentioned above that toluene with B72 performed better hydrophobic character compared acetone. This result verifies previous studies performed with different substrates. In the figure 3.4, shape of the water drop can be observed.

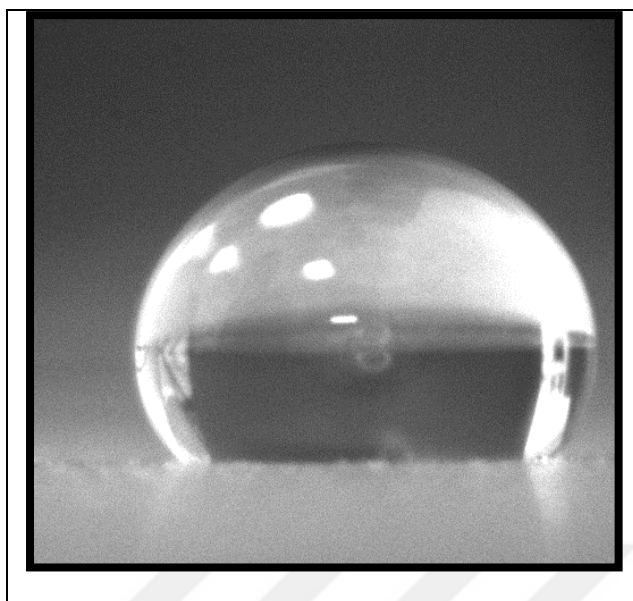


Figure 3.4. SOL4 coated glass substrate with drop

SOL 5, F-silane solution, onto glass substrate gave 91.46° contact angle value which can be considered hydrophobic. In the figure 3.5, it can be seen.

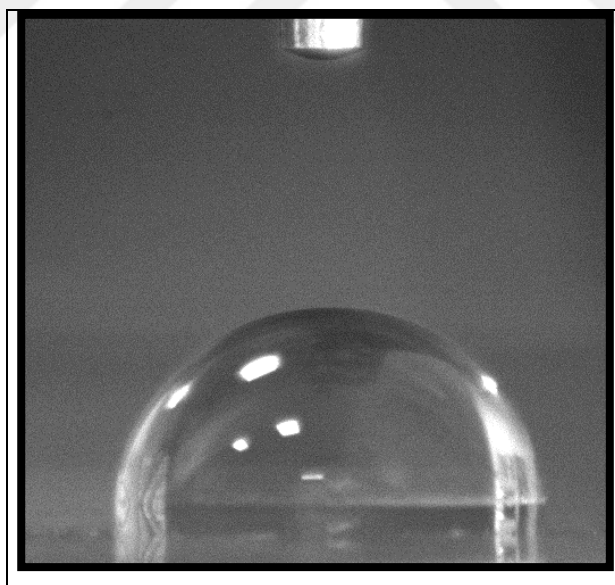


Figure 3.5. SOL5 coated glass substrate

SOL 6-7 were prepared with hexane and nano particulates. This means that there is no backbone that holds the nano structure onto glass. Therefore, these solutions were not applied onto glass surfaces due to their low resistant. Result of the SOL8 was measured and it was 103.98° . It should be noted that drop onto SOL8 easily slide away when it was

compared other solutions. In the below figure (Figure 3.6), shape of the drop onto substrate can be seen.

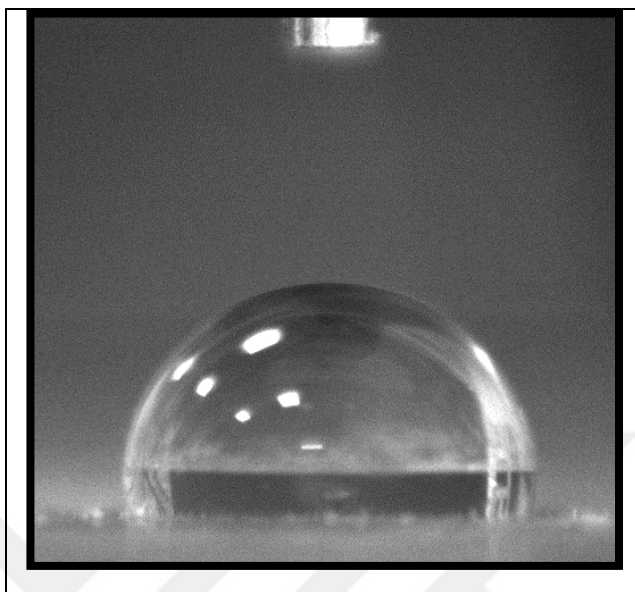


Figure 3.6. SOL6 coated glass substrate

In summary for glass substrate, each solutions have hydrophobic character however, it should ne also noted that only one of these solutions, namely SOL4, turned glass surface to superhydrophobic surface. As it was reported before [120] toluene containing solution fabricates superhydrophobic surface with B72 additive and nano silica dispersion. One of the recent studies, silica-based resins coatings fabricate hydrophobic surfaces only after silanization with TCMS [121]. In the Table 3.1, each contact angle values for each coated specimen were reported.

Table 3.1. Contact angle values for glass substrate

Applied Coating Solution	Contact Angle
SOL1	103.70°
SOL2	109.29°
SOL3	94.95°
SOL4	142.36°
SOL5	91.46°
SOL8	103.98°

3.1.1.2. Ahlat Stone

This stone is very porous volcanic ignimbrite where it is located closer to Van lake in Eastern Anatolian region of Turkey [12]. This material was widely used near Ahlat to construct bridges, houses etc. There is a cultural heritage which was constructed by using this specific stone known as Ahlat Tombstone, which was deteriorated due to climate, in temporary list of UNESCO World Heritage [122]. Water capillary and high water absorption of these stones were reported as the main factor for this deterioration [123]. When these stones were compared other materials, their water capillary absorptions were higher [124]. It is also possible to improve toughness of these stone by reducing water component inside the stone [125]. Porosity was reported as main feature of this stone. It is obvious that when graffiti applied onto Ahlat stone, dye can penetrate these porous structures and removing of this dye struggled to conservators. Except SOL5, contact angle values were measured for every solution. For SOL5, due to the masonry surface, goniometer did not perform the measurements and gave the results. However, in pictures, drop onto F-Silane coated Ahlat stone will be shown below.

Recorded contact angle value for the SOL1 is 105.43° . This value shows that this solution created hydrophobic surface onto very porous Ahlat Stone and shape of the water drop can be seen in Figure 3.7.

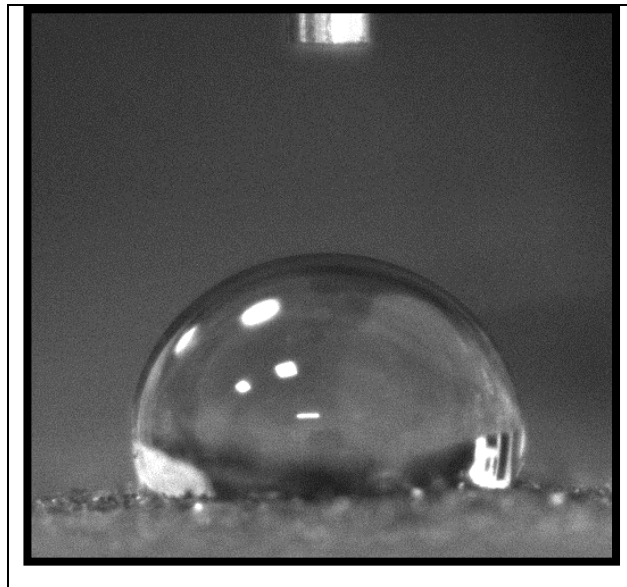


Figure 3.7. SOL1 coated Ahlat stone with water drop

For the SOL2, contact angle value was measured as 102.27° . Unless it was reported above that Toluene containing solution performed better performance in terms of hydrophobicity, it should be noted that these values are very close to each other. In the Figure 3.8, drop onto SOL2 coated Ahlat stone can be seen.

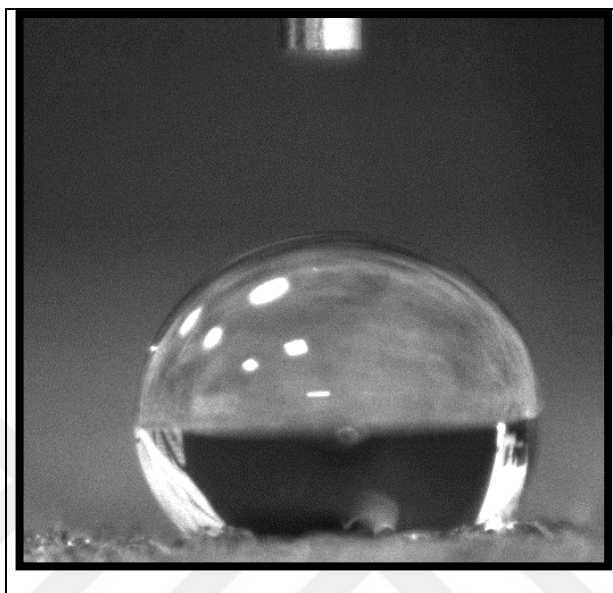


Figure 3.8. SOL2 coated Ahlat Stone with drop

For the SOL3, contact angle value measured and it was equal to 138.49° . This value is almost superhydrophobic. In the Figure 3.9, it can be seen.

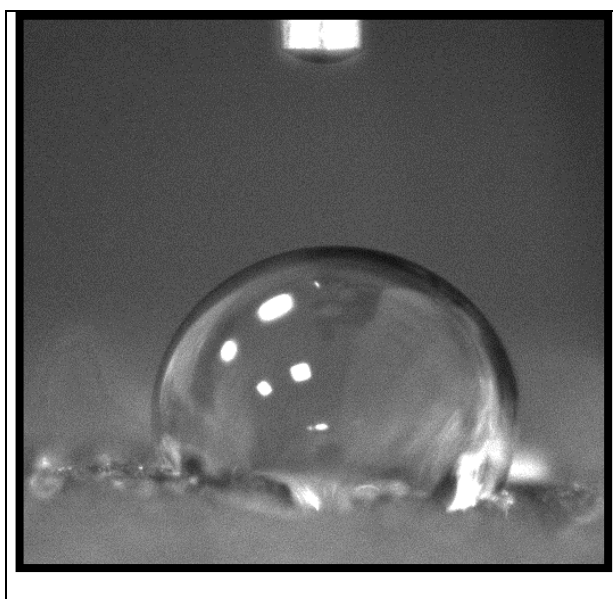


Figure 3.9. SOL3 coated Ahlat Stone with drop onto it

For the SOL4, contact angle was 100.95° . However, this result looks unreliable since how drop placed onto coated surface was seen. In the Figure 3.10, schematic view of this coating can be seen. Shape of the drop seems almost round and spherical onto coated surface which defines the hydrophobicity of the surface. This contact angle measurement was repeated many times to get proper and matched results with its image since all the results were in between 90 - 100° .

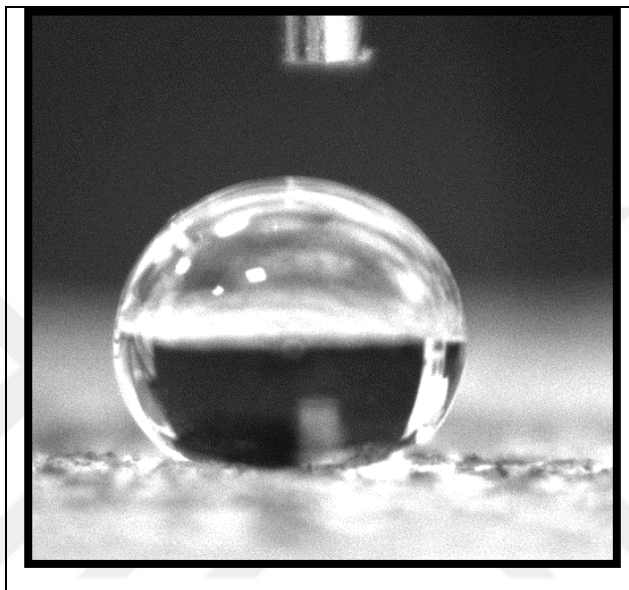


Figure 3.10. SOL4 coated Ahlat stone with its drop

As it was told above, measurement with SOL5 solution could not be performed due to the shape of the Ahlat stone. It cannot be fitted into device to take results. However, its hydrophobic character will be shown following part. For the SOL6, contact angle was 131.56° which is almost superhydrophobic. In the Figure 3.11, drop onto coated surface can be seen.

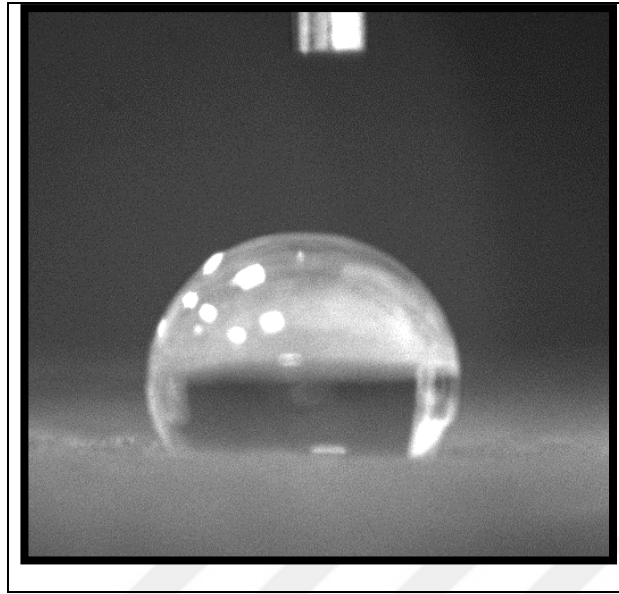


Figure 3.11. SOL6 coated Ahlat Stone with drop

For the SOL7, contact angle was 122.57° which is almost superhydrophobic. In the Figure 3.12, drop onto coated surface can be seen.

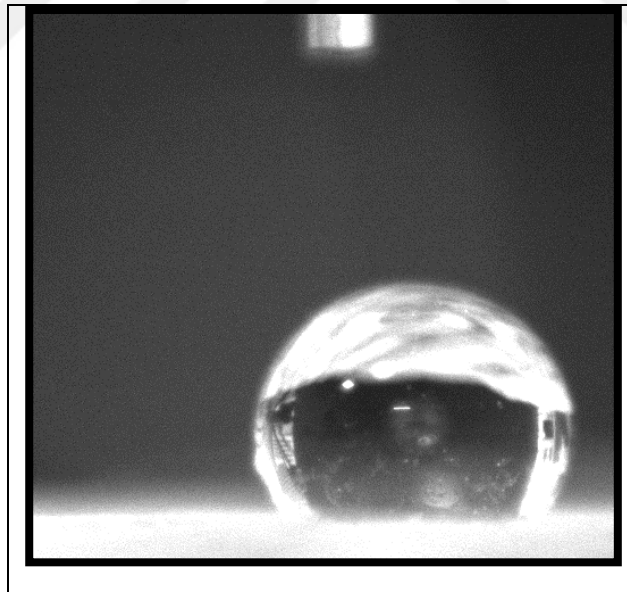


Figure 3.12. SOL7 coated Ahlat stone with drop

For SOL8 solution which contains Desmodur (polyurethane) and surface additives with nano dispersion, its contact angle value is 98.22° . It seems that it is not a hydrophobic coating since it should be noted that drop onto coated area easily slide away from the surface which

is a good property in terms of anti-graffiti coatings. In figure 3.13, SOL8 coated Ahlat stone can be seen with the drop onto it.

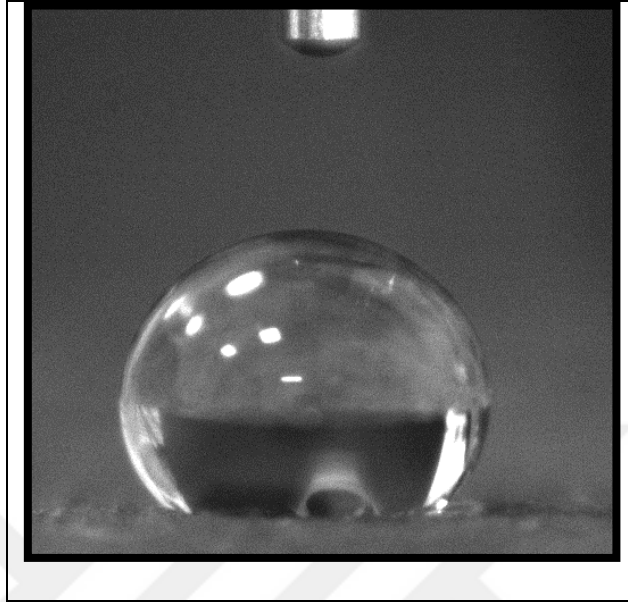


Figure 3.13. SOL8 coated Ahlat stone with drop

Table 3.2. Contact angle values for Ahlat stone substrate

Applied Coating Solutions	Contact Angle Values
SOL1	105.43°
SOL2	102.27°
SOL3	138.49°
SOL4	100.95°
SOL5	131.56 °
SOL7	122.57 °
SOL8	98.22°

3.1.1.3. *Marmara Marble*

Marmara marble (Marmor Proconnesium), from Marmara island, was one of the most preferred construction material with Kufeki stone which were used in cultural heritages in Istanbul [126]. From the cultural heritage perspective and conservations concepts, Marmara Marble is one of the most important stones in Turkey thus, for the graffiti protection, anti-

graffiti coatings should be tested onto them. Until recent times, natural stones were widely used as the main building construction material [127]. Natural marbles have been reported as not being hydrophobic [128]. Therefore, applying the coatings which is able to fabricate hydrophobic surfaces must change the surface characteristic of the marbles. It is also known that marbles are not very porous materials as Ahlat stone [129]. All solutions from SOL1 to SOL8 have been applied onto Marmara marble. Goniometer was employed to measure contact angle values for all these coating onto Marmara marble to identify them as being hydrophobic or not. All the coated marbles were placed into incubator at 150°C and their measurements were performed after 10 days later for curing of the coatings. It should also be noted that Marmara marble is white and goniometer which was employed for these measurements has light problem which struggled to get proper pictures and perform measurements well.

Recorded contact angle value for SOL1 equals to 106.99°, which is clearly hydrophobic. Figure 3.14 represents the shape of the drop onto this coating.

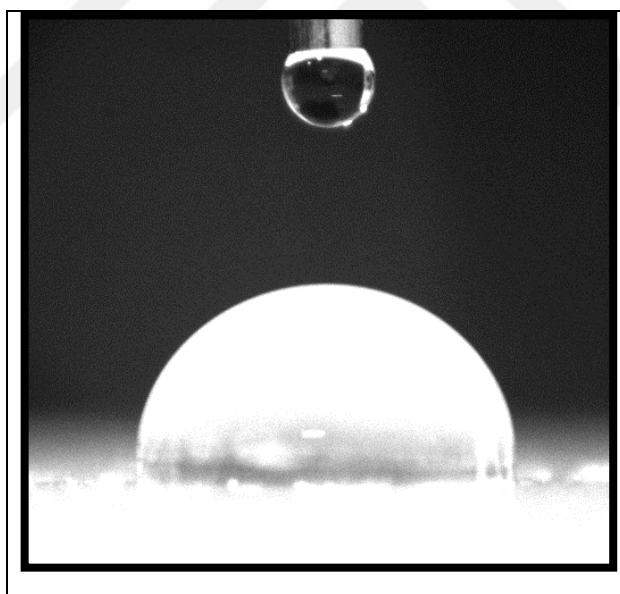


Figure 3.14.SOL1 coated Marmara Marble with drop

Recorded contact angle value for SOL2 equals to 105.58°, which is clearly hydrophobic. Figure 3.15 represents the shape of the drop onto this coating.

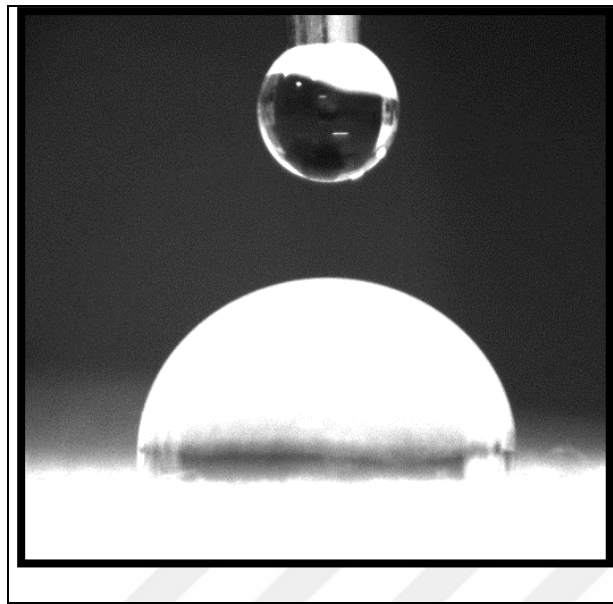


Figure 3.15. SOL2 coated Marmara marble and shape of the drop onto it

Recorded contact angle value for SOL3 equals to 91.94° , which is hydrophobic. Figure 3.16 represents the shape of the drop onto this coating.

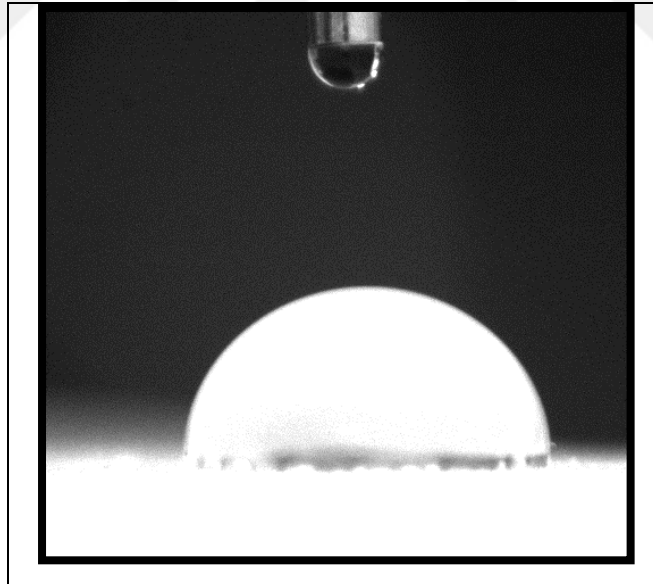


Figure 3.16. SOL3 coated Marmara marble and shape of the drop onto it

Recorded contact angle value for SOL4 equals to 110.06° , which is clearly hydrophobic. It should also be noted that, within this coating, water drop was easily slide away from the surface when a little slope was given to the system. Figure 3.17 represents the shape of the

drop onto this coating. The drop had very spherical shape onto coated are of the marble substrate.

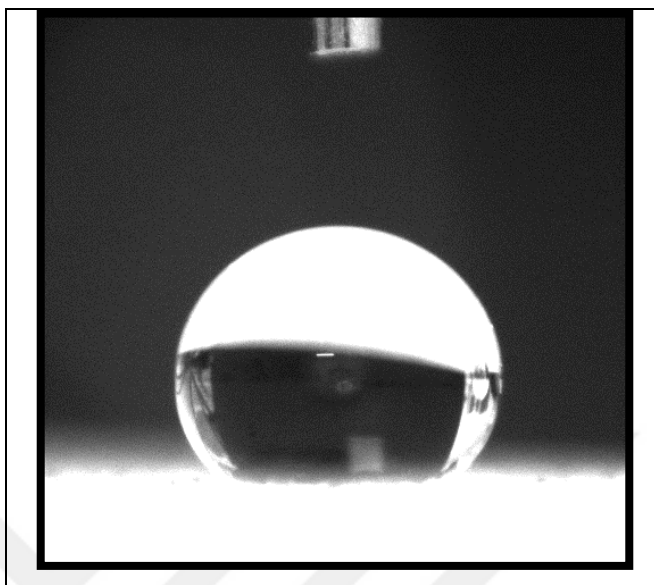


Figure 3.17. SOL4 coated Marmara marble with drop

Recorded contact angle value for SOL5 equals to 102.34° , which is hydrophobic as it is expected from fluorine containing silane solutions by lowering the surface free energy. Figure 3.18 represents the shape of the drop onto this coating.

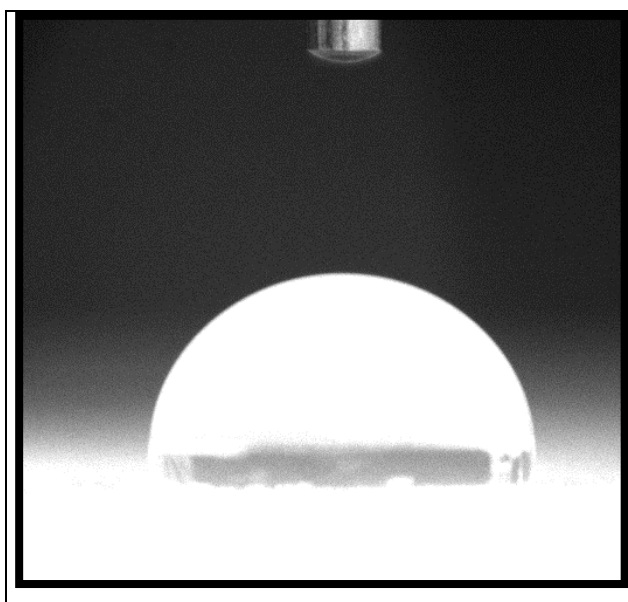


Figure 3.18. SOL5 coated Marmara marble with drop

Recorded contact angle value for SOL6 equals to 69.50° , which is not hydrophobic and almost equal to non-coated marble specimen [128]. Figure 3.19 represents the shape of the drop onto this coating.

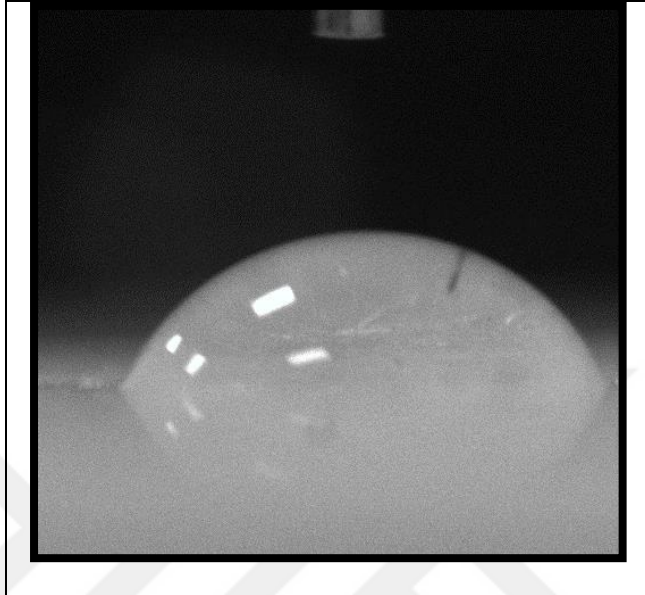


Figure 3.19. SOL6 coated Marmara marble with drop

Recorded contact angle value for SOL8 equals to 121.64° , which is hydrophobic and very close to superhydrophobic. Figure 3.20 represents the shape of the drop onto this coating.

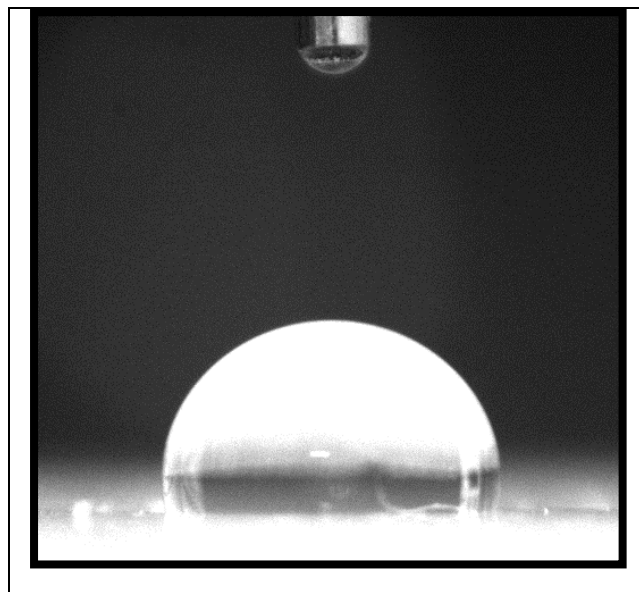


Figure 3.20. SOL8 coated Marmara Marble with drop

Finally, SOL7 is the same solution with SOL6 in chemical way unless amount of the nano silica dispersion varied in these coatings. It will be discussed below since results of the SOL6 made the measurements of SOL7 redundant.

Table 3.3. Contact angle values for Marmara Marble Substrate

Coated Solution	Contact Angle Values
SOL1	106.99°
SOL2	105.58°
SOL3	91.94°
SOL4	110.06°
SOL5	102.34°
SOL6	69.50°
SOL8	121.64°

3.1.2. High-Definition Photographic Characterization

3.1.2.1. Ahlat Stone

In this part, coated Ahlat stones which are very porous materials as it was mentioned above, placed in front of the high-def camera and pictures of dye from coated and uncoated sides were taken to see how drop placed onto substrates which represents the hydrophobic character of the coatings. In this part, for all dispersions, experimental setup was constructed, and procedure was applied. Red dye was employed for experimental procedure.

From SOL1-SOL4, they are broad range stones which their surface was able to be coated 2 different coatings and middle of these coatings can be blanked which is uncoated surface. For SOL1 and SOL3, which are Acetone based Paraloid solutions one of them was pure and other one, SOL3, contains nano silica dispersion. Lefts side of the stone was coated with SOL1, acetone based Paraloid solution which did not contain any amount of nano silica dispersion and right side of the stone was coated with same acetone-based solution solely, additional nano-silica dispersion included. Middle of the stone was not coated any kind of solutions therefore it can be called naked part of the stone which can be evaluated identical

with famous Ahlat tombstones located closer to Lake Van. In the Figure 3.21, how uncoated and coated Ahlat stones responded red dye and water drop can be seen.



Figure 3.21. SOL1 (left) coated, uncoated (middle) and SOL3(right) coated Ahlat stone with red dye and water drops



Figure 3.22. SOL1 (left) coated, uncoated part (middle) and SOL3(right) coated Ahlat stone with red dye and water drops after 20 seconds

As it can be seen (Figure 3.22), 20 seconds after dopped the water and dye onto substrate, uncoated part of the stone rapidly absorbed the dye and water inside through its pores. It should be also noted that water seems more hydrophobic into substrate than red dye. Colour variations onto coated parts of the stone can easily been observed by the uneducated eyes which is very important criteria for a coating which can be applicable in cultural heritage area as it is predicted.

In Figure 3.23, SOL2-SOL4 coated and uncoated Ahlat stone can be seen with water and red dye drop.



Figure 3.23. SOL2 (left) coated, uncoated (middle) and SOL4 (right) coated Ahlat stone with red dye and water drops

It is very clear that SOL4, which contains nano silica dispersion, changed the colour, and turned it almost white. For the SOL4, better performance against dye and water comparing to SOL2 can easily be observed (Figure 3.23). Even there was no contact angle measurements for dye, in terms of eye observations, Toluene based paraloid solutions fabricate more hydrophobic surfaces on the contrary contact angle measurements which were performed with water showed better performance with acetone-based solutions (Table 3.2). In the Figure 3.24, SOL2-SOL4 coated Ahlat stone with water drop can be seen. It is very clear that nano silica fabricated more hydrophobic surface than non-silica containing surface unless there are intolerable colour variations in SOL4 surface.



Figure 3.24. SOL2 (left) coated, uncoated (middle) and SOL4 (right) coated Ahlat stone with water drops



Figure 3.25. SOL5 coated (right) and uncoated (left) Ahlat stone with dye and water drops

It should be noted that there is still colour variation when the stone was coated. F-Silane solution was able to fabricate hydrophobic surface onto very porous Ahlat stone as it can be seen. Figure 3.26 is another view of the F-Silane coated Ahlat stone.



Figure 3.26. SOL5 coated (right) and uncoated (left) Ahlat stone with dye and water drops

For the SOL6, which is hexane-nano silica dispersion in w/w %2, was controlled by using red dye and water (Figure 3.27).



Figure 3.27. SOL6 coated (right) and uncoated (left) Ahat stone

There is still colour variation onto substrate exposed to coating. It should also be noted that, for SOL6, taking the pictures were struggled due to drop motion onto stone surface. They were easily slide away thus capturing them onto substrate was difficult. It also means that this coating fabricates the surface which it was projected as an anti-graffiti coating. In figure 3.28, another view of this substrate can be seen.



Figure 3.28. SOL6 coated (right) and uncoated (left) Ahat stone

3.1.2.2. *Marmara Marble*

In this part, coated Marmara marbles were exposed to red coloured dye to evaluate effectiveness of the developed coatings against graffiti. All solution were coated onto

Marmara marble and then these marbles were exposed to red coloured dye then, pictures had been taken.

For the SOL1, which is identified as the solution containing Acetone-Paraloid solution without any nano dispersion, it is obvious that dye and water drops take more spherical shape than the drops on the left part of the marble surface (Figure 3.29). Due to the white colour of Marmara marbles, implemented coating did not crate colour change which can be easily recognized and approved by eye observations.

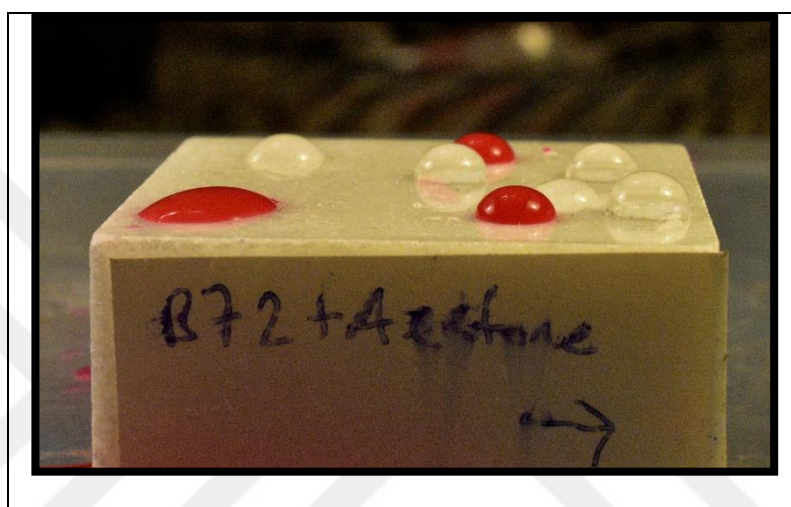


Figure 3.29. SOL 1 coated (right side) Marmara Marble exposed dye and water

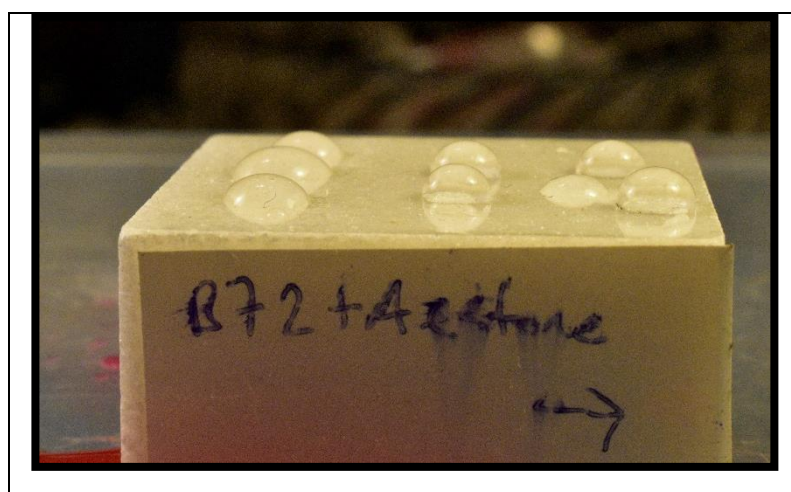


Figure 3.30. SOL 1 coated (right side) Marmara Marble exposed water

For the SOL2, which the toluene was chosen as its solvent as it was mentioned above, was coated onto right side of the marble by using brush. As it can be seen in Figure 3.31 SOL2 was able to fabricate targeted surface onto Marmara marble. The difference between coated

and uncoated is noticeable. Colour change, which can be caused as a result of coating, is not prominent due to the original colour of the Marmara marble.

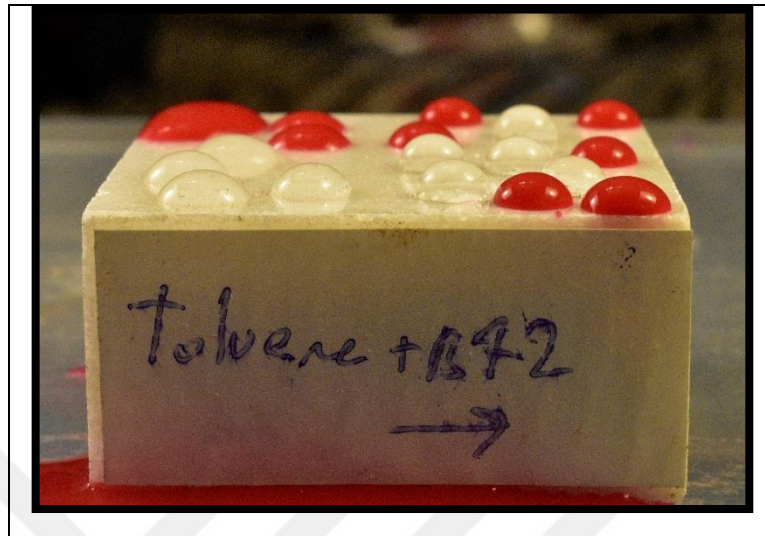


Figure 3.31. SOL 2 coated (right side) Marmara Marble exposed dye and water

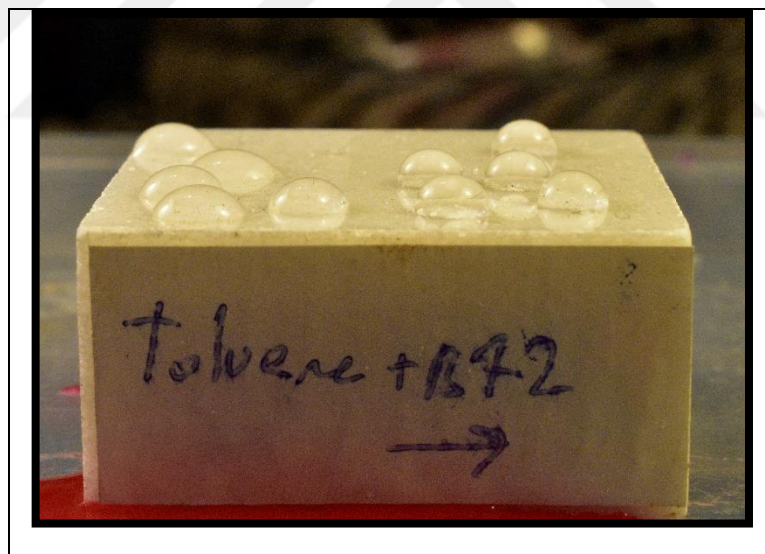


Figure 3.32. SOL 2 coated (right side) Marmara Marble exposed water

In the Figure 3.33, SOL3 which is acetone based Paraloid and nano-silica dispersion, was applied onto Marmara marble. There is a certain difference between coated and uncoated parts of Marmara marble in terms of dye shape onto coated substrate areas. It should be also noted that nano dispersion included coating fabricate noticeable colour change onto marble surface by making it whiter than its original state.

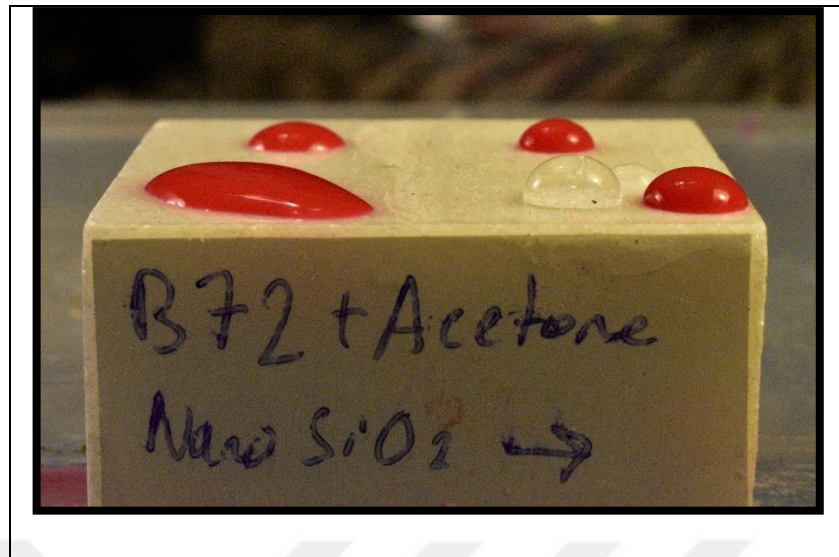


Figure 3.33. SOL 3 coated (right side) Marmara Marble exposed dye and water

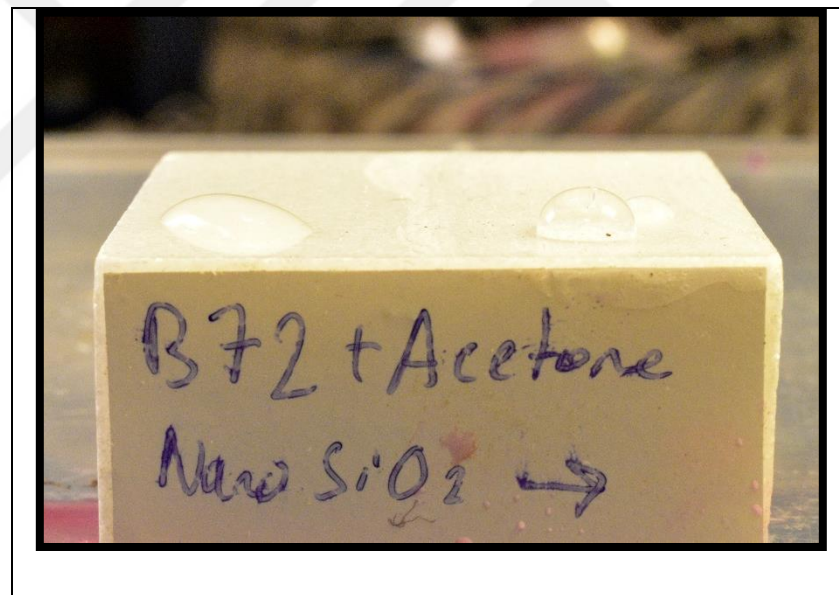


Figure 3.34. SOL 3 coated (right side) Marmara Marble exposed water

SOL4 coated Marmara marble was also exposed red dye and water. In the Figure 3.35, the shape of these drops can be seen. The shape of drops in terms of being more spherical is very noticeable in the below figure. There is also whiter colour in the right part where the coating was performed of the substrate.

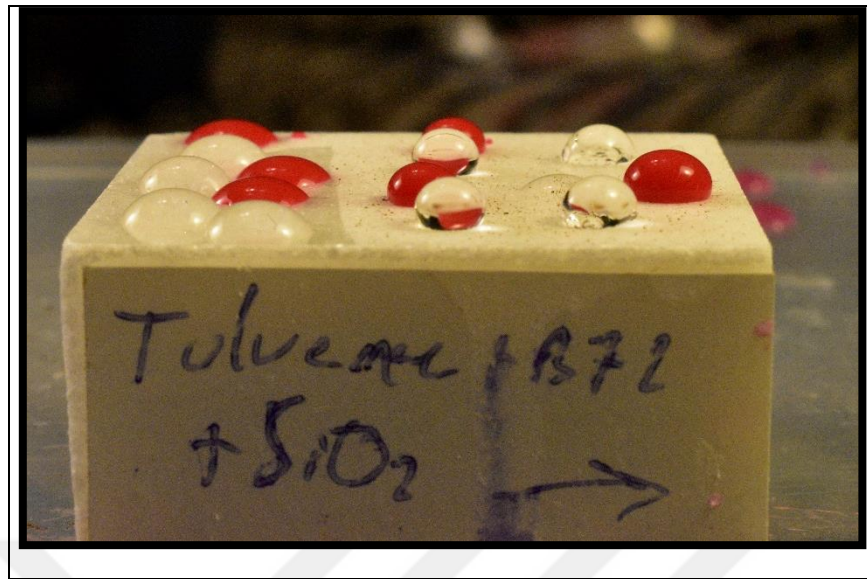


Figure 3.35. SOL 4 coated (right side) Marmara Marble exposed dye and water

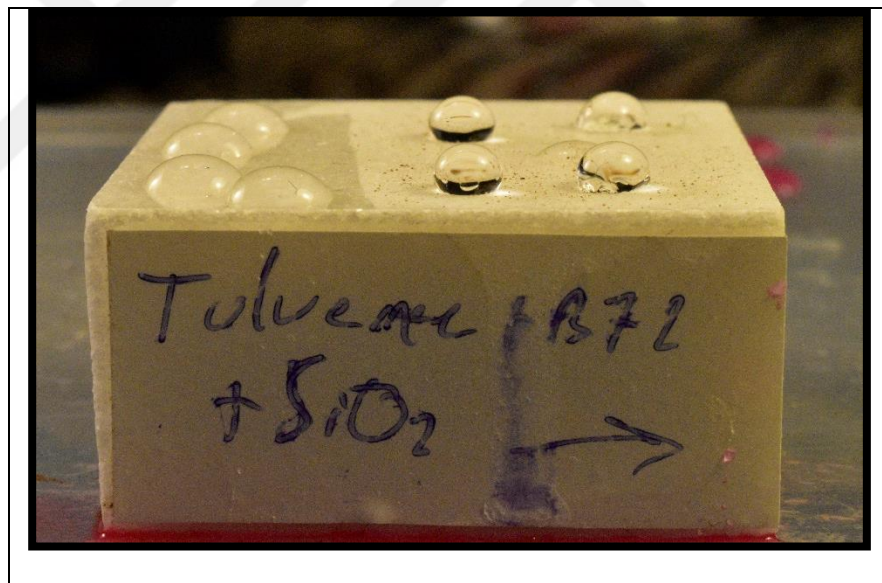


Figure 3.36. SOL 4 coated (right side) Marmara Marble exposed water

In the Figure 3.37, SOL5 was exposed to water and red dye then the picture was taken. When this solution was applied onto stone, there was any noticeable colour change onto substrate.



Figure 3.37. SOL 5 coated (left side) Marmara Marble exposed dye and water



Figure 3.38. SOL 5 coated (left side) Marmara Marble exposed water

Water drops seems more spherical than red dye drops when these two figures compared. Colour change is also imperceptible.

SOL6 and SOL7 were applied onto one marble substrate. As it can be seen in Figure 3.39, left side of the marble was coated with SOL6 and right part was coated with SOL7 while middle part of the substrate was blanked and identified as 'normal'.

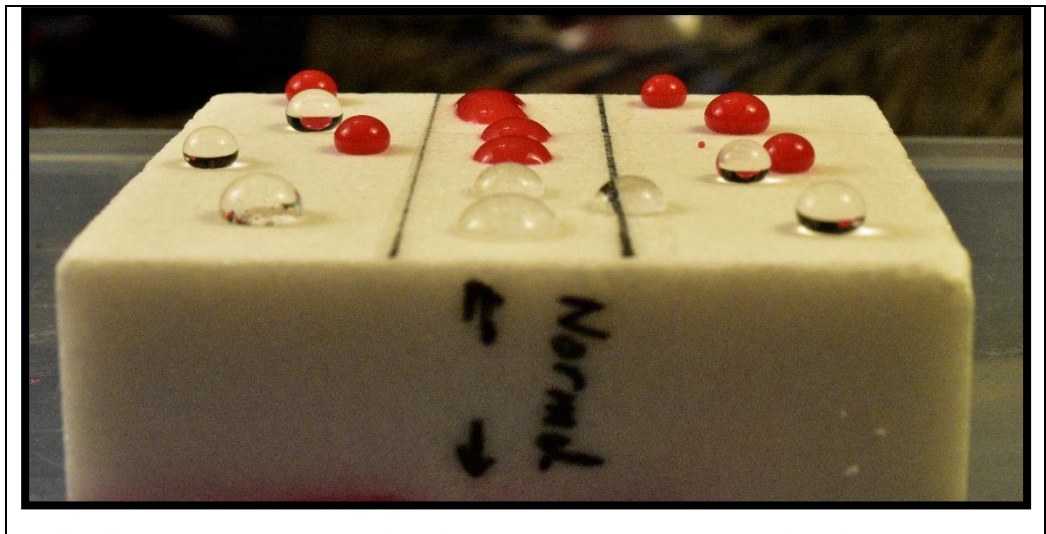


Figure 3.39. SOL 6 (left side) and SOL7 (right side) coated specimen with uncoated middle part 'normal'

There is no huge colour change which can be recognized by eye observations easily due to colour of the marble and applied coatings.

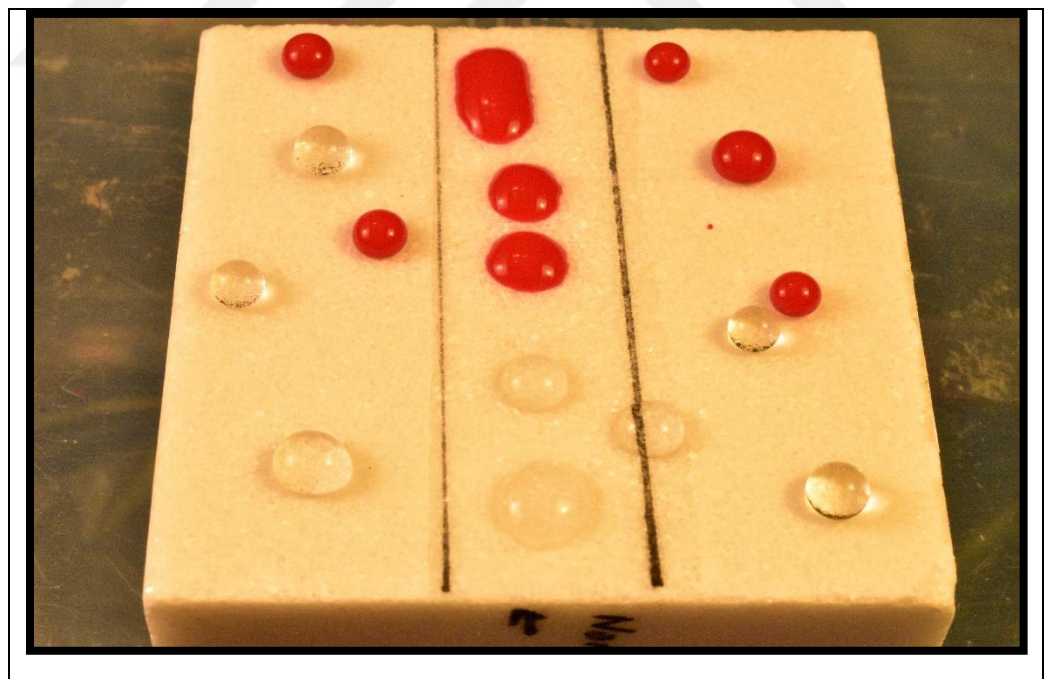


Figure 3.40. SOL 6 (left side) and SOL7 (right side) coated specimen with uncoated middle part 'normal'

Last coating solution applied onto Marmara marble was the SOL 8. This is the polyurethane (Desmodur) based nano dispersion coating. In the Figure 3.41, surface which was fabricated by this solution can be observed.

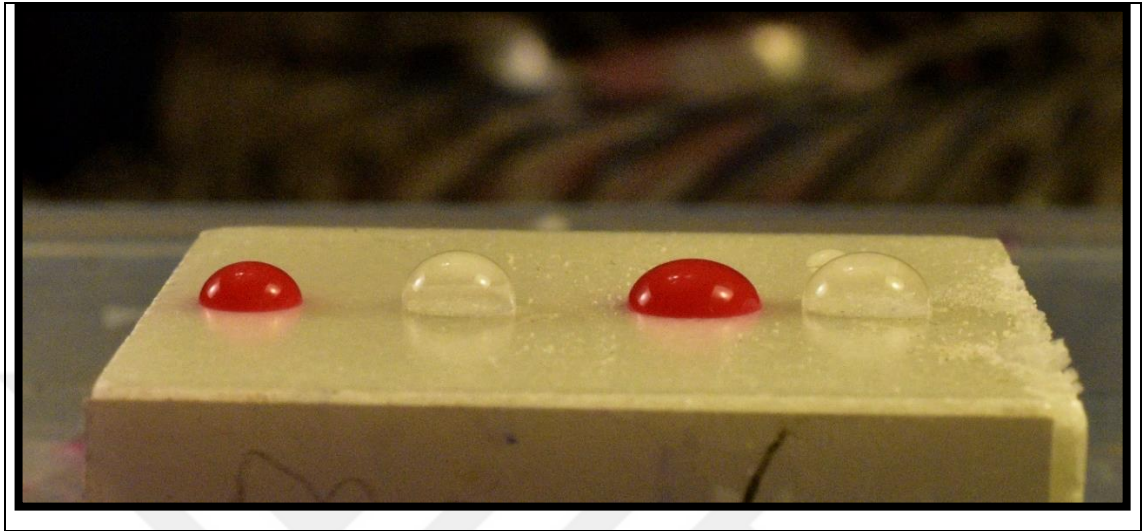


Figure 3.41. SOL8 coated Marmara marble

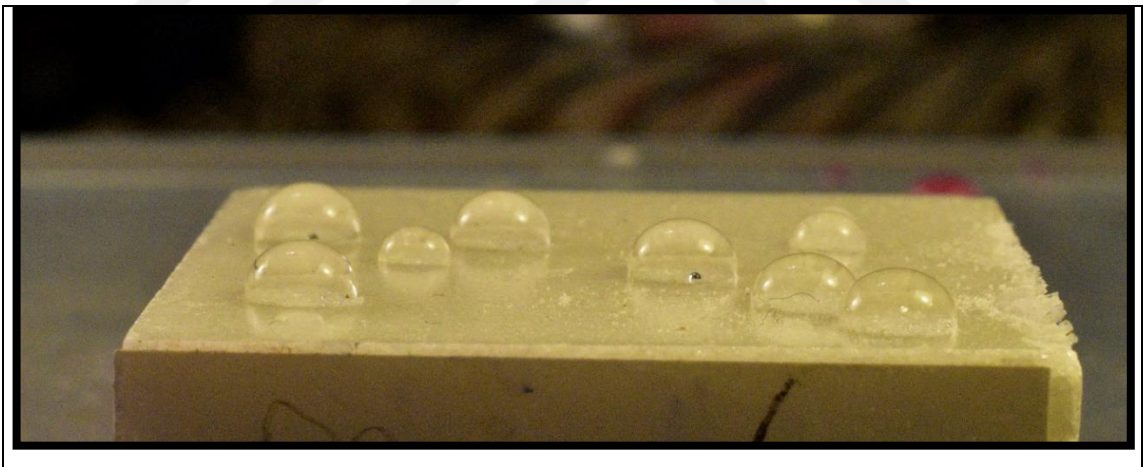


Figure 3.42. SOL8 coated Marmara marble

3.1.2.3. Facing Stone

In this part, very porous facing stone was preferred to be applied given solutions. The colour of this stone is white, and its porous characteristic can lead to collect valuable information for the identical white and porous stones which were mostly used as masonry for cultural heritage. In this part SOL1,2,3,4, 6 and 7 were chosen because of their promised candidacy. In Figure 3.43, Sol 1, 2 and 4 applied facing stone with its uncoated area can be seen.

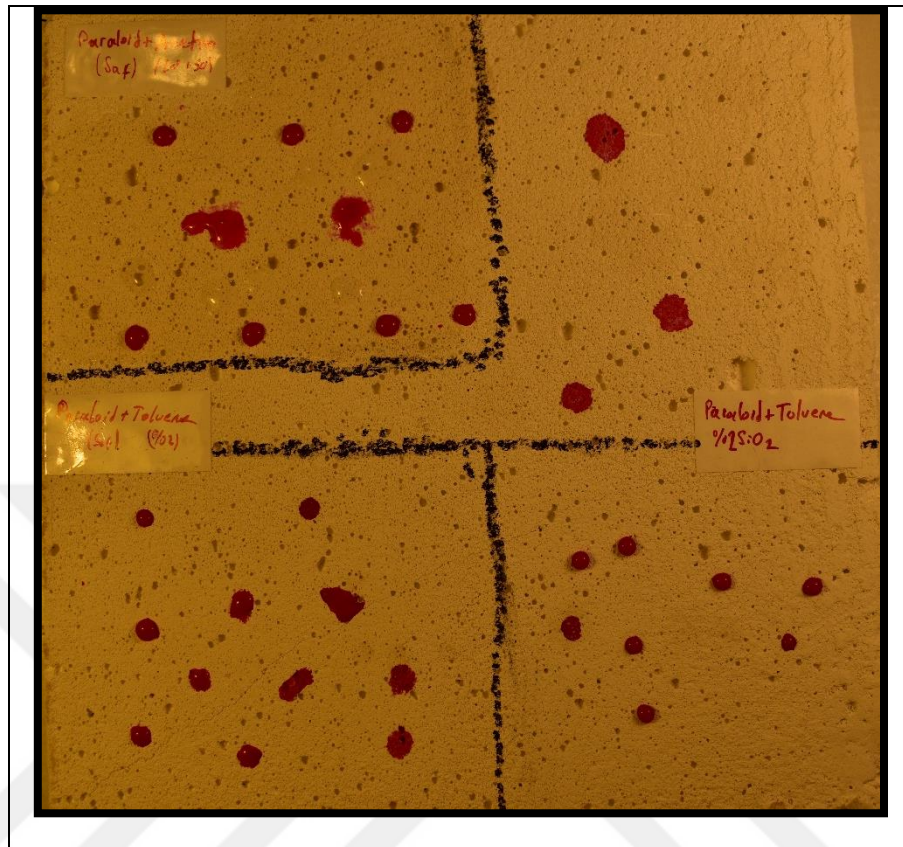


Figure 3.43. SOL 1,2, 4 applied facing stone with its uncoated area its upper right part

It can be easily seen that when the uncoated area faced with dye, it absorbed it into its pores unless coated part gave the drops spherical shapes due to its low surface free energy and rough character according to wettability phenomenon.

In the below figure, Figure 3.44, SOL6 and SOL7 applied facing stone with its uncoated middle part was shown. In this part, SOL6 and SOL7 also created barrier onto specimen and protect its from dye absorption which is good for anti-graffiti behavior.



Figure 3.44. SOL6-7 Coated Facing Stone With its uncoated middle part

In the Figure 3.45, SOL 3 (Right part) and SOL5 (left part) coated was shown. Middle part of the specimen was the uncoated area which absorbs whole dye.



Figure 3.45. SOL 3 (right) SOL 5 (left) coated and uncoated facing stones

Sol 8 was also applied onto facing stone and then it was dyed. In the Figure 3.46, coated and uncoated facing stone specimen can be seen.



Figure 3.46. SOL8 Coated and uncoated facing stone specimen

It is clear that SOL 8 was performed well onto porous facing stone. It created barrier effect onto specimen and protect it from dye attacks. This behavior is reason for preference for anti-graffiti coatings

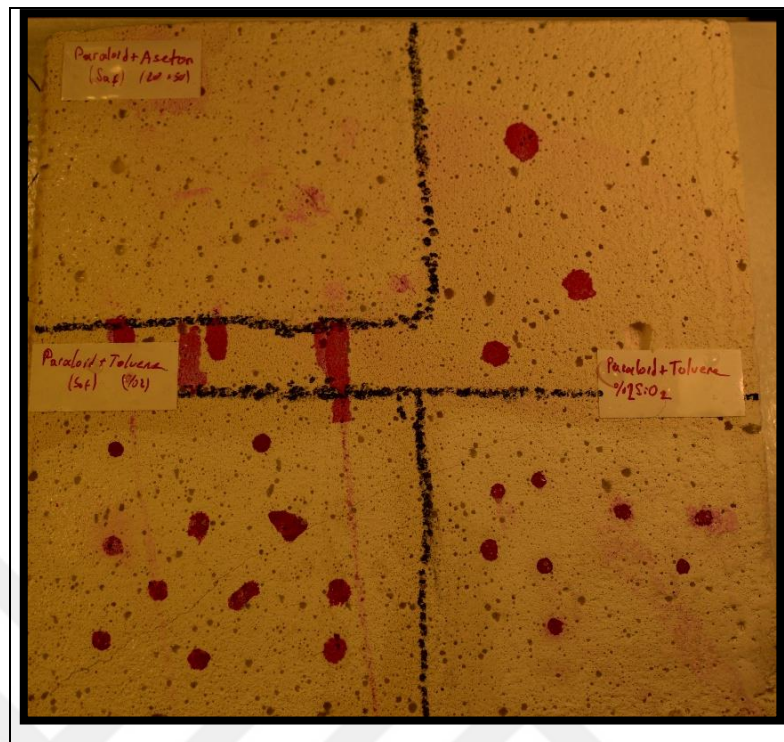


Figure 3.47. SOL1,2,4 and Uncoated Specimen after short and low-pressure water treatment

It should also be noted that for the SOL1, in the Figure 4.43, some part of this solution seems that it absorbs dye when it was painted. However, as it can be seen in the Figure 3.47, after short and low-pressure water treatment, it was cleaned well compared to other parts of the specimen. It makes the solution preferable for anti-graffiti applications due to its ease-to-clean character.

4. DISCUSSION

As it was mentioned, Anti-graffiti coatings requirement and new cleaning applications gaining importance from the beginning of the second half of 20th century due to some political reasons or economic struggles which affected behaviour of the people. With all of these, progress in the dye technologies give opportunity to people from everywhere to perform what they want to do with dye. Despite law and precaution, it is not easy to avoid people to use dyes onto masonry structures. All around the world, countries and their cultural heritage were affected from these dye attacks and these attacks must always be considered differently from street art. In addition to precautions and cleaning technologies, cultural heritages are widely open to these attacks due to their open-air character. Therefore, especially from the beginning of the 21th century, many projects are funded especially by European Union. As a result of these projects, there many coatings available on the market to protect cultural heritage from these attacks. In terms of cleaning procedures, there are some conventional applications and ideas however, for the coating applications, due to their recent progress, there is not any conventional rules which can be followed by conservators. Some implications were given above to develop acceptable coatings for masonry cultural heritage. Most important thing is for Anti-Graffiti coatings, they should create superhydrophobic surfaces onto applied surfaces. It can be seen that if a masonry heritage is coated by using Anti-graffiti coatings, first of all this coating must create superhydrophobic or at least hydrophobic surface onto masonry.

In the experimental procedure, due to its major importance, first requirement of the anti-graffiti coatings, which is hydrophobicity, was studied. To understand efficacy and behaviour of the coatings, different substrates were chosen and tested by using very commonly used red dye. There were four different specimens which were used as substrate and eight different coatings to observe the behaviour of the coatings onto different substrates and efficacy of different substrates which were developed different compounds. Both wettability models which were about surface roughness and surface free energy were studied and reported above. Specimens which were chosen as substrates can be listed as Ahlat Stone, which is a cultural heritage material in Eastern Anatolian part of Turkey used in Ahlat tombstones, Marmara marble, which is widely used cultural heritage material in Turkey also, glass, and facing stone which was chosen because of its very porous character with its white

colour which makes it identical with used stones while constructing cultural heritage. By doing this, one of the other implications was also ensured which was performing experiments for all kinds of coatings onto specified specimen before applying it.

After preparation of the coating solutions with sol-gel process, different specimens were coated. For the contact angle measurements, goniometer was occupied to understand wetting behaviour of the coatings onto substrates with water. Contact angle measurements were conducted for glass, Ahlat stone and Marmara marble and results were given above. From Table 3.1-3.3, contact angle values can be seen for glass, Ahlat stone and Marmara marble, in this order. Apart from SOL6 on marble, all coatings were able to create at least hydrophobic barrier surfaces onto specimens. For the case of SOL6, coating probably peeled off from the surface for some reason and marble surface acted as uncoated specimen. It should be noted that, for the Marmara marble, SOL 8 was the highest contact angle values even though it did not fulfil the conditions to be superhydrophobic since it had an acceptable value. Other solutions on the Marmara marble created hydrophobic surfaces.

For the Ahlat stone, which was the most important one due to its direct application for cultural heritage in Eastern Anatolia, SOL3 and SOL5 created highest contact angle values which are 138.49 and 131.56 respectively. They were still far from fulfilling conditions for being superhydrophobic surfaces. SOL7 also had good values in terms contact angle since it was still just hydrophobic. SOL3 and SOL5 demonstrated that by changing surface roughness with nano-silica dispersion and varying the surface free energy with Fluorine containing silane, it is possible to create good hydrophobic surfaces closer to the superhydrophobic conditions to develop anti-graffiti coatings for Ahlat stone. It is also remarkable that all coatings created barrier effects onto Ahlat stone and avoid penetration of the dyes into pores. In terms of porous Ahlat stones, if dye can penetrate this porous structure, it is obvious that removing the dye from masonry goes more difficulty. Therefore, for the Ahlat stone case, having the coatings onto specimens could always give opportunity to conservators for removing step avoiding harm to masonry structure and its artistical importance. For the first staining- removing cycle, coatings make the procedure easy when compared with uncoated part of the Ahlat stone. It should be noted that further investigations are still needed to advise these coatings after confirming implications which were suggested for the anti-graffiti coatings. For the first implication, being superhydrophobic or at least

hydrophobic, coatings worked well onto very porous Ahlat stone specimen, and this porous character also helps the coating to be absorbed into stone make their connection stronger when it compared to Marmara marble case.

For the glass specimen, it was the hydrophilic and nonporous substrate, coatings were able to create hydrophobic surfaces. Especially for the SOL4, contact angle was measured as 142.36 which is the closest value for the superhydrophobic conditions (higher than 150) for all specimen and coatings. For the SOL4, when it was applied other substrates, there was no such high contact angle value since it was one the best coatings in terms of sliding angle. This phenomenon was not performed during the experimental procedure mathematically, however, it was observed that when the little slope was given to substrate, dye and water drops slide away easily. Although SOL4 was not recorded as superhydrophobic contact angle, it acted very good to force the drop slide away from the substrate. For the glass specimen, SOL6 and SOL7 were not allowed to get results from goniometer since drops were not held onto specimen, they slide away. These two coatings also gave the glass white colour which makes them impossible to use as coatings due to changing transparency of the glass.

According to the results from both goniometer and high-definition photographs of the dyes onto coatings, they were able to create barrier effects and ensure protection to the specimens against dye or water attacks without noticing being porous or less porous. From the pictures, it is easier to observe the contribution of the coating onto surface of chosen specimen. They were always acted as barrier and make difficult for the dye adhering to surface of the specimen or penetrating pores of specimen. In this way, they were all good candidates for anti-graffiti application for different substrates.

Results also prove that one of implications of these coating application which is about applying those coating for specified substrates when it is needed. It means that coatings should not be applied onto masonry structures directly before performing it onto specimen. Each coating must be applied specimen and get results before general application. After that, according to results, coatings could be applied onto different kinds of masonry structures. Results clearly demonstrated that different coatings created different surface characteristic in terms of contact angle measurements as well as both coatings create hydrophobic surfaces.

Properties of the substrates led to change correlation between coatings and substrate which affected the contact angle measurements and wettability of the surface. These results provide that implication which is about preliminary tests for all coatings for each masonry is very important and conservators should follow that rule.

It should also be noted that, lower contact angle values mean this coating has no anti-graffiti behaviour. In terms of SOL1 onto facing stone, drops did not show spherical character which is a prove being hydrophobic surface, however, only low-pressure water treatment easily removes the dye from the surface.



5. CONCLUSION

At the end, eight different coating dispersion and 4 different substrates were occupied to create superhydrophobic surfaces. According to contact angle measurement, none of these coatings were able to create a superhydrophobic barrier onto specimen. However, it should be also noted that all coatings created hydrophobic surfaces for porous and non-porous surfaces. They were also able to provide surfaces that makes easier for the drops slide away with little slopes without dying to surface. This is good for an anti-graffiti coating but not the best. These coatings should also be observed in terms of colour and gloss change after applying to stone and results must be less than 3, which is the value which cannot be detected by human eye. For the further applications, colour and gloss changes must be controlled.

Aging tests were also not performed. To understand long-term durability and protection under atmospheric condition, aging tests must be conducted and at least eight staining-cleaning cycles must be performed.

For these results, these coatings seem to be good candidate for anti-graffiti coatings they still needed further tests to ensure that they could be used these materials. It should also be noted that, if some other substrate is used with one of these coatings, these contact angle and wettability experiments must be performed again.

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