



Chemico-physical characterization and evaluation of coating properties of two commercial organosilicons

Hydrophase[®] and Disboxan 450[®]

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Abstract

Two commercial organosilicons, Hydrophase[®], a monomeric dispersion, and Disboxan 450[®], an oligomeric dispersion, were studied in pure form and applied on acrylic paint replicas. Their physico-chemical characteristics, coating properties, and interaction with acrylic paint replicas were evaluated by TG, DSC, FTIR, and contact angle measurements. Hydrophase[®] showed a higher interaction when used on the top of acrylic paint replicas than Disboxan 450[®]. No appreciable modification was detected after two years of natural ageing.

Keywords TG-FTIR · Differential scanning calorimetry · ATR-FTIR · Contact angle · Organosilicon coatings · Hydrophase[®] · Disboxan 450[®] · Acrylic paint coating interactions · Natural ageing

Introduction

Commercially available organosilicon compounds are extensively used as anticorrosive [1, 2], ice-retarding [3], self-cleaning/antireflective [4], and flame/heat/fire retardants [5] and in microelectronics as precursors for oxide films formation [6]. In particular, they have been used as protective coatings. In fact, polysiloxanes are polymers that possess both organic and inorganic properties and can react with the surface, forming durable covalent bonds at the interface [7]. These bonds are hydrolysable; however, they can reform easily, resulting in improved coating adhesion

and surface durability [7–9]. They have often been applied as restoring and conserving agents of buildings and monuments [7, 8, 10]. Polysiloxanes have been used as monomers, oligomers, or preformed polymers. Their handling and penetration properties are largely determined by the degree of condensation as well as by the solvent. Some of them exhibit their protecting and dirt repelling effects after cross-linking in situ [7–9]. Polysiloxanes used as protective coatings can degrade with prolonged use in outdoor conditions [7, 11]. FTIR, and particularly ATR-FTIR, is often used to study the stability and modification of these coatings [12, 13].

Thermal stability of various polysiloxanes has been evaluated in the literature by using thermogravimetry (TG) [14–17], thermogravimetry coupled with Fourier transfer infrared spectroscopy (TG-FTIR) [17–19], and DSC [17]. The physical–chemical interactions with building materials as stones and cured cement pastes also have been investigated through XPS analysis [12, 20]. On the contrary, studies on the interaction with paints used in outdoor artistic murals are missing. In order to fill this gap, the physico-chemical characterization and the evaluation of the coating properties of two commercial hydrophobic silicone varnishes, and namely Disboxan 450[®] (purchased from Caparol) and Hydrophase[®] (purchased from Phase

A. Spepi and S. Pizzimenti have contributed equally to this work.

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Restauro), were carried out in this work by using DSC, TG coupled with FTIR, ATR-FTIR, and contact angle measurements. Hydrophase[®] and Disboxan 450[®] have been selected for the treatment of the acrylic wall painting “Tuttomondo” painted in 1989 by Keith Haring on the external wall of the church of Sant’ Antonio in Pisa. [21].

Chemical formulas of Hydrophase[®] and Disboxan 450[®] are unknown since they are protected by patents. The only available information is that Hydrophase[®] is a ready-to-use monomeric coating agent, with no film-forming properties and a comparable molecular size to water molecules (5–10 Å), while Disboxan 450[®] is a micro-emulsion composed of an oligomeric alkyl alkoxy silane [21]. Hydrophase[®] and Disboxan 450[®] have been studied in the literature for their ability of reducing water penetration and bioreceptivity of a surface. Considering the hydrophobicity related to the bioreceptivity of the building materials, Urzi et al. [22] demonstrated that Hydrophase Superfici[®] (an alkyl alkoxy silane) and Hydrophase Malte[®] (an alkyl tri-alkoxy silane)—produced by Phase Restauro, are not effective when they are applied alone and need to be combined with a biocide. In the field of underwater archaeology, Crisci et al. [23] investigated capillary water absorption and simulated solar ageing to evaluate hydrophobic and consolidating properties of formulations composed of Hydrophase[®] and a biocide, applied on marble samples. After the ageing cycles, the formulations with Hydrophase[®] appeared stable and showed a good resistance to exposure to solar lamp. Furthermore, the capillary water test revealed that the formulations containing Hydrophase[®] showed an unpredictable further decrease in water absorption.

Both Hydrophase[®] and Disboxan 450[®] have been applied on Caparol acrylic paint replicas (the same paint brand used by K. Hering). The focus was on two main points:

1. The interaction of Disboxan 450[®] and Hydrophase[®] with Caparol acrylic paints;
2. The effect of two years of outdoor natural ageing on coated paint samples;

In this perspective, the coated paint films were systematically examined after drying using DSC, TG, FTIR, and contact angle measurements, before and after two years of natural outdoor ageing.

Experimental

Materials

Hydrophase[®] was purchased from Phase Restauro (Milan, Italy) and Disboxan 450[®] from Caparol (Pisa, Italy). The acrylic colours were purchased from Caparol (Pisa, Italy).

Paint replicas were prepared by applying a layer of Caparol acrylic colour on the wall surface miming material Capatec Putz. Both siloxane coatings were micro-sprayed onto paint replicas. Disboxan[®] was previously diluted 1:10 (v/v) with water and then applied. A set made up of each typology of siloxane coating/acrylic colour paint replica was naturally aged outdoors for two years.

Thermogravimetry (TG)

A TA Instruments Thermobalance model Q5000IR equipped with a FTIR Agilent Technologies spectrophotometer model Cary 640 for evolved gas analysis was used. TG measurements were taken at a rate of 10 °C min⁻¹, from 20 to 800 °C under air flow (25 mL min⁻¹). The amount of sample in each TG measurement varied between 2 and 4 mg. Each experiment was performed three times.

TG-FTIR measurements were performed at a heating rate of 20 °C min⁻¹, from 20 to 800 °C under nitrogen/air flow (90 mL min⁻¹), from 600 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹. To reduce the strong background absorption from water and carbon dioxide in the atmosphere, the optical bench was usually purged with nitrogen. In addition, a background spectrum was collected before the beginning of each analysis in order to zero the signal in the gas cell and to eliminate any contribution from the amount of ambient water and carbon dioxide. The amount of sample in each TG-FTIR measurement varied between 6 and 8 mg. Data were collected using Agilent Resolution Pro version 5.2.0.

DSC

A Perkin-Elmer Pyris Diamond differential scanning calorimeter was used. The measurements were performed in the temperature range 30–300 °C at 10 °C min⁻¹, under air as the purging gas. The sample masses ranged from 5 to 6 mg and were placed in aluminium pans. Each experiment was performed three times.

Fourier Transform Infrared Spectroscopy

Infrared spectra were recorded using a FTIR Agilent Technologies Spectrophotometer model Cary 640, equipped with a universal attenuated total reflectance accessory (ATRU). A few micrograms of sample was used with the following spectrometer parameters: resolution: 4 cm⁻¹, spectral range: 500–4000 cm⁻¹, number of scans: 32. Spectrum software was used to process the FTIR spectra.

Contact Angle

Optical contact angles were performed using the sessile drop technique. The experimental setup for the contact

angle measurements consisted in an HD webcam mounted on a horizontal microscope to acquire a digital image of a drop of deionized water placed onto a treated glass slide. The instrument was positioned in a room with controlled environment (relative humidity of 30% and temperature of 20 °C). The water was dispensed through a micro-syringe, and the drop volume was $(2.0 \pm 1.0) \mu\text{L}$. The contact angle was obtained by fitting the drop profile with the Young–Laplace model using the drop analysis plugin of ImageJ [24]. The reported values were the average of the contact angles of three static drops on different areas on the surface of the films.

Results and discussion

Physico-chemical characterization of Hydrophase® and Disboxan 450®

Thermal degradation of pure Hydrophase® and Disboxan 450® has been studied by TG, DSC, and FTIR. The TG curve and the corresponding derivative curve, recorded under nitrogen or air flow, are reported in Fig. 1. Table 1 reports the maximum temperature of each mass loss and the corresponding mass loss percentage obtained under air or nitrogen flow.

The mechanism of thermal decompositions of Hydrophase® and Disboxan 450® was different if carried out in an inert (nitrogen) or oxidative (air) atmosphere. Under nitrogen flow, both Hydrophase® and Disboxan 450® pyrolyse with a single mass loss at 509 °C and 520 °C, respectively (Fig. 1 and Table 1). Under air flow, the main degradation step, corresponding to an exothermic peak in the DSC curve (Fig. S1 in the Supporting

Information), occurs at a lower temperature (from 150 to 400 °C for Hydrophase® and from 400 to 800 °C for Disboxan 450®) and the TG profile presents a shoulder at higher temperatures (540 °C for Hydrophase® and 471, 622 °C for Disboxan 450®).

Sun and co-workers [25] investigated the thermal degradation process, under an inert argon atmosphere, of a derivative of polydimethylsiloxane (PDMS), the poly(methylphenylsiloxane), and proved that it can proceed according two different mechanisms: “unzip degradation” and “rearrangement degradation.” The first mechanism generates cyclic siloxanes and occurs at about 400–500 °C. The second, above 500 °C, is caused by heterolytic cleavage and rearrangement of the Si–O–Si bond in the main chain and generates low molecular weight species and cyclic siloxanes [17].

In a TG-FTIR experiment carried out under nitrogen atmosphere on a sample of Hydrophase®, the spectrum of the volatiles evolved at 520 °C (Fig. S2) showed the presence of CH_4 (3015 cm^{-1} , C–H stretching and 1304 cm^{-1} , C–H bending), indicative of the homolytic scission of the Si– CH_3 bond followed by H abstraction [26] and of aliphatic saturated (between 2820 and 2960 cm^{-1} , C–H stretching, and between 1370 and 1460 cm^{-1} , C–H bending) and unsaturated (3090 cm^{-1} , =C–H stretching, and 1652 cm^{-1} , C=C stretching) hydrocarbon compounds [27, 28]. The spectrum of the volatiles evolved, in the same conditions, by Disboxan 450® at 510 °C (Fig. 2S) showed FTIR bands that are ascribable to the presence, together with CH_4 , of cyclic siloxane compounds. Figure 2 shows the FTIR profiles at fixed wavenumbers of gases evolved with time by Hydrophase® (3015 cm^{-1} , C–H stretching of CH_4) and Disboxan 450® (1090 cm^{-1} , Si–O stretching vibration of cyclic siloxane compounds).

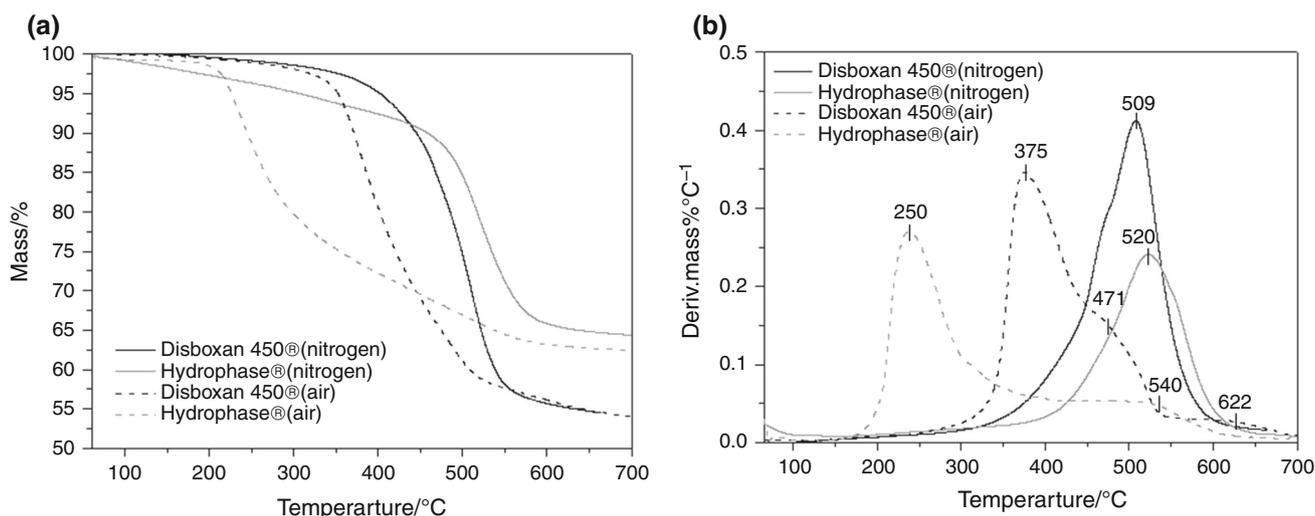
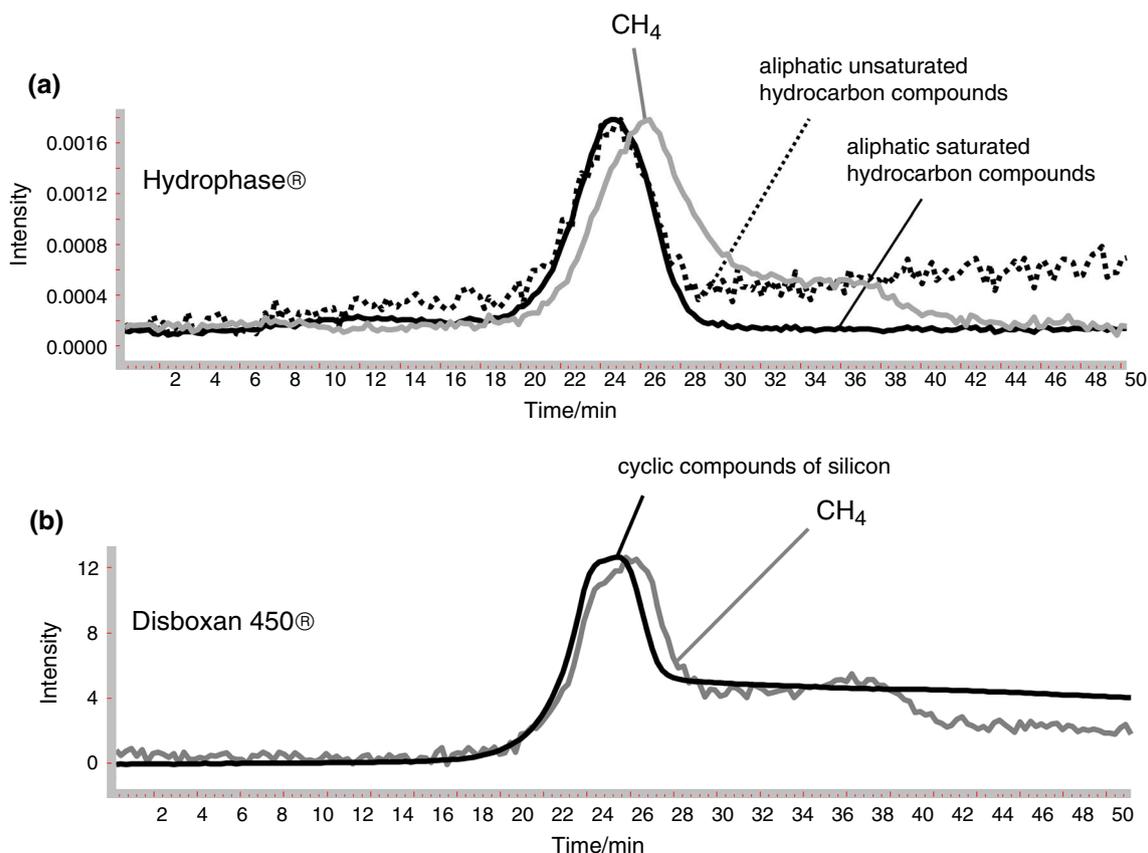


Fig. 1 TG curve of Hydrophase® and Disboxan 450® (a) and the corresponding derivative (b), under nitrogen and air flow at 10 °C min^{-1} heating rate

Table 1 Experimental maximum temperatures and the percentage mass losses of the corresponding degradation steps under air and nitrogen flows of the pure coatings

Step	Hydrophase® (air)	Hydrophase® (nitrogen)	Disboxan 450® (air)	Disboxan 450® (nitrogen)
1	250 °C (33%)	–	–	–
2	–	–	375 °C (38.8%)	–
3	540 °C (10%)	–	471 °C (shoulder)	–
4	–	520 °C (35.4)	–	509 °C (46.5%)
5	–	–	622 °C (7.6%)	–
Residual mass (700 °C)	57.0%	64.6%	53.6%	53.5%

**Fig. 2** Evolved gas analysis profiles under nitrogen flow in function of time at fixed wavenumbers of (a) Hydrophase® (3015 cm⁻¹, C–H stretching of CH₄) and (b) Disboxan 450® (1090 cm⁻¹, ν Si–O of cyclic siloxane compounds)

Under air flow, above 350 °C, the thermo-oxidative degradation of Hydrophase® produces carbon dioxide and water (indicating the combustion of the organic part of the sample), while Disboxan 450® (Fig. S3), in addition to the peaks typical of carbon dioxide and water, shows peaks ascribable to the presence of siloxane oligomers (bands between 810 and 1260 cm⁻¹). These results suggest that Hydrophase® degrades with the simplest pathway (homolytic Si–CH₃ breakage), while Disboxan 450® has a typical PDMS derivative pathway, which occurs with “rearrangement degradation” leading to the formation of

cyclic siloxanes [17, 29], thus confirming the monomeric nature of Hydrophase® and oligomeric nature of Disboxan 450® [21].

These results are supported by the FTIR-ATR spectra of Hydrophase® and Disboxan 450® reported in Fig. 3 (and Table S2 for the main FTIR absorptions and the corresponding vibrational assignments).

The FTIR-ATR spectra of both coatings show the peaks typical of methyl siloxane derivatives. The absorption bands of the alkylic portion of the samples can be totally ascribed to the methyl groups present. Note that the OH

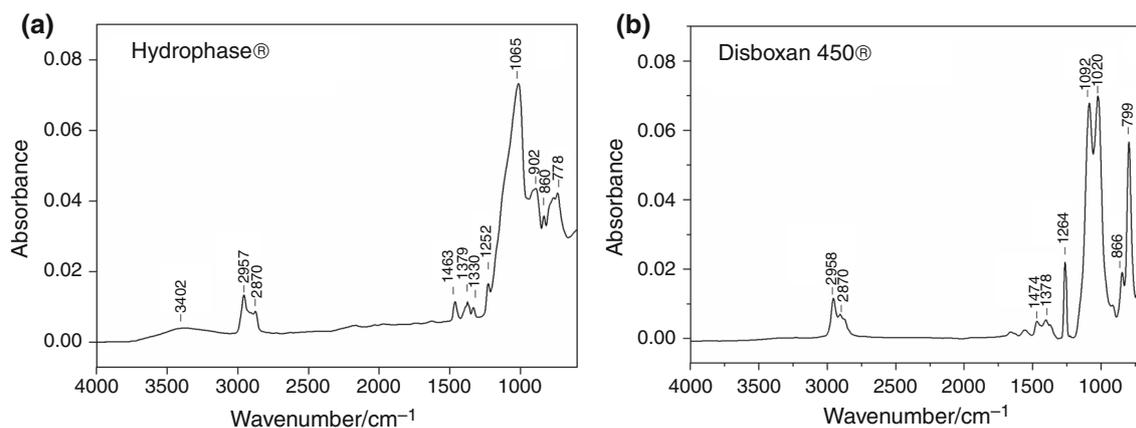


Fig. 3 FTIR-ATR spectra in the range 4000–600 cm^{-1} : Hydrophase[®] (a), and Disboxan 450[®] (b)

stretching band (3402 cm^{-1}) is present only in Hydrophase[®] samples and that the absorption bands related to Si–O vibrations are different for Hydrophase[®] compared to Disboxan 450[®]. In particular, the ν_s and ν_{as} Si–O of Disboxan 450[®] are at 1092 and 1020 cm^{-1} , respectively, while those of Hydrophase[®] at 1065 and 902 cm^{-1} . This could be due to the monomeric nature of Hydrophase[®]. In fact, when silanol (Si–OH) groups are present in the siloxane structure, the absorption of Si–O bond shifts to a lower wavenumber [30].

Hydrophase[®] and Disboxan 450[®] coating properties

In order to investigate the coating properties of Hydrophase[®] and Disboxan 450[®] and their interactions with the acrylic paints, paint/Hydrophase[®] and paint/Disboxan 450[®] replicas were prepared according to the procedure described in the experimental section and studied by TG, DSC, FTIR-ATR, and contact angle measurements.

The Caparol acrylic colour is composed of a styrene/*n*-butyl acrylate copolymer [26]. Table 2 reports the temperatures and the mass losses, under air flow, of the acrylic paint alone or coated with Hydrophase[®] or Disboxan 450[®]. The same quantities for the two pure coatings are reported in Table 1. (A) shows the TG curves under air flow, and the corresponding derivative curves, of samples of acrylic

paint and of acrylic paint covered with Hydrophase[®]. The curves of the acrylic paint alone show the typical behaviour of these copolymers [31], with a first small mass loss in the range 25–260 °C (shoulder at 220 °C in the derivative curve), the main mass loss at 347 °C, due to the degradation of the acrylate unit, and a third decomposition step in the range 390–500 °C (shoulder at about 417 °C), due to the degradation of the styrene unit. The DSC curve of the acrylic paint (Fig. 4b) reveals the presence of three exothermic effects in the temperature range 25–500 °C, which are related to the main decomposition steps highlighted by thermogravimetry.

The TG analysis of the acrylic paint coated with Hydrophase[®] still shows three degradative steps, but they occur at higher temperatures. The first step (at about 270 °C) is only partially due to the degradation of the acrylic paint and can be mainly attributed to the main decomposition step of Hydrophase[®] (250 °C), the second step, with the main mass loss, is shifted at 374 °C, while the third step is shifted at about 450 °C (Fig. 4a, Table 2). An analogous behaviour can be observed in the DSC curves, with the strengthening of the exothermic effect at about 250 °C due to thermoxidation of Hydrophase[®] and the shift to higher temperatures of the two remaining peaks (Fig. 4b, Table 2). These results demonstrate an effective interaction between the acrylic resin and Hydrophase[®] and highlight the greater stability of the coated paint. On the

Table 2 Experimental temperature and mass loss percentage of thermal degradation steps under air of acrylic paint alone or covered by Hydrophase[®] and Disboxan 450[®]

N° step	Acrylic paint	Acrylic paint + Hydrophase [®]	Acrylic paint + Disboxan 450 [®]
1	25–260 °C (4.1%)	25–299 °C (4.6%)	25–260 °C (3.7%)
2	347 °C (20.5%)	374 °C (12.9%)	345 °C (17.5%)
3	390–500 °C (4.1%)	390–500 °C (2.4%)	360–500 °C (6.3%)
Residual mass (500 °C)	71.2%	80.1%	72.4%

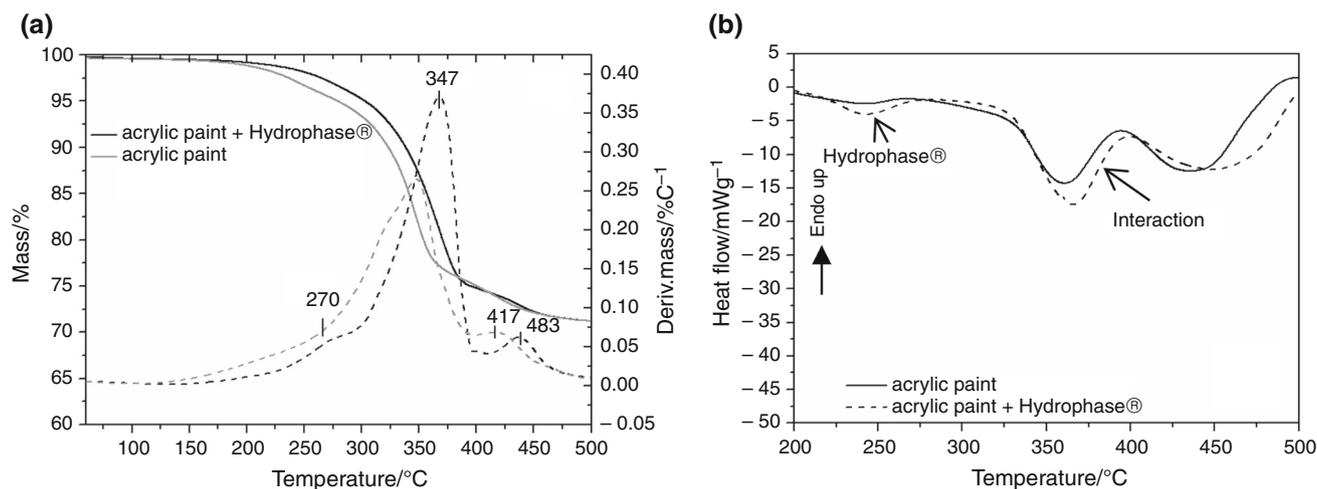


Fig. 4 TG curve and its derivative of the acrylic paint, alone and covered with Hydrophase[®], performed under air flow at 10 °C min⁻¹ heating rate (a). DSC curve of the acrylic paint alone and covered with Hydrophase[®] under air flow at 10 °C min⁻¹ heating rate (b)

contrary, both the DSC and the TG curves of acrylic paint are practically unaffected by the coating with Disboxan 450[®] (See Fig. S4).

The FTIR-ATR spectrum of the acrylic paint alone is reported in Fig. S5. The interactions of Hydrophase[®] and Disboxan 450[®] with acrylic paints have been investigated also by FTIR-ATR measurements. The spectra of the acrylic paint coated with Hydrophase[®] (Fig. S6) clearly show a decrease in the OH stretching absorbance at about 3300 cm⁻¹ and an increase in the Si–O stretching absorbance in the range 1000–1120 cm⁻¹ (Fig. S6). These evidences prove the reduction in the free OH content due to the corresponding formation of a bond between siloxanes and acrylic paint and confirm the increased thermal stability of the coated samples. Moreover, the Hydrophase[®] coating causes an increase in the C–H stretching absorbance (2870–2965 cm⁻¹) on the spectra of acrylic paint replicas due to the presence of alkyl groups bonded to Si atoms of the coating.

Figure 5 shows the FTIR spectra of fresh paint replicas coated with Hydrophase[®] compared to those naturally aged outdoors for two years. The FTIR spectra of the fresh and aged paint coated with Disboxan 450[®] are reported in Fig. S7. Hydrophase[®]-coated paint replica is less stable over time than that coated with Disboxan 450[®]. Its decomposition can lead to the breakage of Si–C bonds and the formation of CH₄ and SiO₂ through radical reactions catalysed by light or by heat during outdoor exposure. As a result, a decrease in the absorption bands is observed in the range 2830–2960 (C–H bonds) and 900–1100 cm⁻¹ for the Si–O bonds, respectively. Regarding the stability of Disboxan 450[®], Wang et al. [32] attributed the ageing resistance of this coating to the inability of the ultraviolet rays to break the siloxane bond (Si–O–Si).

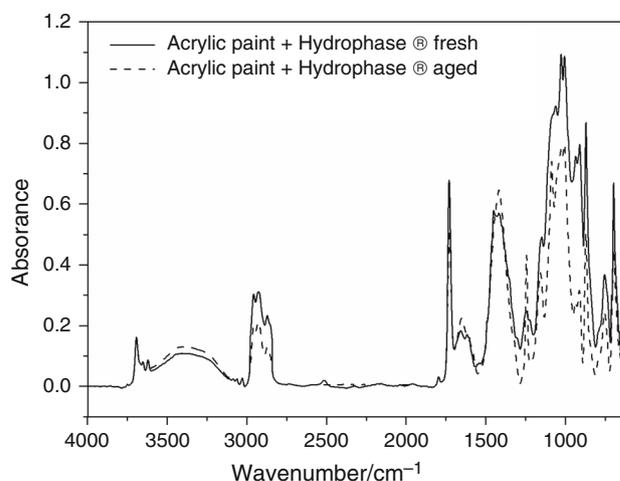


Fig. 5 FTIR spectra of Hydrophase[®]-coated paint fresh and 2 years naturally outdoor aged

Commercial siloxanes are commonly used as water-repellent coatings for wall paints. For this reason, it is important to study the wettability of the coated surface and the stability of the coating over time. The wettability of the two coatings was studied by contact angle measurements. Contact angle value is a simple and a powerful parameter suitable to characterize three-phase junctions and thus to determine the wettability of surfaces with respect to a specific liquid. Sessile drop is today the most widely used method to measure this parameter [24].

Contact angle values can be affected by various factors: surface roughness, morphology, temperature, heterogeneity, and reactivity of surface with water drops [12]. For this reason, we made some assumptions that allowed us to determine and interpret these data:



Fig. 6 Water droplet images captured immediately after droplet deposition on blue paint replicas (a), on paint replica coated with fresh Disboxan 450[®] (b), and on blue paint replicas coated with Disboxan 450[®] after two years of natural outdoor ageing (c)

- (1) All the samples have the same roughness, so the contact angle values are comparable;
- (2) All the samples are homogeneous, or the actual heterogeneity is the same in all the samples;
- (3) There is no swelling, absorption, spreading, or detectable evaporation of water droplets in the time frame of the analysis;
- (4) All the measurements have been collected in the same temperature conditions, and the effect of temperature changes is negligible;
- (5) The Young–Laplace equation gives the best value of the equilibrium contact angle.

On the basis of these assumptions, and in line with the widely accepted theories[33], the contact angle values, measured for the pure acrylic colours, suggested a low hydrophilicity ($\theta \approx 60^\circ$) of the acrylic paint sample. The coating with both Hydrophase[®] and Disboxan 450[®] modify the surface properties. The paint replicas coated with Disboxan 450[®] showed an increase in contact angle value ($\theta \approx 95^\circ$) and the surface became hydrophobic (Fig. 6). On the other hand, the paint replicas coated with Hydrophase[®] showed only a small increase in contact angle ($\theta \approx 68^\circ$), and this indicates that the treatment with Hydrophase[®] promotes only small changes in the wettability of the surface, which maintains its hydrophilicity.

Ageing promotes only small changes in the surface wettability, thus confirming the stability of the two coatings over time. Both naturally aged coated paint replicas showed a small decrease in the contact angle value (Disboxan 450[®]-coated samples, $\theta \approx 92^\circ$; Hydrophase[®]-coated samples, $\theta \approx 64^\circ$). These results indicate an increase in the polarity and hydrophilicity of the film surface, due to the action of pollutants, light, and rain. After two years of natural outdoor ageing, the Hydrophase[®]-coated samples show a contact angle similar to the fresh sample, with a low hydrophilicity. The surface of the Disboxan 450[®]-coated samples remained hydrophobic with $\theta > 90^\circ$.

Conclusions

This work provides the physical chemical characterization of two commercial polysiloxanes, namely Hydrophase[®] and Disboxan 450[®], commonly used as water-repellent coatings for wall paints and artistic wall murals. It also highlights some differences in the behaviour of the two coatings, which can be useful to the restorers to choose the best solution.

Hydrophase[®] coating is less stable in air than Disboxan 450[®], and its thermal degradation occurs via a simple mechanism due to the homolytic scission of the Si-CH₃ bond followed by H abstraction. Differently, the Disboxan 450[®] decomposes through heterolytic cleavage and rearrangement of the Si-O-Si bond in the main chain. This different behaviour may be attributed to the monomeric nature of Hydrophase[®] while Disboxan 450[®] is an oligomeric polysiloxane. On the other hand, Hydrophase[®] interacts with the underlying acrylic paint more strongly than Disboxan 450[®]. In fact, the FTIR spectra clearly show a decrease in the intensity of the OH stretching absorbance (3300 cm^{-1}) in the acrylic paint replicas when they are coated with Hydrophase[®] or Disboxan 450[®], more marked in the case of Hydrophase[®]. This decrease confirms the interaction between the coating siloxanes and the acrylic colour that leads to the formation of a Si-O bond and the consequent reduction of the free OH content. However, Disboxan 450[®] does not induce any modifications in the thermal stability of the acrylic support, while the interaction of Hydrophase[®] causes an increase in the resin's thermal stability as demonstrated by the shifts of the decomposition temperatures to higher values. Moreover, upon two years of natural ageing, FTIR analyses reveals that Hydrophase[®] coating is less stable over time compared to the oligomeric Disboxan 450[®] coating. Contact angle measurements show that the coating with Disboxan 450[®] increases the hydrophobicity of the paint surface and that Hydrophase[®] promotes only small changes in the wettability of the surface which maintains its hydrophilicity. Both replicas of naturally aged coated paint showed only a small decrease in the value of the contact angle, indicating good resistance to the action of pollutants, light and rain.

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References

1. Ammar S, Ramesh K, Vengadaesvaran B, Ramesh S, Arof AK. Amelioration of anticorrosion and hydrophobic properties of epoxy/PDMS composite coatings containing nano ZnO particles. *Prog Org Coat*. 2016;92:54–65. <https://doi.org/10.1016/j.porgcoat.2017.05.012>.
2. Blanco I, Abate L, Bottino FA. Synthesis and thermal behaviour of phenyl-substituted POSSs linked by aliphatic and aromatic bridges. *J Therm Anal Calorim*. 2018;131(2):843–51. <https://doi.org/10.1007/s10973-017-6608-6>.
3. Li J, Zhao Y, Hu J, Shu L, Shi X. Anti-icing performance of a superhydrophobic PDMS/modified nano-silica hybrid coating for insulators. *J Adhes Sci Technol*. 2012;26(4–5):665–79. <https://doi.org/10.1163/016942411X574826>.
4. Kapridaki C, Maravelaki-Kalaitzaki P. TiO₂–SiO₂–PDMS nanocomposite hydrophobic coating with self-cleaning properties for marble protection. *Prog Org Coat*. 2013;76(2–3):400–10. <https://doi.org/10.1016/j.porgcoat.2012.10.006>.
5. Jagdale P, Salimpour S, Islam MH, Cuttica F, Hernandez FCR, Tagliaferro A, et al. Flame retardant effect of nano fillers on polydimethylsiloxane composites. *J Nanosci Nanotechnol*. 2018;18(2):1468–73. <https://doi.org/10.1166/jnn.2018.15251>.
6. Ermakova E, Sysoev S, Nikolaev R, Nikulina L, Lis A, Tsyrendorzhieva I, et al. Thermal properties of some organosilicon precursors for chemical vapor deposition. *J Therm Anal Calorim*. 2016;126(2):609–16. <https://doi.org/10.1007/s10973-016-5563-y>.
7. Witucki GL. A silane primer: chemistry and applications of alkoxy silanes. *J Coat Technol*. 1993;65:57.
8. Tsakalof A, Manoudis P, Karapanagiotis I, Chrissoulakis I, Panayiotou C. Assessment of synthetic polymeric coatings for the protection and preservation of stone monuments. *J Cult Herit*. 2007;8(1):69–72. <https://doi.org/10.1016/j.culher.2006.06.007>.
9. Eduok U, Faye O, Szpunar J. Recent developments and applications of protective silicone coatings: a review of PDMS functional materials. *Prog Org Coat*. 2017;111:124–63. <https://doi.org/10.1016/j.porgcoat.2017.05.012>.
10. Kahraman MV, Kuğu M, Menciloğlu Y, Kayaman-Apohan N, Güngör A. The novel use of organo alkoxy silane for the synthesis of organic–inorganic hybrid coatings. *J Non-Cryst Solids*. 2006;352(21–22):2143–51. <https://doi.org/10.1016/j.jnoncrysol.2006.02.029>.
11. Li D, Xu F, Liu Z, Zhu J, Zhang Q, Shao L. The effect of adding PDMS-OH and silica nanoparticles on sol–gel properties and effectiveness in stone protection. *Appl Surf Sci*. 2013;266:368–74. <https://doi.org/10.1016/j.apsusc.2012.12.030>.
12. Fermo P, Cappelletti G, Cozzi N, Padeletti G, Kaciulis S, Brucalè M, et al. Hydrophobizing coatings for cultural heritage. A detailed study of resin/stone surface interaction. *Appl Phys A*. 2014;116(1):341–8. <https://doi.org/10.1007/s00339-013-8127-z>.
13. Brachaczek W. Comparative analysis of organosilicon polymers of varied chemical composition in respect of their application in silicone-coating manufacture. *Prog Org Coat*. 2014;77(3):609–15. <https://doi.org/10.1016/j.porgcoat.2013.11.026>.
14. Thomas TH, Kendrick T. Thermal analysis of polydimethylsiloxanes. I. Thermal degradation in controlled atmospheres. *J Polym Sci Part A 2 Polym Phys*. 1969;7(3):537–49. <https://doi.org/10.1002/pol.1969.160070308>.
15. Jovanovic JD, Govedarica MN, Dvornic PR, Popovic IG. The thermogravimetric analysis of some polysiloxanes. *Polym Degrad Stab*. 1998;61(1):87–93. [https://doi.org/10.1016/S0141-3910\(97\)00135-3](https://doi.org/10.1016/S0141-3910(97)00135-3).
16. Deshpande G, Rezac ME. The effect of phenyl content on the degradation of poly (dimethyl diphenyl) siloxane copolymers. *Polym Degrad Stab*. 2001;74(2):363–70. [https://doi.org/10.1016/S0141-3910\(01\)00186-0](https://doi.org/10.1016/S0141-3910(01)00186-0).
17. Tomer NS, Delor-Jestin F, Frezet L, Lacoste J. Oxidation, chain scission and cross-linking studies of polysiloxanes upon ageings. *Open J Org Polym Mater*. 2012;2(02):13. <https://doi.org/10.4236/ojopm.2012.22003>.
18. Camino G, Lomakin S, Lazzari M. Polydimethylsiloxane thermal degradation Part 1. Kinetic aspects. *Polymer*. 2001;42(6):2395–402. [https://doi.org/10.1016/S0032-3861\(00\)00652-2](https://doi.org/10.1016/S0032-3861(00)00652-2).
19. Camino G, Lomakin S, Lageard M. Thermal polydimethylsiloxane degradation. Part 2. The degradation mechanisms. *Polymer*. 2002;43(7):2011–5. [https://doi.org/10.1016/S0032-3861\(01\)00785-6](https://doi.org/10.1016/S0032-3861(01)00785-6).
20. Stewart A, Schlosser B, Douglas EP. Surface modification of cured cement pastes by silane coupling agents. *ACS Appl Mater Interfaces*. 2013;5(4):1218–25. <https://doi.org/10.1021/am301967v>.
21. Colombini M, Modugno F, Di Girolamo F, La Nasa J, Duce C, Ghezzi L et al. Keith Haring and the city of the Leaning Tower: preservation of the mural “Tuttomondo”. *Conservation Issues in Modern and Contemporary Murals*. Cambridge Scholars Publishing; 2015. ISBN 978-1-4438-7233-1.
22. Urzì C, De Leo F. Evaluation of the efficiency of water-repellent and biocide compounds against microbial colonization of mortars. *Int Biodeterior Biodegrad*. 2007;60(1):25–34. <https://doi.org/10.1016/j.ibiod.2006.11.003>.
23. Crisci GM, La Russa MF, Macchione M, Malagodi M, Palermo AM, Ruffolo SA. Study of archaeological underwater finds: deterioration and conservation. *Appl Phys A*. 2010;100(3):855–63. <https://doi.org/10.1007/s00339-010-5661-9>.
24. Stalder AF, Melchior T, Müller M, Sage D, Blu T, Unser M. Low-bond axisymmetric drop shape analysis for surface tension and contact angle measurements of sessile drops. *Colloids Surf Physicochem Eng Aspects*. 2010;364(1):72–81. <https://doi.org/10.1016/j.colsurfa.2010.04.040>.
25. Sun JT, Huang YD, Cao HL, Gong GF. Effects of ambient-temperature curing agents on the thermal stability of poly(methylphenylsiloxane). *Polym Degrad Stab*. 2004;85(1):725–31. <https://doi.org/10.1016/j.polymdegradstab.2004.03.018>.
26. La Nasa J, Orsini S, Degano I, Rava A, Modugno F, Colombini MP. A chemical study of organic materials in three murals by Keith Haring: a comparison of painting techniques. *Microchem J*. 2016;124:940–8. <https://doi.org/10.1016/j.microc.2015.06.003>.
27. Pandeale A, Andronescu C, Ghebaure A, Garea S, Iovu H. New biocompatible mesoporous silica/polysaccharide hybrid materials as possible drug delivery systems. *Materials*. 2019;12(1):15. <https://doi.org/10.3390/ma12010015>.
28. Catauro M, Tranquillo E, Salzillo A, Capasso L, Illiano M, Sapio L, et al. Silica/Polyethylene glycol hybrid materials prepared by a sol-Gel method and containing chlorogenic acid. *Molecules*. 2018;23(10):2447. <https://doi.org/10.3390/molecules23102447>.
29. González-Rivera J, Iglío R, Barillaro G, Duce C, Tinè M. Structural and thermoanalytical characterization of 3D porous PDMS foam materials: the effect of impurities derived from a

- sugar templating process. *Polymers*. 2018;10(6):616. <https://doi.org/10.3390/polym10060616>.
30. Hofman R, Westheim JGF, Pouwel I, Fransen T, Gellings PJ. FTIR and XPS studies on corrosion-resistant SiO₂ coatings as a function of the humidity during deposition. *Surf Interface Anal*. 1996;24(1):1–6. [https://doi.org/10.1002/\(SICI\)1096-9918\(199601\)24:1%3c1:AID-SIA73%3e3.0.CO;2-I](https://doi.org/10.1002/(SICI)1096-9918(199601)24:1%3c1:AID-SIA73%3e3.0.CO;2-I).
 31. de la Fuente JL, Fernández-García M, López Madruga E. Characterization and thermal properties of poly(*n*-butyl acrylate-*g*-styrene) graft copolymers. *J Appl Polym Sci*. 2001;80(5):783–9. [https://doi.org/10.1002/1097-4628\(20010502\)80:5%3c783:AID-APP1155%3e3.0.CO;2-5](https://doi.org/10.1002/1097-4628(20010502)80:5%3c783:AID-APP1155%3e3.0.CO;2-5).
 32. Wang ZY, Liu FC, Han EH, Ke W. Ageing resistance and corrosion resistance of silicone-epoxy and polyurethane topcoats used in sea splash zone. *Mater Corros*. 2013;64(5):446–53. <https://doi.org/10.1002/maco.201106269>.
 33. Baudys M, Krýsa J, Zlámál M, Mills A. Weathering tests of photocatalytic facade paints containing ZnO and TiO₂. *Chem Eng J*. 2015;261:83–7. <https://doi.org/10.1016/j.cej.2014.03.112>.

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