

Journal of Thermal Analysis and Calorimetry

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--Manuscript Draft--

Manuscript Number:	
Full Title:	Chemico-physical characterization and evaluation of coating properties of two commercial organosilicons: Hydrophase and Disboxan 450
Article Type:	S.I. : AICAT2018
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Funding Information:	University of Pisa (PRA2017_17) Prof. Maria Rosaria Tinè
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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 aging.

Keywords: *ATR-FTIR, differential scanning calorimetry, contact angle, organosilicon coatings, evolved gas analysis, paint-coating interactions, polysiloxane, thermal stability, thermogravimetric analysis, therm(oxy)dative degradation.*

27 Introduction

28 Polysiloxanes are polymers that possess both organic and inorganic properties and can react
29 with the surface, forming durable covalent bonds at the interface [1]. These bonds are
30 hydrolysable; however, they can reform easily, resulting in improved coating adhesion and
31 surface durability [1-3]. They have often been applied as restoring and conserving agents of
32 buildings and monuments [1, 2, 4]. Polysiloxanes have been used as monomers, oligomers, or
33 preformed polymers. Their handling and penetration properties are largely determined by the
34 degree of condensation as well as by the solvent. Some of them exhibit their protecting and
35 dirt repelling effects after cross-linking *in situ* [1-3]. Polysiloxanes used as protective coatings
36 can degrade with prolonged use in outdoor conditions [1, 5]. FTIR, and particularly ATR-
37 FTIR, is often used to study the stability and modification of these coatings [6, 7].

38 Thermal stability of various polysiloxanes has been evaluated in the literature by using
39 thermogravimetry (TG) [8-11], thermogravimetry coupled with infrared spectroscopy (TG-
40 FTIR) [12, 13, 11] and DSC [11]. The physical-chemical interaction with building materials
41 as stones and cured cement pastes has also been investigated through XPS analysis [6, 14].
42 On the contrary, studies on the interaction with paints used in outdoor artistic murals are
43 missing. In order to fill this gap, the physico-chemical characterization and the evaluation of
44 the coating properties of two commercial hydrophobic silicone varnishes, and namely
45 Disboxan 450 (purchased from Caparol) and Hydrophase (purchased from Phase Restauro),
46 were carried out in this work by using DSC, TG coupled with FTIR, ATR-FTIR and contact
47 angle measurements.

48 Chemical formulas of Hydrophase and Disboxan 450 are unknown since they are
49 protected by patents. The only available information is that Hydrophase is a ready-to-use
50 monomeric coating agent, with no film-forming properties and a comparable molecular size
51 to water molecules (5-10 Å), while Disboxan 450 is a micro-emulsion composed of an
52 oligomeric alkyl alkoxysilane. Hydrophase penetrates deeply into the walls thus precluding

53 the absorption of water, the damage due to ice formation, and the corrosion induced by
54 pollutants and acid rain. On the contrary, given its higher molecular size, Disboxan 450 does
55 not penetrate deep into the support and its interaction with the substrate takes place mainly on
56 the surface. Hydrophase and Disboxan 450 have been studied in the literature for their ability
57 of reducing the water penetration and the bioreceptivity of a surface. Considering the
58 hydrophobicity related to the bioreceptivity of the building materials, Urzi et al.,[15]
59 demonstrated that Hydrophase Superfici (an alkyl alkoxy silane) and Hydrophase Malte (an
60 alchyl tri-alkoxy silane) - produced by Phase Restauro are not effective when they are applied
61 alone, and need to be combined with a biocide. In the field of underwater archaeology, Crisci
62 et al. investigated capillary water absorption and simulated solar aging to evaluate
63 hydrophobic and consolidating proprieties of formulations composed of Hydrophase and a
64 biocide, applied on marble samples. After the aging cycles, the formulations with Hydrophase
65 appeared stable and showed a good resistance to exposure to solar lamp. Furthermore, the
66 capillary water test revealed that the formulations containing Hydrophase showed an
67 unpredictable further decrease in water absorption. [16]

68 The present study was carried out within the cleaning and restoration activities of the
69 acrylic wall painting “Tuttomondo” painted in 1989 by Keith Haring on the external wall of
70 the church of Sant' Antonio in Pisa. Both Hydrophase and Disboxan 450 have been applied on
71 Caparol acrylic paint replicas (the same paint brand used by K.Hering). The focus was on two
72 main points:

- 73 1. The interaction of Disboxan 450 and Hydrophase with Caparol acrylic paints;
- 74 2. The effect of two years of outdoor natural aging on coated paint samples;

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

78

79 **Experimental**

80 **Materials**

81 Hydrophase® was purchased from Phase Restauro (Milan-Italy), and Disboxan 450®
82 from Caparol (Pisa-Italy). The acrylic colours were purchased from Caparol (Pisa-Italy). Paint
83 replicas were prepared by applying a layer of Caparol acrylic colour on the wall surface
84 miming material Capatec Putz. Both siloxane coatings were micro-sprayed onto paint
85 replicas. Disboxan was previously diluted 1:10 with water and then applied. A set made up of
86 each typology of siloxane coating/acrylic colour paint replica was naturally aged outdoors for
87 two years.

89 **Thermogravimetry (TG)**

90 A TA Instruments Thermobalance model Q5000IR equipped with a FT-IR Agilent
91 Technologies spectrophotometer model Cary 640 for Evolved Gas Analysis was used. TG
92 measurements were performed at a rate of 10 °C/min, from 50 °C to 800 °C under air flow
93 (25 ml/min). The amount of sample in each TG measurement varied between 2 and 4 mg.
94 Each experiment was performed three times.

95 TG-FTIR measurements were performed at a rate of 20 °C/min, from 50 °C to 800 °C
96 under nitrogen/air flow (90 ml/min), from 600 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹. To
97 reduce the strong background absorption from water and carbon dioxide in the atmosphere,
98 the optical bench was usually purged with nitrogen. In addition, a background spectrum was
99 taken before the beginning of each analysis in order to zero the signal in the gas cell and to
100 eliminate any contribution from the amount of ambient water and carbon dioxide. The amount
101 of sample in each TG-FTIR measurement varied between 6 and 8 mg. Data were collected
102 using Agilent Resolution Pro version 5.2.0.

104 **DSC**

105 A Perkin Elmer Pyris Diamond Differential Scanning Calorimeter was used. The
106 measurements were performed in the temperature range 30-300 °C at 10 °C/min, under air as
107 the purging gas. The sample masses ranged from 5 to 6 mg and were prepared in aluminium
108 pans. Each experiment was performed three times.

109

110 **Fourier Transform Infrared Spectroscopy**

111 Infrared spectra were recorded using a FT-IR Agilent Technologies Spectrophotometer
112 model Cary 640, equipped with a universal attenuated total reflectance accessory (ATRU). A
113 few micrograms of sample were used with the following spectrometer parameters; resolution:
114 4 cm⁻¹, spectral range: 500-4000 cm⁻¹, number of scans: 32. Spectrum software was used to
115 process the FTIR spectra.

116

117 **Contact Angle**

118 Optical contact angles were performed using the sessile drop technique. The
119 experimental setup for the contact angle measurements consisted in an HD webcam mounted
120 on a horizontal microscope to acquire a digital image of a drop of deionized water placed onto
121 a treated glass slide. The instrument was positioned in a room with controlled environment
122 (relative humidity of 30% and temperature of 20°C). The water was dispensed through a
123 micro-syringe and the drop volume was 2.0 ± 1.0 µL. The contact angle was obtained by
124 fitting the drop profile with the Young-Laplace model using the Drop Analysis plugin of
125 ImageJ [18]. The reported values were the average of the contact angles of three static drops
126 on different areas on the surface of the films.

127

128

129 Results and discussion

130 Physico-chemical characterization of Hydrophase and Disboxan 450

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

135
136 **Fig. 1** TG curve of Hydrophase and Disboxan 450 (left) and the corresponding derivative (right), under nitrogen and
137 air flow at 10°C/min heating rate.

138
139 **Table 1** . Experimental temperatures and the percentage mass losses of the corresponding degradation steps under air
140 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%	64.6 %	53.6 %	53.5 %

142
143 The thermal decompositions of Hydrophase and Disboxan 450 were different if carried
144 out in an inert (nitrogen) or oxidative (air) atmosphere. Under nitrogen, both Hydrophase and
145 Disboxan 450 pyrolyse with a single mass loss at 509 °C and 520 °C, respectively (**Fig. 1** and
146 **Table 1**). Under air flow, the main degradation step, corresponding to an exothermic peak in
147 DSC curve (**Fig. S1** in the Supplementary Material), shifts to a lower temperature (from 520
148 °C to 250 °C for Hydrophase and from 509 to 375°C for Disboxan 450) and the TG profile

149 presents a shoulder at higher temperatures (540°C for Hydrophase and 471, 622°C for
150 Disboxan 450).

151 Sun and coworkers [19] investigated the thermal degradation process, under an inert
152 argon atmosphere, of a derivative of polydimethylsiloxane (PDMS), the
153 poly(methylphenylsiloxane), and proved that it can proceed according two different
154 mechanisms: “unzip degradation” and “rearrangement degradation”. The first mechanism
155 generates cyclic siloxanes and occurs at about 400-500°C. The second, above 500°C, is
156 caused by heterolytic cleavage and rearrangement of the Si-O-Si bond in the main chain, and
157 generates low molecular weight species and cyclic siloxanes [11].

158 In a TG-FTIR experiment carried out under nitrogen atmosphere on a sample of
159 Hydrophase, the spectrum of the volatiles evolved at 520 °C (**Fig.S2**) showed the presence of
160 CH₄ (3015 cm⁻¹, C-H stretching and 1304 cm⁻¹, C-H bending), indicative of the homolytic
161 scission of the Si-CH₃ bond followed by H abstraction [**Error! Bookmark not defined.**], and
162 of aliphatic saturated hydrocarbon compounds (between 2820 and 2960 cm⁻¹, C-H stretching,
163 and between 1370 and 1460 cm⁻¹, C-H bending) and unsaturated (3090 cm⁻¹, =C-H stretching,
164 and 1652 cm⁻¹, C=C stretching). The spectrum of the volatiles evolved, in the same
165 conditions, by Disboxan 450 at 510 °C (**Fig. 2S**) showed FTIR bands that are ascribable to the
166 presence, together with CH₄, of cyclic siloxane compounds. **Fig. 2** shows the FTIR profiles at
167 fixed wavenumbers of gases evolved with time by Hydrophase (3015 cm⁻¹, C-H stretching of
168 CH₄) and Disboxan 450 (1090 cm⁻¹, Si-O stretching vibration of cyclic siloxane compounds).

169 Under air flow, above 350°C, the thermo-oxidative degradation of Hydrophase
170 produces carbon dioxide and water (indicating the combustion of the organic part of the
171 sample), while Disboxan 450 (**Fig. S3**), in addition to the peaks typical of carbon dioxide and
172 water, shows peaks ascribable to the presence of siloxane oligomers (bands between 810 and
173 1260 cm⁻¹). These results suggest that Hydrophase degrades with the simplest pathway
174 (homolytic Si-CH₃ breakage), while Disboxan 450 has a typical PDMS derivative pathway,

175 which occurs with “rearrangement degradation” leading to the formation of cyclic siloxanes
176 [11, 20], thus confirming the monomeric nature of Hydrophase and oligomeric nature of
177 Disboxan 450. [21]

178
179 **Fig. 2 Evolved gas analysis profiles under nitrogen flow in function of time at fixed wavenumbers of**
180 **Hydrophase (3015 cm⁻¹, C-H stretching of CH₄) and Disboxan 450 (1090 cm⁻¹, ν Si-O of cyclic siloxane**
181 **compounds).**

182
183 These results are supported by the FTIR-ATR spectra of Hydrophase and Disboxan 450
184 reported in **Fig. 3** (and **Table S2** for the main FTIR absorptions and the corresponding
185 vibrational assignments).

186
187 **Fig. 3 FTIR-ATR spectra in the range 4000-600 cm⁻¹ - Hydrophase (left), and Disboxan 450 (right).**

188
189 The FTIR-ATR spectra of both coatings show the peaks typical of methyl siloxane
190 derivatives. The absorption bands of the alkylic portion of the samples can be totally ascribed
191 to the methyl groups present. Note that the OH stretching band (3402 cm⁻¹) is present only in
192 Hydrophase samples and that the absorption bands related to Si-O vibrations are different for
193 Hydrophase compared to Disboxan 450. In particular, the ν_s and ν_{as} Si-O of Disboxan 450 are
194 at 1092 and 1020 cm⁻¹ respectively, while those of Hydrophase at 1065 and 902 cm⁻¹. This
195 could be due to the monomeric nature of Hydrophase. In fact, when silanol (Si-OH) groups
196 are present in the siloxane structure, the absorption of Si-O bond shifts to a lower
197 wavenumber [22].

198 **Hydrophase and Disboxan 450 coating properties**

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

203 The Caparol acrylic color is composed of a styrene/*n*-butylacrylate copolymer [17].

204 **Table 2** reports the temperatures and the mass losses, under air flow, of the acrylic paint alone
 205 or coated with Hydrophase or Disboxan 450. The same quantities for the two pure coatings
 206 are reported in **Table 1**. Error! Reference source not found. (left) shows the TG curves under air
 207 flow, and the corresponding derivative curves, of samples of acrylic paint and of acrylic paint
 208 covered with Hydrophase. The thermograms of the acrylic paint alone show the typical
 209 behaviour of these copolymers [23], with a first small mass loss in the range 25-260 ° C
 210 (shoulder at 220°C in the derivative curve), the main mass loss at 347°C, due to the
 211 degradation of the acrylate unit, and a third decomposition step in the range 390–500 °C
 212 (shoulder at about 417°C), due to the degradation the styrene unit. The DSC curve of the
 213 acrylic paint (Error! Reference source not found. – right) reveals the presence of three
 214 exothermic effects in the temperature range 25-500 °C, which are related to the main
 215 decomposition phases highlighted by thermogravimetry.

216 **Fig. 4** TG curve and its derivative of the acrylic paint, alone and covered with Hydrophase, performed under air flow
 217 at 10°C/min heating rate (left). DSC curve of the acrylic paint alone and covered with Hydrophase under air flow at
 218 10°C/min heating rate (right).
 219

220 **Table 2** Experimental temperature and mass loss percentage of thermal degradation steps under air of acrylic paint
 221 alone or covered by Hydrophase and Disboxan 450.
 222
 223

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 %

224
 225 The TG analysis of the acrylic paint coated with Hydrophase still shows three
 226 degradative steps, but they occur at higher temperatures. The first step (at about 270 °C), is
 227 only partially due to the degradation of the acrylic paint and can be mainly attributed to the

228 main decomposition step of Hydrophase (250°C), the second step, with the main mass loss, is
1
2 229 shifted at 374°C while the third step is shifted at about 450°C. (Error! Reference source not
3
4 230 found. left, **Error! Reference source not found.**). An analogous behaviour can be observed
5
6
7 231 in the DSC curves, with the strengthening of the exothermic effect at about 250°C due to
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9 232 thermoxidation of Hydrophase, and the shift to higher temperatures of the two remaining
10
11 233 peaks (Error! Reference source not found. right, **Error! Reference source not found.**). These
12
13
14 234 results demonstrate an effective interaction between the acrylic resin and Hydrophase and
15
16
17 235 highlight the greater stability of the coated paint. On the contrary, both the DSC thermogram
18
19 236 and the TG profile of acrylic paint are practically unaffected by the coating with Disboxan
20
21
22 237 450 (See **Fig. S4**).

24 238 The FTIR-ATR spectrum of the acrylic paint alone is reported in **Fig. S5**. The
25
26 239 interactions of Hydrophase and Disboxan 450 with acrylic paints have been investigated also
27
28
29 240 by FTIR-ATR measurements. The spectra of the acrylic paint coated with Hydrophase (**Fig.**
30
31 241 **S6**) clearly show a decrease in the OH stretching absorbance at about 3300 cm⁻¹ and an
32
33
34 242 increase in the Si-O stretching absorbance in the range 1000-1120 cm⁻¹ (**Fig. S6**). These
35
36 243 evidences prove the reduction in the free OH content due to the corresponding formation of a
37
38
39 244 bond between siloxanes and acrylic paint and explain the increased thermal stability of the
40
41 245 coated samples. Moreover, the Hydrophase coating causes an increase in the C-H stretching
42
43 246 absorbance (2870-2965 cm⁻¹) on the spectra of acrylic paint replicas due to the presence of
44
45
46 247 alkyl groups bonded to Si atoms of the coating.

48 248 Error! Reference source not found. shows the FTIR spectra of fresh paint replicas
49
50
51 249 coated with Hydrophase compared to those naturally aged outdoors for two years. The FTIR
52
53 250 spectra of the fresh and aged paint coated with Disboxan 450 are reported in **Fig.S6**.
54
55
56 251 Hydrophase coated paint replica is less stable over time than that coated with Disboxan 450.
57
58 252 Its decomposition can lead to the breakage of Si-C bonds and the formation of CH₄ and SiO₂
59
60
61 253 through radical reactions catalysed by light or by heat during outdoor exposure. As a result,
62
63
64
65

254 absorption decreasing in the range 2830-2960 cm^{-1} (C-H bonds) and in the range 900-1100
1
2 255 cm^{-1} (Si-O bonds) are observed. Regarding the stability of Disboxan 450, Wang et al., [24]
3
4 256 attributed the ageing resistance of this coating to the inability of the ultraviolet rays to break
5
6
7 257 the siloxane bond (Si-O-Si).
8

9 258

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11
12 259 **Fig. 5 FTIR spectra of Hydrophase coated paint fresh and 2 years naturally outdoor aged.**
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14 260

15
16 261 Commercial siloxanes are commonly used as water repellent coatings for wall paints,
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18 262 for this reason, it is important to study the wettability of the coated surface and the stability of
19
20 263 the coating over time. The wettability of the two coatings was studied by contact angle
21
22 264 measurements. Contact angle value is a simple and a powerful parameter suitable to
23
24 265 characterize three-phase junctions, and thus to determine the wettability of surfaces with
25
26 266 respect to a specific liquid. Sessile drop is today the most widely used method to measure this
27
28
29
30 267 parameter [18].
31

32
33 268 Contact angle values can be affected by various factors: surface roughness, morphology,
34
35 269 temperature, heterogeneity and reactivity of surface with water drops [6]. For this reason, we
36
37
38 270 made some assumptions which allowed us to determine and interpret these data:
39

- 40 271 1) all the samples have the same roughness, so the contact angle values are
41
42 272 comparable;
- 43
44 273 2) all the samples are homogeneous, or the actual heterogeneity is the same in all the
45
46
47 274 samples;
- 48
49
50 275 3) there is no swelling, absorption, spreading or evaporation of water droplets in the
51
52 276 time frame of the analysis;
- 53
54
55 277 4) all the measurements have been collected in the same temperature conditions and
56
57 278 the effect of temperature changes is negligible;
- 58
59
60 279 5) the Young-Laplace equation gives the best value of the equilibrium contact angle.
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280 On the basis of these assumptions, and in line with the widely accepted theories, the
1
2 281 contact angle values, measured for the pure acrylic colours, suggested a low hydrophilicity (θ
3
4 282 $\approx 60^\circ$) of the acrylic paint sample. The coating with both Hydrophase and Disboxan 450
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6
7 283 modify the surface properties. The paint replicas coated with Disboxan 450 showed an
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9
10 284 increase in contact angle value ($\theta \approx 95^\circ$) and the surface became hydrophobic (**Fig. 6**). On the
11
12 285 other hand, the paint replicas coated with Hydrophase showed only a small increase in contact
13
14 286 angle ($\theta \approx 68^\circ$) and this indicates that the treatment with Hydrophase promotes only small
15
16
17 287 changes in the wettability of the surface which maintains its hydrophilicity.

18
19 288 Aging promotes only small changes in the surface wettability, thus confirming the
20
21
22 289 stability of the two coatings over time. Both naturally-aged coated paint replicas showed a
23
24 290 small decrease in contact angle value (Disboxan 450 coated samples, $\theta \approx 92^\circ$; Hydrophase
25
26
27 291 coated samples, $\theta \approx 64^\circ$) and this indicates an increase in the polarity and hydrophilicity of the
28
29 292 film surface, due to the action of pollutants, light and rain. After two years of natural outdoor
30
31
32 293 ageing, the Hydrophase coated samples shows a contact angle similar to the fresh sample,
33
34 294 with a low hydrophilicity, while, in the Disboxan 450 coated samples, the surface remained
35
36 295 hydrophobic with $\theta > 90^\circ$.

37
38
39 296

40
41 297 **Fig. 6** Water droplet images captured immediately after droplet deposition on blue paint replicas (A), on paint replica
42 298 coated with fresh Disboxan 450 (B) and on blue paint replicas coated with Disboxan 450 after two years of natural
43 299 outdoor ageing (C).

44 300

45 301 **Conclusions**

46

47
48 302 This work provides the physical chemical characterization of two commercial
49
50
51 303 polysiloxanes, Hydrophase and Disboxan 450, commonly used as water repellent coatings for
52
53 304 wall paints and artistic wall murals and highlights some differences in the behaviour of the
54
55 305 two coatings which can be useful to the restorers in the choice of the best solution.

56
57
58 306 Hydrophase coating is less stable in air than Disboxan and its thermal degradation
59
60 307 occurs with a simple mechanism, due to the homolytic scission of the Si-CH₃ bond followed

308 by H abstraction. Differently, the Disboxan decomposes through heterolytic cleavage and
309 rearrangement of the Si-O-Si bond in the main chain. This different behavior may be
310 attributed to the monomeric nature of Hydrophase while Disboxan is an oligomeric
311 polysiloxane. On the other hand, Hydrophase interacts with the underlying acrylic paint
312 more strongly than Disboxan. In fact, the FTIR spectra clearly show a decrease in the
313 intensity of the OH stretching absorbance (3300 cm^{-1}) in the acrylic paint replicas when they
314 are coated with Hydrophase or Disboxan 450, more marked in the case of Hydrophase This
315 decrease confirms the interaction between the coating siloxanes and the acrylic colour that
316 leads to the formation of a Si-O bond and the consequent reduction of the free OH content.
317 However, Disboxan 450 does not induce any modifications in the thermal stability of the
318 acrylic support while the interaction of Hydrophase, causes an increase in the resin's thermal
319 stability with the shifts of the decomposition temperatures to higher values. Moreover, upon
320 two years of natural aging, FTIR analyses reveals that Hydrophase coating is less stable over
321 time compared to the oligomeric Diboxan coating. Contact angle measurements show that the
322 coating with Disboxan 450 increases the hydrophobicity of the paint surface, while
323 Hydrophase promotes only small changes in the wettability of the surface which maintains its
324 hydrophilicity. Both replicas of naturally aged coated paint showed only a small decrease in
325 the value of the contact angle, indicating good resistance to the action of pollutants, light and
326 rain.

327 **Acknowledgements**

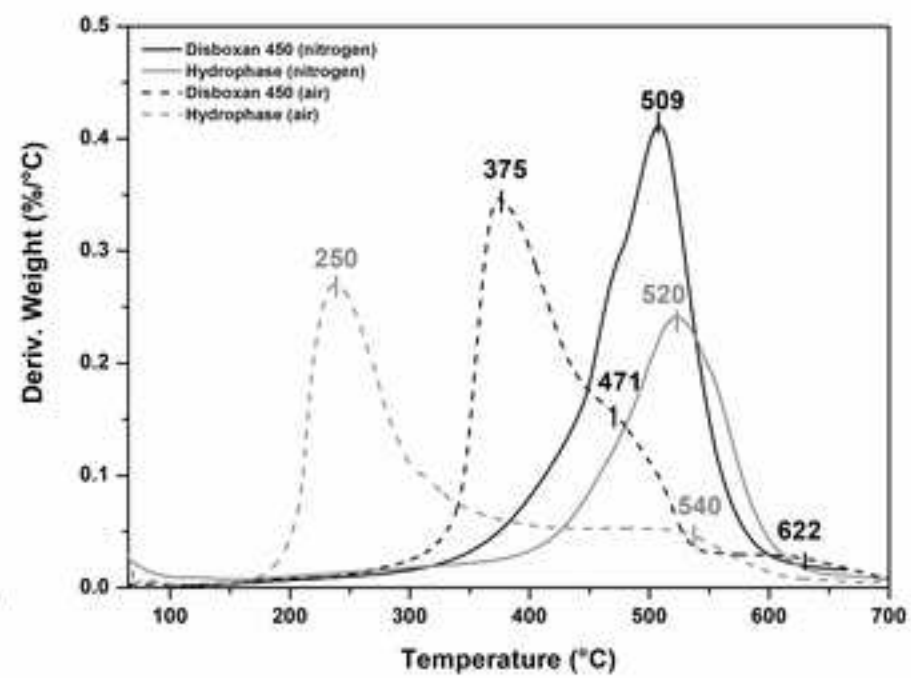
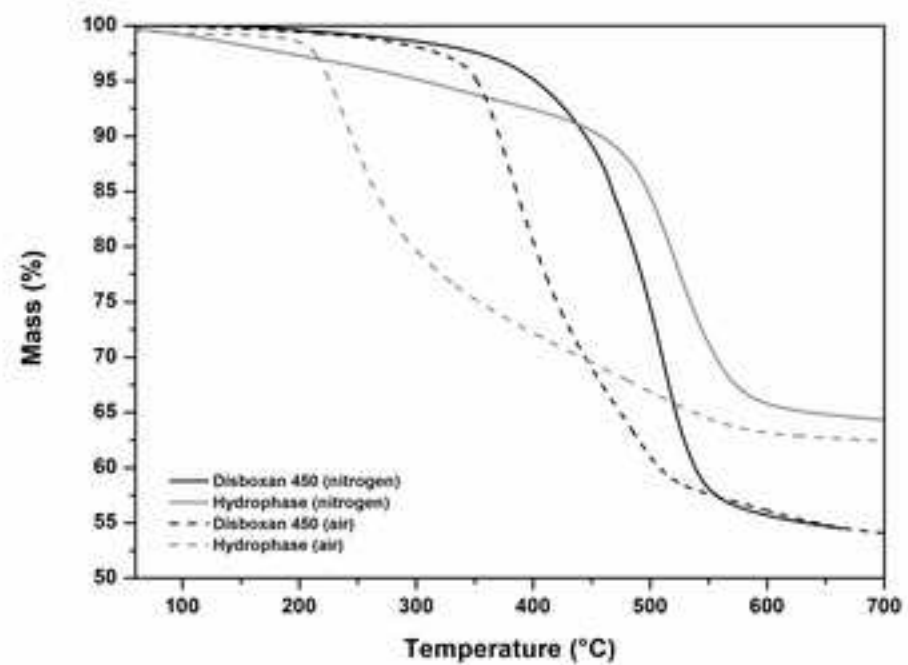
328 This work was supported by PRA_2017_17 funded by University of Pisa

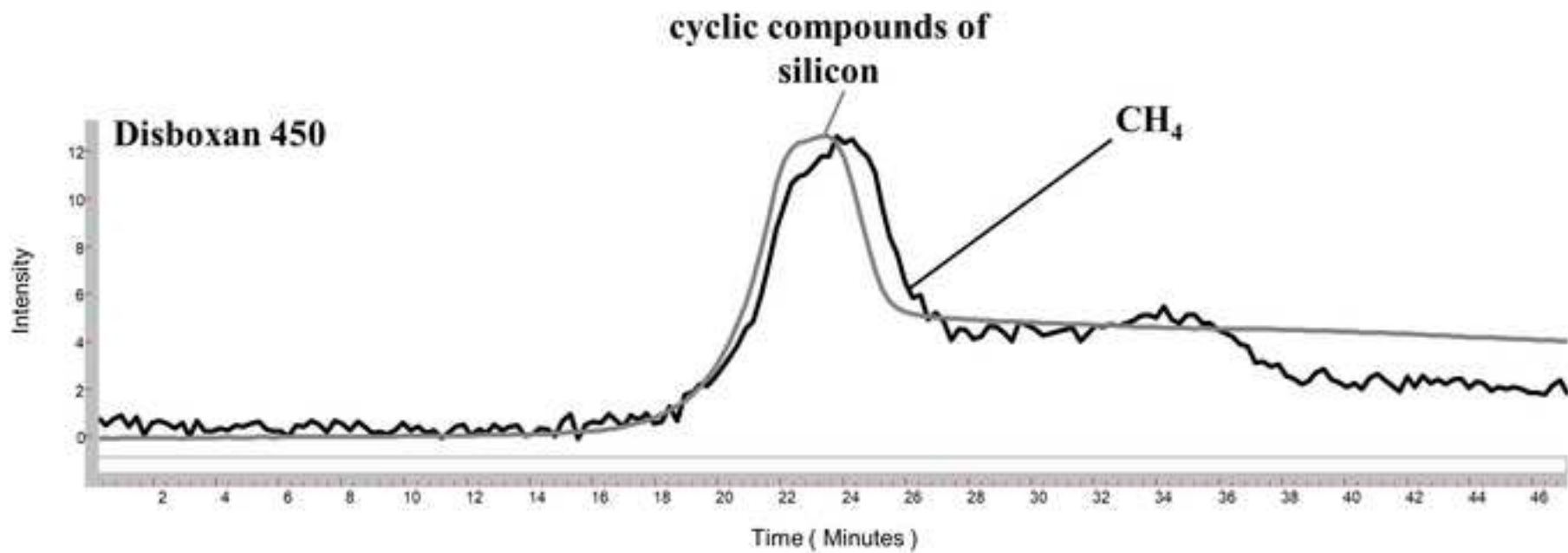
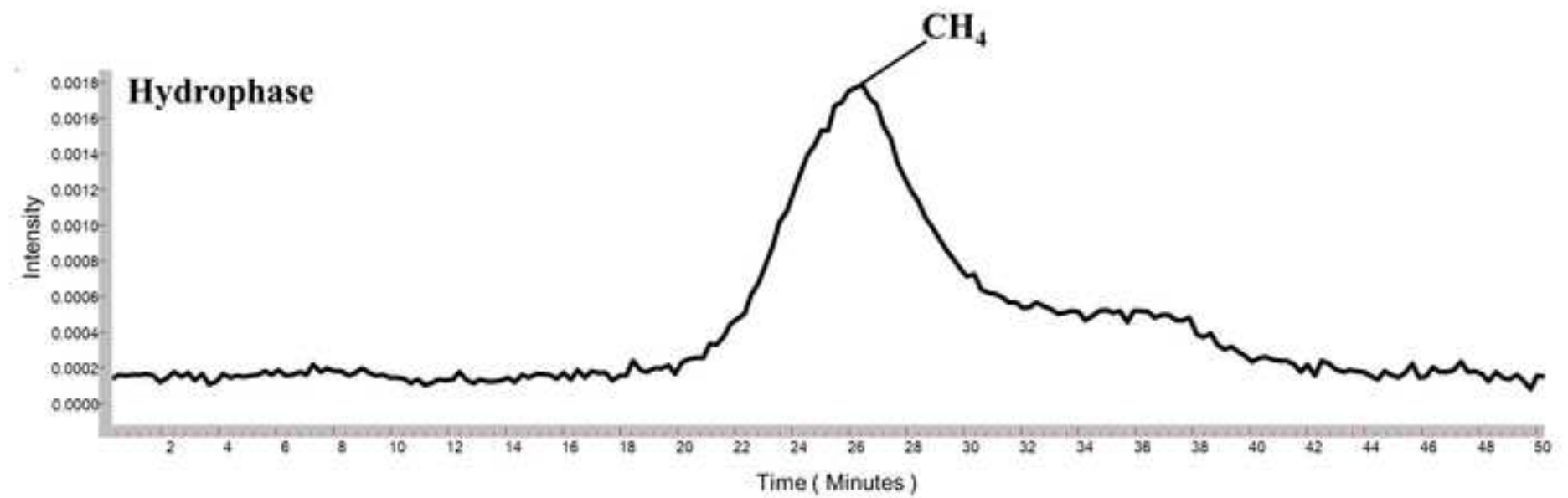
329 **References**

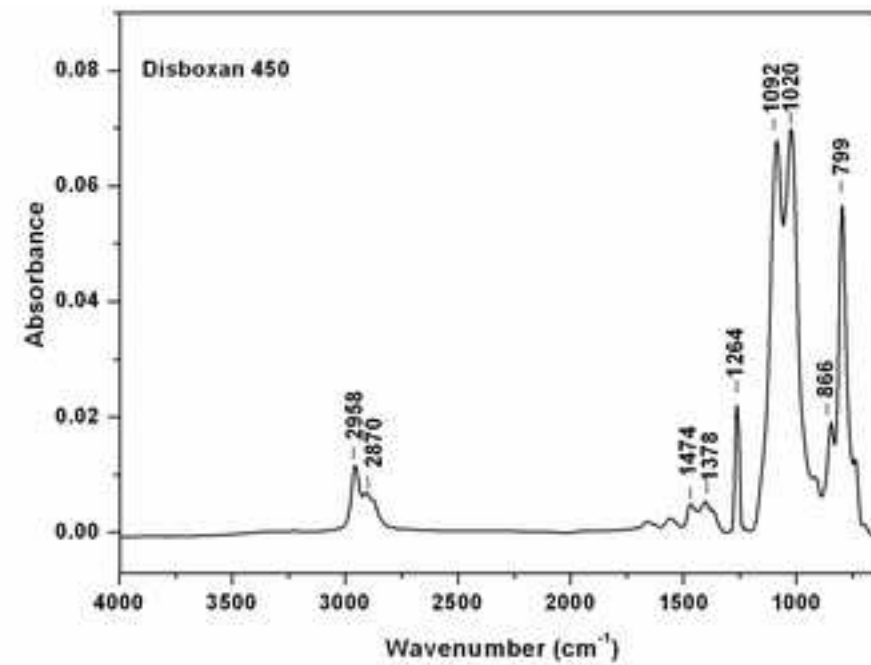
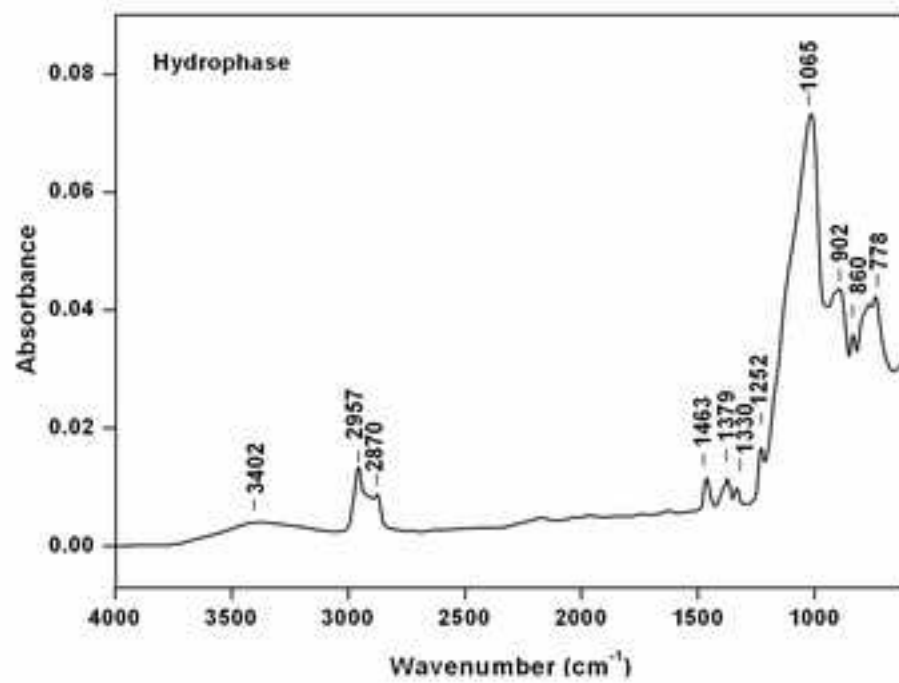
- 330 1. Witucki GL. A silane primer: chemistry and applications of alkoxy silanes. *Journal of*
331 *coatings technology.* 1993;65:57-.
- 332 2. Tsakalof A, Manoudis P, Karapanagiotis I, Chryssoulakis I, Panayiotou C. Assessment of
333 synthetic polymeric coatings for the protection and preservation of stone monuments. *J Cult*
334 *Herit.* 2007;8(1):69-72.

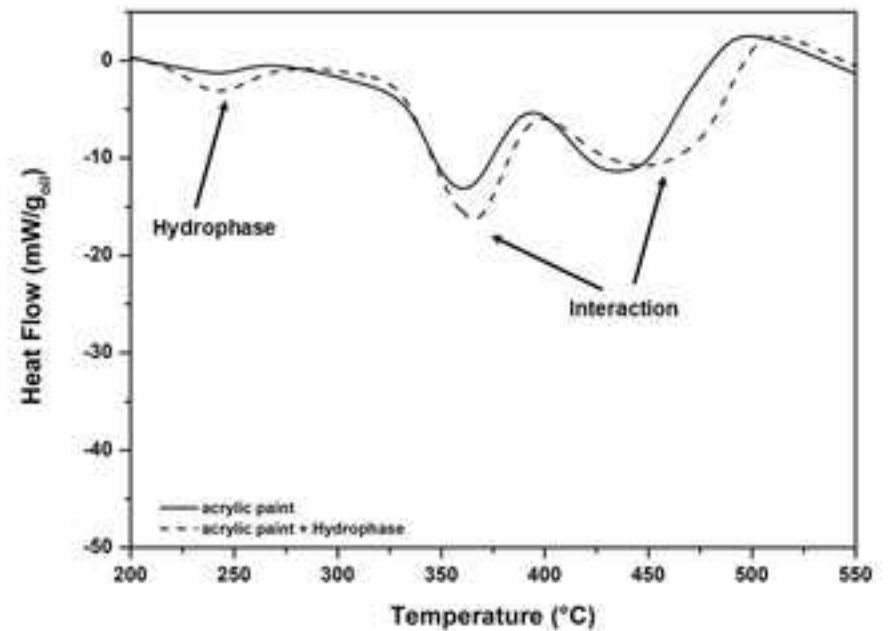
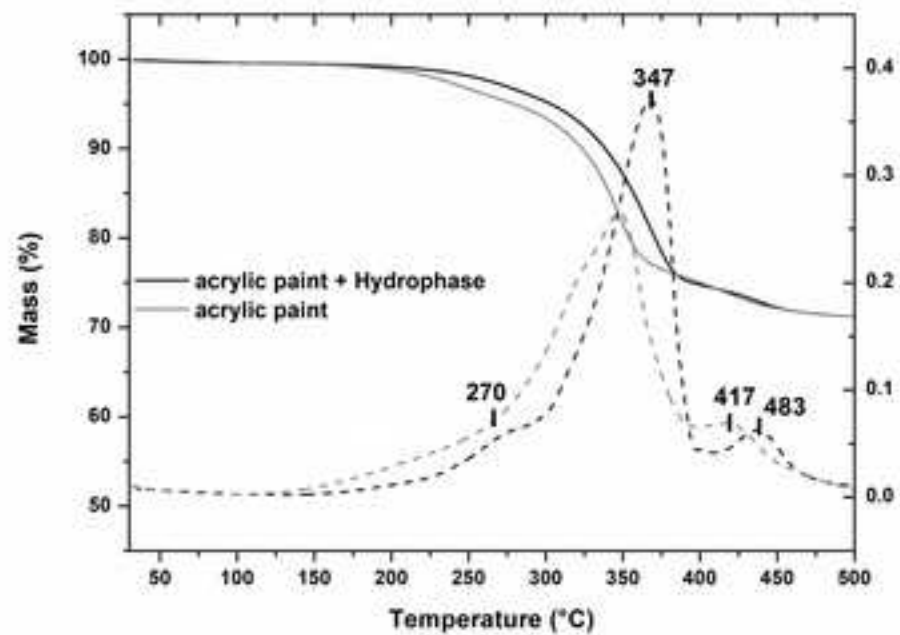
- 336 3. Eduok U, Faye O, Szpunar J. Recent developments and applications of protective silicone
1 337 coatings: A review of PDMS functional materials. *Prog. Org. Coat.* 2017;111:124-63.
2 338 doi:<https://doi.org/10.1016/j.porgcoat.2017.05.012>.
- 3 339 4. Kahraman MV, Kuğu M, Menceloğlu Y, Kayaman-Apohan N, Güngör A. The novel use of
4 340 organo alkoxy silane for the synthesis of organic–inorganic hybrid coatings. *J. Non-Cryst.*
5 341 *Solids.* 2006;352(21-22):2143-51.
- 6 342 5. Li D, Xu F, Liu Z, Zhu J, Zhang Q, Shao L. The effect of adding PDMS-OH and silica
7 343 nanoparticles on sol–gel properties and effectiveness in stone protection. *Appl. Surf. Sci.*
8 344 2013;266:368-74.
- 9 345 6. Fermo P, Cappelletti G, Cozzi N, Padeletti G, Kaciulis S, Brucale M et al. Hydrophobizing
10 346 coatings for cultural heritage. A detailed study of resin/stone surface interaction. *Appl. Phys.*
11 347 *A.* 2014;116(1):341-8.
- 12 348 7. Brachaczek W. Comparative analysis of organosilicon polymers of varied chemical
13 349 composition in respect of their application in silicone-coating manufacture. *Prog. Org. Coat.*
14 350 2014;77(3):609-15.
- 15 351 8. Thomas TH, Kendrick T. Thermal analysis of polydimethylsiloxanes. I. Thermal
16 352 degradation in controlled atmospheres. *Journal of Polymer Science Part A- 2: Polymer*
17 353 *Physics.* 1969;7(3):537-49.
- 18 354 9. Jovanovic JD, Govedarica MN, Dvornic PR, Popovic IG. The thermogravimetric analysis
19 355 of some polysiloxanes. *Polym. Degrad. Stab.* 1998;61(1):87-93.
- 20 356 10. Deshpande G, Rezac ME. The effect of phenyl content on the degradation of poly
21 357 (dimethyl diphenyl) siloxane copolymers. *Polym. Degrad. Stab.* 2001;74(2):363-70.
- 22 358 11. Tomer NS, Delor-Jestin F, Frezet L, Lacoste J. Oxidation, chain scission and cross-linking
23 359 studies of polysiloxanes upon ageings. *Open Journal of Organic Polymer Materials.*
24 360 2012;2(02):13.
- 25 361 12. Camino G, Lomakin S, Lazzari M. Polydimethylsiloxane thermal degradation Part 1.
26 362 Kinetic aspects. *Polymer.* 2001;42(6):2395-402.
- 27 363 13. Camino G, Lomakin S, Lagueard M. Thermal polydimethylsiloxane degradation. Part 2.
28 364 The degradation mechanisms. *Polymer.* 2002;43(7):2011-5.
- 29 365 14. Stewart A, Schlosser B, Douglas EP. Surface modification of cured cement pastes by
30 366 silane coupling agents. *ACS applied materials & interfaces.* 2013;5(4):1218-25.
- 31 367 15. Urzì C, De Leo F. Evaluation of the efficiency of water-repellent and biocide compounds
32 368 against microbial colonization of mortars. *Int. Biodeterior. Biodegrad.* 2007;60(1):25-34.
33 369 doi:<https://doi.org/10.1016/j.ibiod.2006.11.003>.
- 34 370 16. Crisci GM, La Russa MF, Macchione M, Malagodi M, Palermo AM, Ruffolo SA. Study
35 371 of archaeological underwater finds: deterioration and conservation. *Appl. Phys. A.*
36 372 2010;100(3):855-63. doi:10.1007/s00339-010-5661-9.
- 37 373 17. La Nasa J, Orsini S, Degano I, Rava A, Modugno F, Colombini MP. A chemical study of
38 374 organic materials in three murals by Keith Haring: A comparison of painting techniques.
39 375 *Microchem. J.* 2016;124:940-8. doi:<https://doi.org/10.1016/j.microc.2015.06.003>.
- 40 376 18. Stalder AF, Melchior T, Müller M, Sage D, Blu T, Unser M. Low-bond axisymmetric
41 377 drop shape analysis for surface tension and contact angle measurements of sessile drops.
42 378 *Colloids Surf. Physicochem. Eng. Aspects.* 2010;364(1):72-81.
43 379 doi:<https://doi.org/10.1016/j.colsurfa.2010.04.040>.
- 44 380 19. Sun JT, Huang YD, Cao HL, Gong GF. Effects of ambient-temperature curing agents on
45 381 the thermal stability of poly(methylphenylsiloxane). *Polym. Degrad. Stab.* 2004;85(1):725-31.
46 382 doi:<https://doi.org/10.1016/j.polymdegradstab.2004.03.018>.
- 47 383 20. González-Rivera J, Iglío R, Barillaro G, Duce C, Tinè M. Structural and Thermoanalytical
48 384 Characterization of 3D Porous PDMS Foam Materials: The Effect of Impurities Derived from
49 385 a Sugar Templating Process. *Polymers.* 2018;10(6):616.

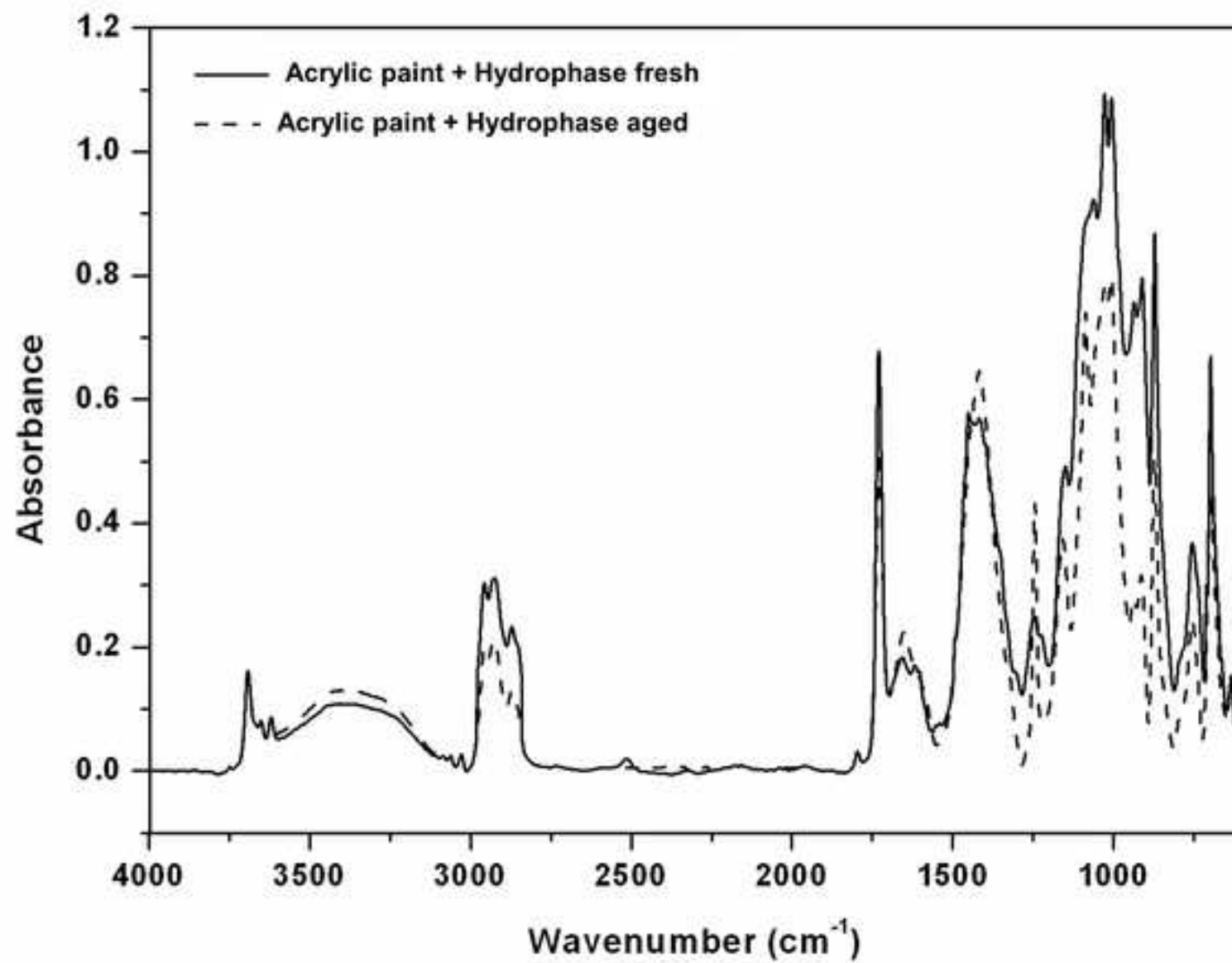
- 386 21. Colombini M, Modugno F, Di Girolamo F, La Nasa J, Duce C, Ghezzi L et al. Keith
1 387 Haring and the city of the Leaning Tower: preservation of the mural " Tuttomondo". 2015.
2 388 22. Hofman R, Westheim JGF, Pouwel I, Fransen T, Gellings PJ. FTIR and XPS Studies on
3 389 Corrosion-resistant SiO₂ Coatings as a Function of the Humidity during Deposition. Surf.
4 390 Interface Anal. 1996;24(1):1-6. doi:doi:10.1002/(SICI)1096-9918(199601)24:1<1::AID-
5 391 SIA73>3.0.CO;2-I.
6 392 23. de la Fuente JL, Fernández-García M, López Madruga E. Characterization and thermal
7 393 properties of poly(n-butyl acrylate-g-styrene) graft copolymers. J. Appl. Polym. Sci.
8 394 2001;80(5):783-9. doi:doi:10.1002/1097-4628(20010502)80:5<783::AID-
9 395 APP1155>3.0.CO;2-5.
10 396 24. Wang ZY, Liu FC, Han EH, Ke W. Ageing resistance and corrosion resistance of silicone-
11 397 epoxy and polyurethane topcoats used in sea splash zone. Mater. Corros. 2013;64(5):446-53.
12 398 doi:doi:10.1002/maco.201106269.
13 399
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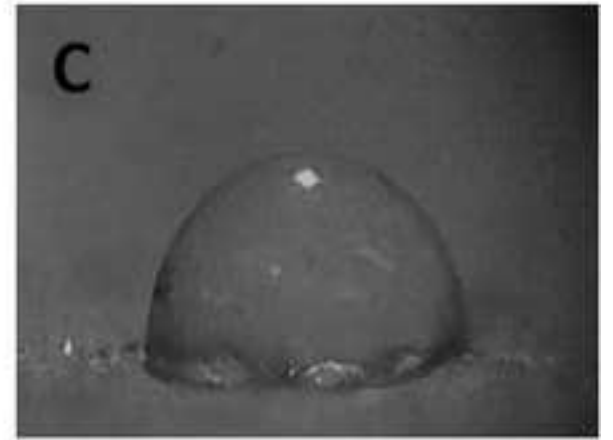
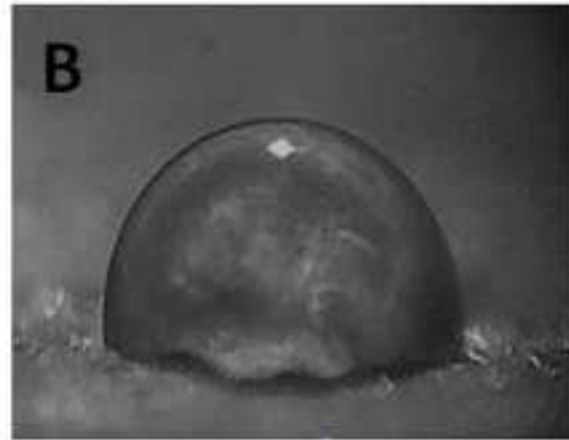
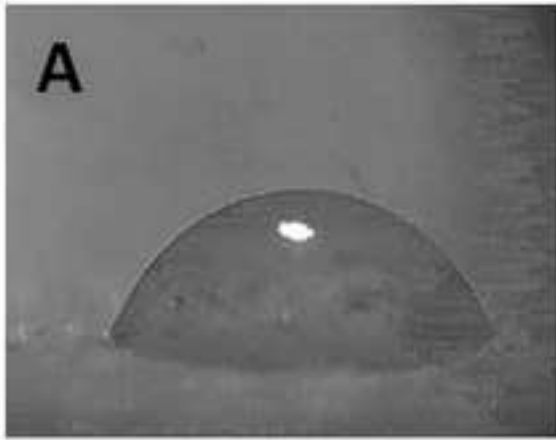














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