SURFACE DISPERSIVE ENERGY DETERMINED WITH IGC-ID IN ANTI- GRAFFITI-COATED BUILDING MATERIALS

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Abstract

Coating building materials with anti-graffiti treatments hinders or prevents spray paint adherence by generating low energy surfaces. This paper describes the effect of coating cement paste, lime mortar, granite, limestone and brick with two anti-graffiti agents (a water-base fluoroalkylsiloxane, “Protectosil Antigraffiti®”, and a Zr ormosil) on the dispersive component of the surface energy of these five construction materials. The agents were rediluted in their respective solvents at concentrations of 5 and 75 % and the values were determined with inverse gas chromatography at infinite dilution (IGC-ID).

The dispersive energy of the five materials prior to coating, ranked from highest to lowest, was as follows: limestone > granite > cement paste > brick > lime mortar. After application of the two anti-graffiti compounds, CF₃ terminals (Protectosil) were found to reduce the surface energy of both basic (limestone and lime mortar) and acidic (granite) substrates more effectively than CH₃ (ormosil) terminals.

Keywords: Inverse gas chromatography; Construction materials; Surface energy; Anti-graffiti coatings; Ormosil; Contact angle

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1. Introduction

Water is one of the main, not to say the main decay-inducing agent in building materials [1], occasioning deterioration via freeze-thaw cycles [2,3], acid attack [4], salt crystallization [5], concrete steel corrosion [6], micro-organisms and so on.

Construction materials have been routinely treated with protective, consolidating, water-repellent and similar agents to conserve historic buildings and civil engineering infrastructure since the mid nineteen sixties [7]. Ideally, today's products are multifunctional, with the versatility required to adapt to different needs depending on the stimulus. The compounds known as anti-graffiti agents, for instance, generate low surface energy conditions to facilitate the removal of spray paint from building materials while at the same time waterproofing their surfaces. As a rule, graffiti applied to these protective barriers can be removed with low pressure water and a detergent or solvents [8].

The protective effectiveness of these products is analyzed with the system conventionally used to evaluate other surface treatments. This involves determining the new physical properties (hydric, surface appearance and so on) of the substrates [9,10] as well as treatment durability [11], and analyzing the cleanliness of the protected surfaces after graffiti is removed with a variety of procedures [12].

Very few studies have been published on the surface characteristics of materials coated with protective treatments, however. In particular, scant attention has been paid to surface energy, which is usually evaluated indirectly by determining the static or dynamic contact angle. The value of this angle, 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), represents the minimum free energy in the system.

Surface energy and surface roughness have been reported as crucial factors affecting anti-adhesion properties of coating materials [13]. The low surface energy of anti-graffiti protective treatments hinders the adherence of likewise low surface tension spray paint.

Inverse gas chromatography (IGC) is a technique used to characterize the surface energy of powdery materials whose surfaces (characterized by the presence of different adsorption sites) can be examined in terms of dispersive energy (the highest energy sites) and acid/base properties. This technique quantifies interactions with apolar, amphoteric and basic probe molecules ($\gamma_s = \gamma_s^d + \gamma_s^{sp}$; γ_s = surface energy, γ_s^d = dispersive component (non-specific or London-type force), γ_s^{sp} = specific component (Lewis acid-base)) [14]. When adsorption takes place at infinite dilution (ID), the adsorbed molecules do not interact. Consequently, interactions are to be found on the surface of the solid only.

The chief limitation to this method is its sensitivity to the presence of high energy adsorption sites that renders the analysis of uneven surfaces more difficult. Coating these materials progressively is one way of side-stepping this drawback, for polymer adsorption on the highest energy sites would facilitate the access of the gas to the lower energy sites [15]. This may prove to be a novel and highly useful technique for evaluating the protective effectiveness of anti-graffiti surface treatments on different substrates.

The aim of the present study was, then, to compare the performance of two anti-graffiti treatments and the effect of concentration on the reduction of the high surface energy (dispersive or London force) component in five building materials (cement paste, lime mortar, limestone, granite and brick), whose surface wetting properties were also investigated by measuring their dynamic contact angle.

2. Experimental

2.1. Materials

Cement paste and cement mortar specimens measuring 70x60x10 mm were prepared with CEM I 42.5 N cement, a water/cement ratio of 1/2, the latter with a sand/cement ratio of 3/1, and cured for 28 days at 21 °C and 95 % relative humidity as specified in European standard UNE-EN 196-1 [16]. The commercial lime mortar, containing limestone aggregate, portlandite and a certain amount of cement (Calhidro, Spain), was

mixed with the necessary amount of water to attain normal consistency [17] (binder+aggregate/water ratio = 4.6/1) and moulded into 70×60×10 mm specimens.

“Gris Quintana” variety granite (from the Spanish province of Badajoz), with a bush-hammered surface, and “Blanco Paloma” limestone (from Seville) were used. (The original size of these samples was 4x4x16 and 10x10x3 cm). Both these stones are characterized petrographically in Carmona-Quiroga et al. [9]. The fair face brick used, supplied by Hermanos Díaz Redondo (Toledo), had a factory standard water-repellent coating consisting of potassium methyl siliconate, applied to combat salt efflorescence during construction, primarily induced by mortar.

The five substrates (cement paste instead cement mortar to simplify the system interactions) were ground to a particle size of 250 to 425 µm in order to be analyzed by IGC-ID. The particles were coated with the two anti-graffiti treatments selected, a water-base fluoroalkylsiloxane (“Protectosil Antigraffiti” marketed by Degussa) and an organically modified silicate (ormosil) synthesized from a polymer chain (polydimethyl siloxane, PDMS) and two network-forming alkoxides (Zr propoxide and methyl triethoxy silane, MTES) dissolved in n-propanol [18].

The two anti-graffiti agents had to be rediluted to ensure a longer gas circulation time through the chromatographic columns at different analytical temperatures. The 250-425-µm substrate particles were submerged in the diluted agents (1g in 25 cm³, 5 or 75 % (vol.) of Protectosil dissolved in water; 1 g in 10 cm³, 5 or 75 % of ormosil dissolved in n-propanol) and stirred for 6 hours. The samples were subsequently filtered (using 20 to 25-µm pore filter paper) and dried in a stove for 16 hours at 40 °C.

Prismatic specimens of the five construction materials, on which the dynamic contact angle was measured, were cut to an approximately size of 2x1.5x0.3 and 2.5x2x0.3 cm, and immersed for 1 minute into the anti-graffiti coatings.

2.2. Methods

The dispersive component of surface energy (London constant) was determined for the powdery substrates (250 to 425-µm fraction) before and after immersion in different

concentrations of the anti-graffiti treatments using inverse gas chromatography at infinite dilution (IGC-ID) on a Perkin-Elmer Sigma 2 instrument fitted with a flame ionization detector.

The particles were placed inside 3-mm diameter Teflon chromatographic columns and degasified for 18 hours at 60 °C to prevent coating degradation.

Dispersive energy was determined by injecting n-alkanes (from n-hexane to n-dodecane) into the samples at 40, 50 and 60 °C with a 0.1-μl syringe at a rate of 20 ml/min. At least five trials were run per apolar probe molecule and all the results were used to calculate the surface energy.

Dynamic contact angles (advancing and receding) were determined with a DCA-315 CAHN analyzer, before and after the substrates were coated with the anti-graffiti. The mean value of three measurements for each sample was taken as the result. The dynamic contact angle hysteresis was also calculated to estimate surface roughness.

3. Results and discussion

3.1. Untreated building materials

The standard free energy generated when one mol of a gaseous probe molecule is adsorbed is related to the net retention volume as follows:

$$\Delta G_A^0 = -RTL \ln(Vr) + C \quad [1]$$

Fig. 1 shows the retention volumes for n-alkanes, molecules capable only of London-type interactions (they have no specific character; $\gamma_s^{sp} = 0$, i.e., they are apolar) on the surface of the five building materials studied, at 40, 50 and 60 °C. The result is a straight line (one for each temperature) whose slope is related to the dispersive energy of the material as indicated in the following equation:

$$\Delta G_{CH_2} / (N_A \cdot a_{CH_2}) = 2(\gamma_{CH_2} \cdot \gamma_s^d)^{1/2} \quad [2]$$

Where ΔG_{CH_2} is the slope of the line (i.e., the increase in adsorption free energy per CH_2 group in the n-alkane) (Table 1), N_A is Avogadro's number, a_{CH_2} is the area of each CH_2 group, γ_{CH_2} is the surface tension of a molecule with an infinite number of CH_2 groups (polyethylene for instance) and γ_s^d is the dispersive component of surface energy.

The regression coefficients for the lines were over 0.99 in all cases except granite at 60 °C, where $R^2=0.97$. The slopes declined with rising temperature (Table 1) and were less pronounced in lime mortar than in the other materials.

The dispersive or London component of surface energy, γ_s^d , at 40, 50 and 60 °C is given in Table 1 for all the building materials studied. Sample dispersive energy consistently declined with rising temperature, an indication that the n-alkanes and the material surfaces interacted physically (adsorption).

The findings for cement paste (Table 1) were similar to the results reported by Oliva et al. [19] (54-67 mJ/m^2 at 35 to 80 °C with a flow rate of 40 ml/min). These authors also obtained much higher energy, 81.8 mJ/m^2 at 60 °C (column conditioned for 15 hours) when a lower flow rate (25 ml/min) was used. Baeta Neves et al. [20] observed a slightly lower value, 42.2 mJ/m^2 , for pastes prepared with the same w/c ratio as used in this study. These differences in the γ_s^d values may be related to the differences in water content in the samples. Since the presence of water minimizes interactions, an increase in temperature would induce surface desorption and a concomitant rise in paste dispersive energy until degeneration of its hydrated structure leads to a decline in energy levels [21].

Of the materials studied, lime mortar exhibited the lowest dispersive surface energy, 41.49 mJ/m^2 at 40 °C (Table 1). Although the literature contains no reference to this type of materials, the values obtained were similar to the findings for cement pastes (40-45 mJ/m^2 at 35 °C) [20-22].

Limestone, by contrast, had the highest London component values at 40 and 50 °C (84.98 and 70.98 mJ/m^2 respectively, Table 1), which are characteristic of fairly high energy surfaces, such as MgO (95.6 mJ/m^2 at 25 °C) [23] or silica (98.2 mJ/m^2 at 20 °C)

[24]. The high energy surface of calcium carbonate particles is due to the ionic and electronegative oxygen atom charges on the carbonate ion [25].

Evidence of the importance of the flow rate and the conditions for preparing chromatographic columns [19,26] can be found in the wide range of dispersive surface energy values for limestone reported in the literature: 57 mJ/m² (column at 110 °C, conditioned for 12 to 16 hours at 140 °C) [25], 44.4 mJ/m² (70 °C, flow rate 20 ml/min) [27], 55 mJ/m² (at 100 °C after conditioning the sample at 50 °C) [26]. Keller et al. [26] observed much higher values, 255 mJ/m², when the conditioning temperature was much higher (200 °C), due to water desorption in the highest energy sites on the surface. Perruchot et al. [21] reported similar results (236 mJ/m² at 35 °C). As these authors themselves pointed out, however, values depend on the nature, origin and composition of the surface in question, as well as on whether the interaction takes place in higher (crystal vertices) or lower (crystal planes) energy sites.

After limestone, granite was the material with the highest dispersive component of the surface energy. The 44.13 mJ/m² (60°C) exhibited by the stone studied here was in between the value reported for another variety, 29.38 mJ/m² (60 °C) [28], and for a quartz sand, 55.5 mJ/m² (60 °C) [29]. The values obtained at any temperature were much lower than found for silica at ambient temperature, 78-100 mJ/m² [24,30,31], or inorganic materials such as mica (100 mJ/m² [32]) or schist (140 and 96.8 mN/m² at 100 and 130°C, respectively) [33], whose laminar structure (porosity) determines their high surface energy.

Contrary to what was observed for the other building materials, the dispersive energy of brick, 49.30 mJ/m² at 40 °C, barely declined with rising temperature. According to Comard et al. [15], this occurs when coatings, in this case a water repellent (potassium methyl silicate), form a thick multi-layer film.

The correlation of the results obtained with IGC and the receding contact angles, of the two dynamic contact angle the one that gives a truer indication of the actual water repellence of the analyzed surfaces [34], is not straightforward, and not only because IGC usually yields higher values for the dispersive surface energy [35] but also because in all of the construction materials selected, except for granite (the less porous of the

selected materials [36]), the value of the receding contact angle could not be measured due to a significant water absorption of the prismatic specimens (Table 2). (The values of the advancing and receding contact angle depend on the roughness of the surface of the construction materials and they can be therefore significantly modified, however, the measurement of the absorption of water by capillarity, that verifies the degree of protection of a surface, directly correlates with the receding contact angle, while a meaningful correlation is not present between absorption and static or advancing contact angle [34]).

3.2. Treated materials

The following discussion addresses the results of determining the dispersive component of surface energy in the five building materials after immersion in different dilutions of the two anti-graffiti agents.

Increasing the concentration of the agents (from 5 to 75 %) induced a greater decline in the dispersive component of the substrates (Fig. 2), evincing the gradual occupation of the active sites on their surfaces. The opposite was observed in the lime mortar only (38.38 mJ/m² with 5 % and 41.36 mJ/m² with 75 %, at 40 °C) (Fig. 2-b). This undesirable rise in surface energy was also reported by Calhoun et al. [25] in propyltriethoxysilane-coated calcium carbonate particles, as a result of the outward orientation of the highest energy functions (formation of an inverted two-layer film). Shui [37] also obtained this type of results when coating calcium carbonate with different concentrations of polyacrylic acid. At low concentrations (1-3 %), the energy level declined, while at 4 % the surface energy rose with temperature. The author attributed these findings to a change in the chain alignment of the molecules on the particle surface when more than the coating consisted of more than one layer (the hydrophilic groups would be oriented toward the surface instead of bonding to active sites on the surface of the calcium carbonate).

In all cases, rising temperatures induced normal behaviour, i.e., surface deactivation (Fig. 2).

In cement paste, the low concentration (5 %) treatments failed to coat the active sites on the surface (Fig. 2-a). The dispersive energy of the treated materials was even higher than in the untreated samples (53.61 and 59.87 mJ/m² in the material respectively coated with 5 % Protectosil and ormosil, compared to 52.87 mJ/m² in the uncoated paste at 40 °C), due to the different water content in the samples (the more active the surface, the lower the water content). Ormosil induced a slightly greater decline in cement paste surface energy than Protectosil when the 75 % products were used. This decline was nonetheless minimal compared to the values found for the other building materials when coated with the high concentration agents.

Of the two anti-graffiti treatments, the fluorinated product (Protectosil) reduced lime mortar and limestone surface energy more effectively (Fig. 2-b,c). In fact, 5 % Protectosil yielded better results than 75 % ormosil. Note that with this treatment the stone, which when untreated exhibited the highest value for the London component of surface free energy, was the least energetic of all the materials studied (Table 1). Extrapolating the findings to 25 °C, only 5 and 75 % Protectosil-coated limestone (23.89 y 20.64 mJ/m², respectively) had values close to the results for Teflon (18 mJ/m²). This is an indication that Protectosil-coated limestone would interact very weakly with any spray paint, indelible felt pens (graffiti) or other type of adsorbed compound.

Of the materials selected for this study, calcium carbonate and cement particles are the ones most frequently analyzed with IGC-ID. The changes in CaCO₃ surface characteristics have been explored by a number of authors (treatment with stearic acid [27], silica coating [30], acrylic coating [38] and so on). Very few studies have been conducted on the effect of functionalized silane surface coatings (of the kind used in anti-graffiti agents) [25], however, while references to anti-graffiti treatments strictly speaking are completely lacking in the literature.

In granite, the more diluted version of Protectosil barely coated the particles, judging by the minimal decline in energy recorded for the stone (Fig. 2-d). When more agent was applied it reduced the dispersive component more effectively than ormosil, although both treatments reduced the surface energy in granite (with limestone, one of the most energetic substrates) to one of the lowest values recorded in this study. This finding

confirmed the greater non-polarity of the fluorinated alkyl groups in Protectosil than the non-fluorinated compounds in ormosil on all manner of surfaces, whether basic (limestone and lime mortar) or acid (granite).

In terms of probe molecule adsorption, the two treatments performed very similarly on the surface of the water-repellent brick, although ormosil reduced the dispersive component slightly more effectively (Fig. 2-e). Of the surfaces studied, brick coated with 75 % ormosil was nonetheless the one that interacted most weakly with n-alkanes.

According to the receding contact angle findings, Protectosil exhibited greater (short-term) water repellence than ormosil in cement mortar, limestone and brick (Table 2). This better overall performance of Protectosil is in agreement with IGC results that showed this fluorinated treatment reduced surface energy more effectively than ormosil. In the less porous material, granite, and in the more porous one, lime mortar, ormosil increased deeper the value of the receding contact angle, but for different reasons. On the granite, the knowing lower surface tension of the CF_3 terminals of Protectosil compared to CH_3 terminals of ormosil [39] could hinder its adsorption on its small porous system. This would explain why granite coated with the fluorinated anti-graffiti showed the low value of the receding contact angle in spite of being the only substrate in which the receding contact angle could be measured when uncoated. Lime mortar results in this regard could be related with the amount (and distribution) of anti-graffiti absorbed, very significative in this material as previously reported by chromatographic determinations. In fact, in spite of being the most porous material, lime mortar exhibited the higher values of receding contact angle when the substrate was coated with the two anti-graffiti.

The cleaning efficiency of the two anti-graffiti on the five construction materials was carried out in previous studies in the laboratory [9,36] where the anti-graffiti protected substrates were painted with red, green and black synthetic enamel spray paint and subsequently cleaned (cyclohexanone, brush and water for rinsing). These definitive results on porous and rough prismatic specimens in terms of anti-graffiti effectiveness at the time of graffiti elimination were correlated with the results of surface energy obtained in powdered substrates in the present study, founding a good agreement between both of them. In fact, further to the post-cleaning chromatic parameters

(CIELab) found, the surfaces coated with Protectosil cleaned more thoroughly than the ormosil-treated materials [36]. Nonetheless, IGC determinations only allowed to predict which anti-graffiti was better graffiti repellent on a given surface but not on which surface (treated with the same anti-graffiti) the cleaning was more satisfactory, because the parameter that ultimately governed spray paint adherence was superficial roughness [36]. For instance, the material with the less rough surface ($R_a = 1.2 \mu\text{m}$), brick, was the only one that did not exhibited visible traces of paint after cleaning (post-cleaning chromatics values of untreated brick reduced the importance of the prior in-plant waterproofing on cleaning efficiency) while on the extreme roughness surface of granite ($R_a = 9.5 \mu\text{m}$), cleaning was ineffective from the first cycle regardless of the treatment, but particularly in the ormosil-coated specimen [36].

The dynamic contact angle hysteresis traditionally allows the estimation of the surfaces roughness and therefore the evaluation of the cleaning properties of surfaces [40]. According to Brugnara et al. [34], in protected materials, the variations of hysteresis are related to variations of roughness only if the surfaces have been covered in an efficient way by the polymer, if not, hysteresis is caused by the heterogeneity produced on the construction materials by applying the protective (not homogeneous surface of polymer). Moreover the anti-graffiti have an intrinsic hereogeneity, related to the complexity of their lateral chains (increasing their complexity, the heterogeneity increases and the hysteresis of the contact angles increases too). Taking into account these considerations, the lower values of hysteresis determined on Protectosil-treated substrates, when compared to the ones obtained in ormosil-treated surfaces (except granite), would coincide with IGC measurements and cleaning tests, in pointing the superior anti-adhesion properties of Protectosil (Table 2). Nonetheless, it is not possible to correlate the results of cleaning efficiency with these results, because the superficial roughness (R_a) of the materials in which chromatic changes were measured was different from R_a of the samples used to determine the contact angle (especially for granite, $R_a = 9.5 \mu\text{m}$ vs. $R_a 1.2 \mu\text{m}$).

4. Conclusions

The dispersive component of surface energy was determined for the first time in building materials coated with anti-graffiti agents. Both products selected, a water-base

fluoroalkylsiloxane (Protectosil Antigraffiti marketed by Degussa) and Zr ormosil, reduced the surface energy of the substrates.

Prior to coating, the surface energies at 40 and 50 °C of the five materials selected could be ranked from highest to lowest as follows: limestone > granite > cement paste > brick > lime mortar.

After coating with Protectosil, the sequence was: cement paste > brick > granite > lime mortar > limestone. And after treatment with 75 % ormosil, it was: cement paste > lime mortar > limestone > granite > brick.

Increasing the concentration of the products used (from 5 to 75 %) induced more effective reduction of substrate surface energy (therefore, the more diluted form of the products failed to coat the entire surface of the materials), providing the coating consisted of no more than one layer. Otherwise, the hydrophilic groups adopted an undesirable outward orientation, raising the surface energy of the substrate (such as in lime mortar coated with 75 % ormosil).

CF₃ terminals (Protectosil) proved to reduce substrate surface energy more effectively than CH₃ terminals (ormosil). This is tantamount to saying that paint molecules are easier to remove from surfaces coated with the fluorinated product, regardless of whether the substrate is acidic (granite) or basic (lime mortar, limestone), as receding contact angle measurements, hysteresis and cleaning test on protected substrates have proved.

The use of such coatings is particularly useful on stone surfaces (limestone and granite), initially the most energetic and the ones in which the dispersive component declined most steeply when treated with an anti-graffiti agent. Nonetheless, in practical situations surface roughness has been reported to be a crucial factor on an effective cleaning.

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Table 1. ΔG_{CH_2} (kJ/mol) and γ_s^d (mJ/m²) values of the building materials studied, at 40, 50 and 60 °C

Sample	ΔG_{CH_2} (kJ/mol)			γ_s^d (mJ/m ²)		
	40°C	50°C	60°C	40°C	50°C	60°C
Cement paste	3.14	3.01	2.86	52.87	48.87	43.96
Lime mortar	2.78	2.73	2.67	41.49	39.93	38.47
Limestone	3.98	3.63	2.85	84.98	70.98	43.70
Granite	3.30	3.05	2.86	58.41	50.13	44.13
Brick	3.03	3.02	3.02	49.30	49.20	48.93

Table 2. Advancing (Θ_a) and receding (Θ_r) contact angle and hysteresis contact angle ($\Theta_h = \Theta_a - \Theta_r$) of the construction materials, uncoated and coated with Protectosil and ormosil

		Θ_a	Θ_r	Θ_h
Cement mortar	Unc.	48 ± 5	n.d.	n.d.
	Pr.	117 ± 6	61.3 ± 0.7	56 ± 7
	Or.	120 ± 7	45 ± 6	75 ± 5
Lime mortar	Unc.	59 ± 5	n.d.	n.d.
	Pr.	123 ± 9	64 ± 4	58 ± 5
	Or.	131 ± 5	71 ± 10	59 ± 5
Limestone	Unc.	$62 \pm 10^*$	n.d.*	n.d.*
	Pr.	$103 \pm 7^*$	$63 \pm 6^*$	$40 \pm 2^*$
	Or.	118 ± 4	48 ± 10	70 ± 14
Granite	Unc.	$32 \pm 5^*$	$21 \pm 8^*$	$11 \pm 8^*$
	Pr.	$123 \pm 7^*$	$53 \pm 8^*$	$70 \pm 10^*$
	Or.	117 ± 2	64 ± 5	53 ± 4
Brick [^]	Unc.	n.d.	n.d.	n.d.
	Pr.	115 ± 3	67 ± 6	48 ± 4
	Or.	122 ± 6	51 ± 4	71 ± 3

n.d.: not determined

* results published elsewhere [9]

[^] specimens cut from the core to avoid unhomogeneity of the faces (e.g. exposed surface or edge)

FIGURE CAPTIONS

Fig.1. N-alkane retention volume at 40, 50 and 60 °C on the surface of a) cement paste, b) lime mortar, c) limestone, d) granite and e) brick particles.

Fig. 2. Dispersive energy, γ_s^d (mJ/m²), of: a) cement paste, b) lime mortar, c) limestone, d) granite and e) brick, untreated and treated with 5 and 75 % Protectosil (P) and ormosil (O) at 40, 50 and 60 °C.

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