Evaluation of dry ice blasting as a sustainable technique for graffiti removal on steel and aluminium substrates coated with acrylic-urethane and acrylic-styrene clear coats

Avaliação do jato de areia com gelo seco como técnica sustentável para a remoção de graffiti em substratos de aço e alumínio revestidos com vernizes de acrílico-uretano e acrílico-estireno

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Abstract

Dry ice blasting is presented as a sustainable alternative to removing unwanted coatings without damaging underlying materials. This study analyses its effectiveness in the removal of aerosols from non-porous surfaces, evaluating the physical, chemical, and micromorphological responses derived from the cryogenic phenomena. Alkyd, polyurethane, acrylic and bitumen aerosols were applied on steel and aluminium substrates coated with acrylic-urethane and acrylic-styrene clear coats. Changes in mechanical properties, such as adhesion and hardness, as well as optical properties like colour and gloss, were evaluated. Additionally, the treated surfaces were analysed using Field Emission Scanning Electron (FESEM) and Fourier Transform Infrared Spectroscopy (FTIR). The results demonstrated that the method preserves the integrity of the coatings; however, traces of aerosol (< 0.5 %) were detected, which affected the surface wettability and gloss in some cases. These findings confirm its potential as a safe alternative for use on non-porous surfaces.

KEYWORDS
Graffiti removal
Dry ice blasting
Non-porous surfaces
Solid CO_2
FTIR
FESEM

Resumo

O jato de gelo seco é apresentado como alternativa sustentável para remover revestimentos indesejados sem danificar os materiais subjacentes. Analisou-se a sua eficácia na remoção de aerossóis em superfícies não porosas, avaliando as respostas físicas, químicas e micromorfológicas derivadas dos fenómenos criogénicos. Foram aplicados aerossóis de: alquídico, poliuretano, acrílico e betume, em substratos de aço e alumínio revestidos por camadas de acrílico-uretano e acrílico-estireno. Avaliaram-se as alterações nas propriedades mecânicas (adesividade e dureza), e nas propriedades óticas (cor e brilho). As superfícies tratadas foram analisadas por microscopia eletrónica de varrimento por emissão de campo (FESEM) e por espectroscopia de infravermelho por transformada de Fourier (FTIR). Os resultados demonstraram que o método preserva a integridade dos revestimentos; contudo, detetaram-se vestígios de aerossol (< 0,5 %), que, em alguns casos, afetaram o humedecimento e o brilho da superfície. Confirmou-se o seu potencial como alternativa segura para a utilização em superfícies não porosas.

PALAVRAS-CHAVE
Remoção de graffiti
Jato de gelo seco
Superfícies não porosas
CO_2 sólido
FTIR
FESEM

Introduction

The impact of graffiti in urban environments represents a global phenomenon that affects a wide variety of materials and surfaces, including street furniture, historic buildings, and cultural resources. This phenomenon poses significant challenges for the conservation of cultural heritage, especially in urban contexts where graffiti can irreversibly damage the affected surfaces. In many cases, these interventions occur on heritage materials, requiring cleaning protocols that ensure the complete removal of paint without compromising the integrity of the underlying substrates. The diversity of substrates and chemical compositions of spray paints significantly increases the complexity of this challenge.

Graffiti vandalism affects thousands of cultural heritage sites worldwide. In Europe alone, approximately 3.5 million protected monuments are affected, placing significant financial burdens on cities [1]. Recent years have seen a rise in research on graffiti removal techniques. The effective preservation of public spaces and historic buildings requires solutions that are simultaneously effective and sustainable.

The materials used by graffiti artists to mark historic monuments and facades vary widely and are often applied in multiple overlapping layers, complicating removal and necessitating the use of sequential methods [1]. Spray paint is the main material used by graffiti artists [2] due to its visual impact, ease of application, and quick drying time. It is composed of pigments that provide colour and opacity, additives that improve specific properties (such as plasticity, fluidity, or thickness), a binder that unifies all the components, and a solvent that ensures the fluidity of the mixture [3]. The hardening of these paints varies according to their chemical composition; some paints harden through the evaporation of the solvent, while others depend on polymerisation, generating cross-linked and insoluble chemical films [4]. Therefore, accurate identification of the type of paint requires advanced analytical techniques, as their compositions are highly variable. For example, Germinario et al. [5] characterised binders, pigments, and additives in 45 spray paints of various brands using a multi-technique approach.

Graffiti removal involves a considerable risk for the treated surfaces. The adhesion of the spray to the substrate affects the efficiency of the treatment. It is crucial to consider factors such as the cohesion of the material, its resistance to treatment, and its porosity or texture. Traditional techniques used for graffiti removal include chemical solvents and abrasive mechanical methods. However, these techniques have important limitations. Chemical solvents can penetrate porous substrates, causing irreversible damage, while mechanical methods, such as sandblasting, can erode the outer layers of treated surfaces [6-7]. Additionally, the multi-layered structure of spray paints makes their removal even more difficult due to the complex interaction between their binders, pigments, and additives [8].

Dry ice blasting has emerged as an innovative and sustainable alternative for graffiti removal [9]. This method combines kinetic action, thermal energy, and sublimation, allowing mechanical cleaning without the risk of abrasion or the generation of secondary waste [10-12]. The process consists of the microprojection of dry ice particles, combined with compressed air, reaching initial temperatures of −79 °C for dry ice and −18 °C for carbonic snow. The projected particles generate a thermomechanical effect that includes projectile-induced cooling, transmitted kinetic energy, and sublimation of the cryogenic material, transforming the residue into a gas [10]. This process has a significant ecological impact as it eliminates the need to manage waste generated by the equipment or the use of solvents.

The advantages of this system compared to other cleaning methods have been evaluated [13]. Firstly, dry ice blasting represents an eco-sustainable option by using recycled CO_2 in the blasting, which significantly reduces water consumption and eliminates the need for solvents that negatively affect the environment and health [14]. Additionally, this method protects treated surfaces by preventing abrasion due to the low hardness of the beads used (2 Mohs) [15] and reduces the air pressure required compared to other mechanical methods.

This method is highly versatile, as it can be adjusted to different operating parameters, allowing its application on delicate surfaces [16]. A comparative study with traditional techniques, such as sandblasting or water, conducted by researchers from the Department of Civil, Architectural, and Environmental Engineering at the University of Miami, showed that this technique requires 19 % less energy and reduces the time of use by 77 %, validating it as an efficient and safe method for treating architectural structures [17].

However, despite its benefits, CO_2 cleaning has inherent limitations due to the nature of the projectile. In particular, it generates greenhouse gas emissions. Although the use of dry ice favours the reuse of carbon dioxide from surplus and by-products derived from other industries, its production is linked to the manufacturing process of other gases such as oxygen, argon, and hydrogen. Therefore, reducing the emission of CO_2 into the atmosphere remains a major challenge for cryogenic studies.

The relevance of this study lies in the need to assess the safety of dry ice blasting on non-porous substrates with multi-layer coatings, which are common on graffiti-affected urban materials. Although the properties of sprayed CO_2 offer significant advantages, there remains a paucity of research that thoroughly analyses the interaction between aerosols of varying compositions and this cleaning method. This knowledge gap limits their safe and effective application in heritage and urban contexts.

The main objective of this study is to evaluate the effectiveness of dry ice blasting for the removal of graffiti on multi-layer coatings, ensuring that this method does not compromise the integrity of the underlying materials. This will be done by analysing the physical, chemical, and micromorphological changes on the treated surfaces to understand the impact of the process and ensure its safety. This research aims to provide a solid basis for developing sustainable and effective conservation protocols, especially in heritage contexts where the preservation of original materials is essential.

Materials and methods

The dry ice blasting system used in the tests was the PolarTech PT-PROsi (Polartech, Odense, Denmark), selected using a quantitative comparative methodology based on the analysis of commercial systems manufactured by leading companies in the market [18]. This equipment (Table 1) allows the independent and simultaneous projection of solid carbon dioxide in pellet form and liquid CO_2 delivered by direct connection to a cylinder with a siphon. The materials tested include metal substrates (Table 2), with coatings applied during manufacture (M and N), and surfaces coated after traditional graffiti cleaning treatment (R).

Table 1. Technical specifications of the tested dry ice blasting system (Source: based on authors elaboration [19]).

Company	PolarTech
Equipment name	PT-PROsi
Dimensions	850 × 550 × 480 mm
Power supply	110-230 V / AC 50-60 Hz
Air pressure	2-14 bar
Air volume flow rate	0.8-9 m^3/min
Sound pressure level	60-120 dB
Tank capacity	25 kg
Pellets ø	1-3 mm
Dry ice consumption	0-75 kg/h
Liquid CO_2 consumption	0.25-1.5 kg/min
Liquid pressure	20-70 bar
Weight without accessories	70 g

Table 2. Supports and coatings tested.

Code	Colour	Support	Coating
M	Purple	Steel	Multi-layer: acrylic-urethane clear coat
N	Orange		
R	Red	Aluminium	Multi-layer: acrylic-styrene clear coat

Table 3. Aerosols used in the tests (Source: authors [13] based on paint data sheets [20-25]).

Code	Manufacturer	Type	Colour	Binder	Solvent
94_A	MTN	MTN 94	RV 30 Electric Blue EX014H0030	Modified alkyd	Aromatic mixture
94_N			Matte Black EX014H0901		
94_R			RV 3001 Vivid Red EX014H3001		
HC	MTN	Hardcore	Silver EX014H0101		
N2G	MTN	NITRO 2G	Black	Acrylic	Butyl acetate
TB	Montana	NITRO	Black Tarblack	Bitumen	-
WB_A	MTN	Water-based	Cobalt Blue EX019W0068M	Modified polyurethane	Water and spirits
WB_N	MTN		Charcoal Black EX019W9011M		
WB_R	MTN		Naphthol Red EX019W3020M		

Nine spray paints of varying compositions were applied, representative of the most common binders in street art: modified alkyd (94; HC), modified polyurethane (WB), acrylic (N2G), and bitumen (TB). These paints included representative colours such as silver (HC), blue (A), black (N), and red (R), and their characteristics are summarised in Table 3. The specimens were prepared by spraying aerosols manually on the described substrates. Three shots were fired for each aerosol, maintaining a constant distance, pressure, and volume of projected material. Solid state, commercial quality CO_2 was sprayed as 3 mm diameter pellets, at a pressure of 9 bar, a distance of 25 cm, and an average consumption of 1.25 kg/min. A convergent-divergent nozzle with a minimum diameter of 7 mm was used, setting the exposure time per area and recording it with measuring equipment.

The effectiveness of dry ice blasting for spray paint removal was evaluated using analytical methods that integrated aesthetic, mechanical, and chemical criteria, ensuring a multidisciplinary approach to assess both immediate and long-term effects on treated surfaces. To evaluate the visual changes, colourimetric and photometric analyses were carried out using a Konica Minolta CM-2600d (Konica Minolta, Tokio, Japan) spectrophotometer and a Rhopoint Novo-Gloss 20/60/85 (Rhopoint Instruments, St Leonards, United Kingdom) glossmeter, in accordance with UNE-EN 15886 [26] and UNE-EN ISO 2813 [27] standards. These analyses made it possible to identify variations in the optical and chromatic properties of the substrates before and after treatment.

Table 4. Rating scale and description (Source: based on standard UNE-EN ISO 2409 [30]).

Value	Description	% of area with coating detachment
0	Clean cuts without detachment	0
1	Small losses at intersections	< 5
2	Detachment at edges and intersections	5-15
3	Partial loss in strips or in several squares	15-35
4	Total separation in some frames, with bands around the cuts	35-65
5	Loss in excess of that described in classification 4	> 65

Surface alteration was also evaluated by measuring the static contact angle according to the UNE-EN 15802 standard [28] with deionised water as a reference liquid, allowing for the determination of changes in the wettability of the treated surfaces, as well as their relevance for the adhesion of subsequent coatings. However, some procedures were adapted to better reflect the conditions of the coatings studied. Instead of polishing the surface, as recommended in the standard, a 10 μL drop of distilled water was applied directly to the unpolished surface. The drop was pipetted, and an image was taken 5 seconds after deposition. Five measurements were taken for each substrate, both before and after each cleaning process, ensuring a distance of approximately 7 mm between drops. Additionally, surface hardness was analysed using an HTTK-37D (PCE Deutschland GmbH, Meschede, Germany) digital Shore D durometer, according to UNE-EN ISO 868 [29], identifying possible mechanical alterations induced by the cleaning process and their impact on the functionality and resistance of the substrate. Cohesion of the multi-layer coatings was assessed by lattice shear tests using a NEURTEK NK2000 (Neurtek Instruments, Eibar, Spain) according to ISO 2409 [30]. This method enabled the analysis of paint delamination after cross-cutting the surface (Table 4), with the results scored on a scale from 0 (no delamination) to 5 (total material loss). Assessments were made between 7 and 14 days after treatment.

The morphological changes on the surfaces and cross-sections of the specimens were studied by field emission scanning electron and optical microscopy (FESEM and OM). For this analysis, a Leica MZ AP0 (Leica, Wetzlar, Germany) optical microscope and a Zeiss ULTRA 55 FESEM (Zeiss, Jena, Germany) were used, guaranteeing an accurate evaluation at the microstructural level. To assess potential chemical changes in the specimens as a result of the cleaning treatment, the samples were analyzed using Fourier Transform Infrared Spectroscopy (FTIR) and Field Emission Scanning Electron Microscopy with (FESEM). The analyses were conducted with a Vertex 70 spectrometer (Bruker Optics GmbH & Co. KG, Ettlingen, Germany) equipped with an Attenuated Total Reflection (ATR) system and a FESEM coupled with an Energy Dispersive X-Ray Spectroscopy (EDX) EDS X-Max 80 (Oxford Instruments, Abingdon, United Kingdom) system.

Results

Study of optical and chromatic properties

The chromatic parameters L* (lightness), a* (chromaticity on the red-green axis), and b* (chromaticity on the yellow-blue axis) were obtained to evaluate the effectiveness of the cryocleaning process on each of the sprayed substrates. The initial and final measurements of these parameters are plotted in Figure 1, showing the Lab* chromatic coordinates for the treated areas before and after cleaning. In the graphs obtained, it can be seen that the variations in the L* parameter are small. The brightness values remain close to the initial range in all the areas analysed, suggesting that the cryogenic cleaning preserved the brightness of the clear coats. The chromatic values a* (red-green axis) and b* (yellow-blue axis) also show minimal deviations from the initial values in most cases. These variations are concentrated close to the reference values, indicating a high effectiveness in the recovery of the original chromaticity of the coatings.

To quantify the chromatic variations, the value of ΔE was calculated according to the UNE-EN 15886 [26] standard. The results obtained are presented in Table 5, showing the chromatic differences between the untreated coatings and the cleaned areas.

The initial and final gloss values (ΔGloss) were evaluated at an angle of 20 °, according to UNE-EN ISO 2813:2015 [27]. The results (Figure 2) have indicated a different behaviour between the M, N, and R supports.

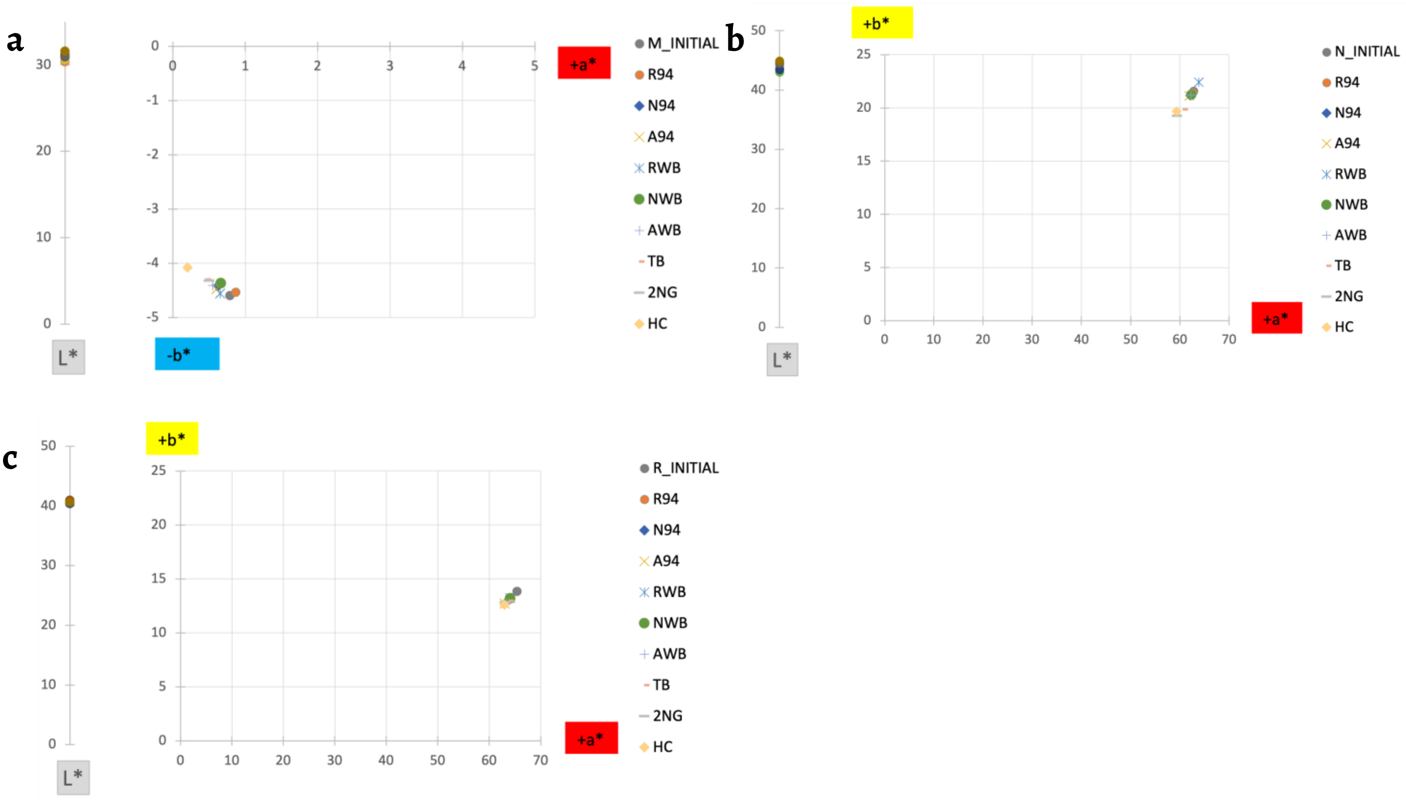

Figure 1. Representation of the variation of the L*, a*, and b* coordinates: *a)* Coat M; *b)* Coat N; *c)* Coat R.

On the M substrate, the initial gloss values were high and homogeneous, ranging between 75 and 80 UB. After dry ice blasting, the treated areas maintained values very close to the original ones, with variations of less than 10 UB, indicating an almost complete recovery of the initial gloss. The N support showed greater variability, with areas such as HC, 2NG, TB, and RWB retaining moderately high levels of brightness, while other areas such as N94, R94, A94, NWB, and AWB showed significant losses, with N94 and R94 being the most affected. Finally, the Styrene acrylic clearcoat (R) showed heterogeneous results, with the N94 and A94 areas displaying pronounced losses, while the HC, 2NG, and TB areas showed brightness values close to the initial values.

Table 5. ΔE* values for each test area.

ΔE*			
Code	**ΔE_M**	**ΔE_R**	**ΔE_N**
HC	1.244	0.767	1.121
TB	0.656	0.615	0.850
2NG	0.510	0.682	1.169
AWB	0.699	0.669	1.145
NWB	0.444	0.440	1.559
RWB	0.457	0.538	0.931
A94	0.247	0.755	0.329
N94	0.204	0.544	0.760
R94	0.193	0.386	0.356

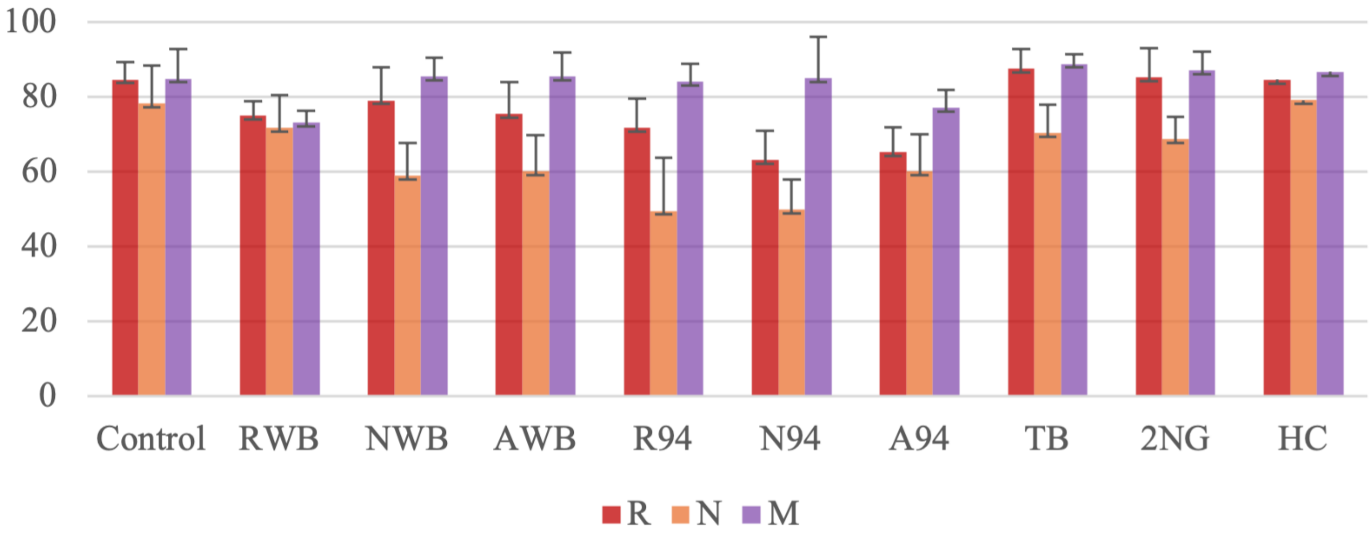

Figure 2. Gloss values of coatings subjected to CO_2 projection. The control measurement is followed by the values of the areas after removal of the aerosol HC, N2G, TB, 94 (A, N, and R), and WB (A, N, and R).

Assessment of physical and mechanical properties

The adhesion results, measured in accordance with ISO 2409 [30] (Table 6) indicate that the multi-layer coatings subjected to dry ice blasting kept their original cohesion levels without compromising the structural integrity of the film.

Table 6. Measurement of adhesion of coatings subjected to CO_2 microspraying. The control sample is indicated, followed by measurement of the areas after removal of the aerosol HC, N2G, TB, 94 (A, N, and R), and WB (A, N, and R).

Material	Control	HC	N2G	TB	A94	N94	R94	AWB	NWB	RWB
M	0	0	0	0	0	0	0	0	0	0
N	1	1	1	1	1	1	1	1	1	1
R	1	1	1	1	1	1	1	1	1	1

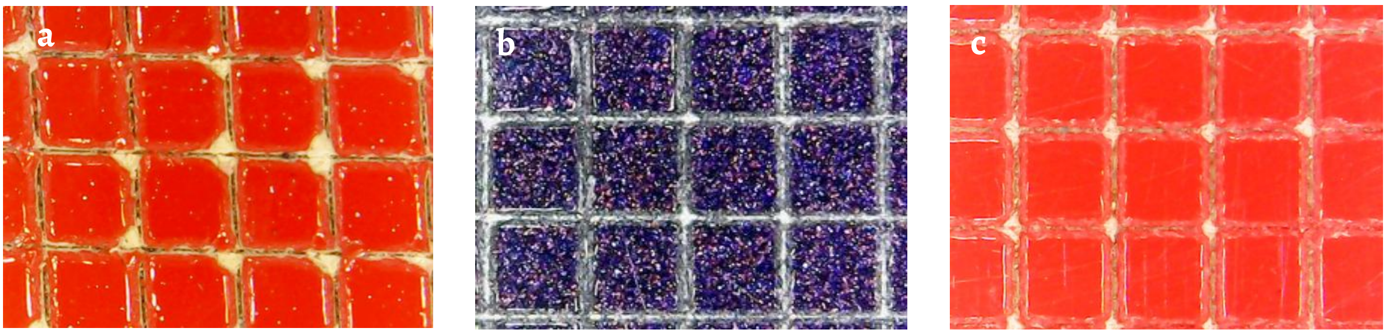

Figure 3. Control adhesion tests: *a)* N substrate; *b)* M substrate; *c)* R substrate.

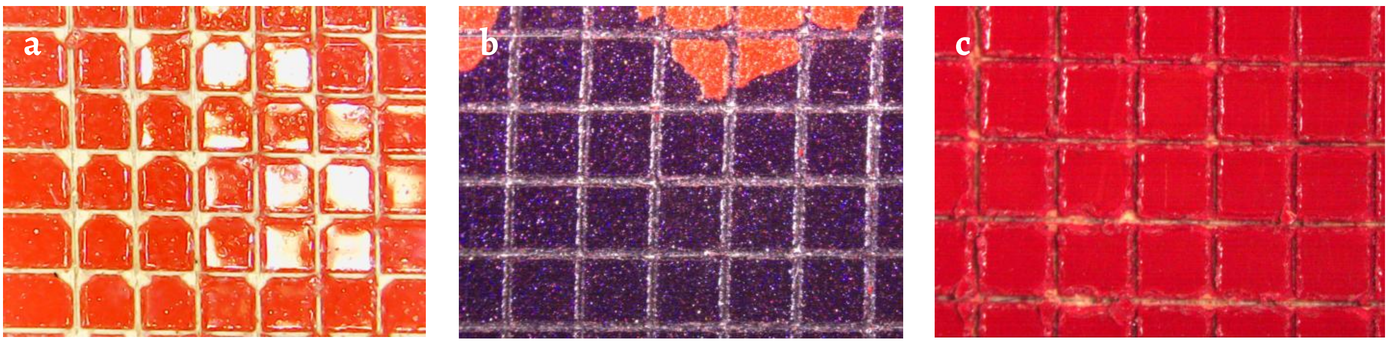

Figure 4. Adhesion tests after CO_2 projection: *a)* N substrate, NWB zone; *b)* M substrate, R94 zone; *c)* R substrate, NWB zone.

For the M support, initially classified as value 0, 100 % of the cuts performed showed complete integrity before and after cleaning. On the other hand, the N and R supports, initially graded as 1, showed less than 5 % damage after treatment. These results indicate that the dry ice blasting process did not have a negative effect on the adhesion of the treated layers. Figure 3 and Figure 4 show detailed images of the adhesion test results.

Changes in the surface hardness of the coatings were assessed by five strategically distributed measurements to provide an accurate representation of variations. Acrylic urethane coatings M and N showed average values of 90.1 HD and 82.5 HD, respectively, indicating very hard multi-layer coatings. Substrate R displayed lower initial values of 73.3 HD, corresponding to an acrylic-styrene coating. This reflects lower mechanical strength due to the linear structure of acrylic-styrene compared to the cross-linked acrylic-urethane.

The average hardness measurements after CO_2 microprojection (Figure 5) were evaluated. Substrate M showed 88.7 Shore D, a slight decrease from 90.1 Shore D, indicating no significant structural alteration. Substrate N recorded 82.1 Shore D, with a minor change from 82.5 Shore D. Small individual variations in measurements show the coating retained its hardness, suggesting minimal structural change.

The orange substrate's initial values, averaging 82.5 Shore D with a standard deviation of 2.26, indicate heterogeneity in hardness due to variations in coating thickness or internal microstructures. This could influence adhesion and cleaning effectiveness. Finally, substrate R's hardness increased slightly to 75.1 HD from 73.3 HD, showing no significant change.

The evaluation of wettability was carried out by measuring the static contact angle, in accordance with the UNE-EN 15802 [28] standard. The results compare the initial and post-cleaning values for the different graffiti applied on the tested substrates (Figure 6).

The static contact angle values indicate that all surfaces, including the control and those treated for paint removal, exhibit moderate wettability, with angles ranging between approximately 60 ° and 80 °. This suggests that the surfaces retain a balanced behavior, neither strongly hydrophobic (above 90 °) nor highly hydrophilic (below 40 °). The paint removal treatments generally do not significantly alter the surface's hydrophobic character, as all treated surfaces display similar contact angles to the control. Minor variations between treatments, such as TB or N2G, may reflect slight differences in surface modifications or residues left after cleaning.

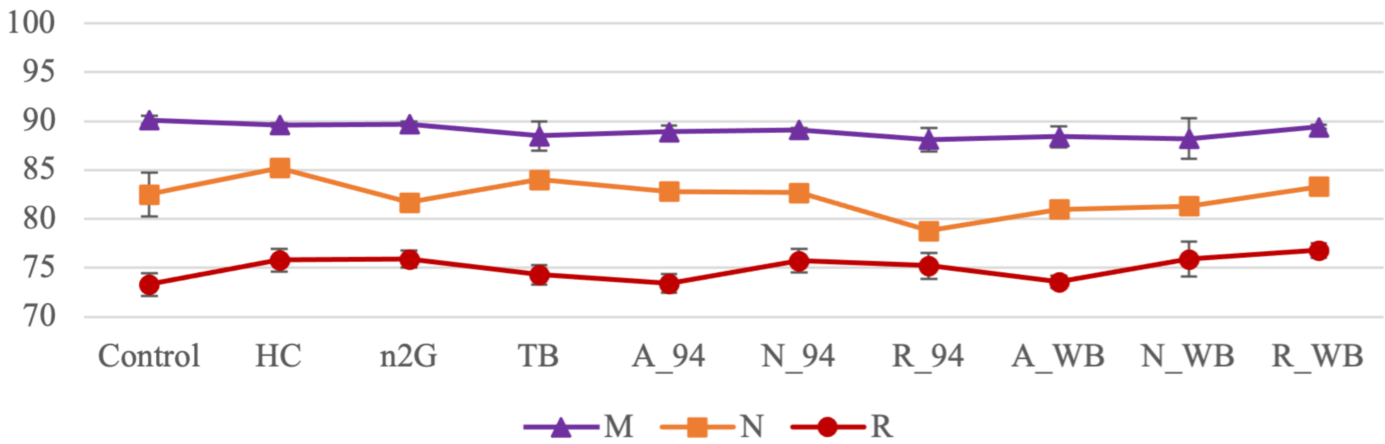

Figure 5. Shore D hardness measurement of coatings subjected to cryogenic cleaning. The control values are indicated, followed by the measurements of the zones after removal of the aerosol HC, N2G, TB, 94 (A, N, and R), and WB (A, N, and R).

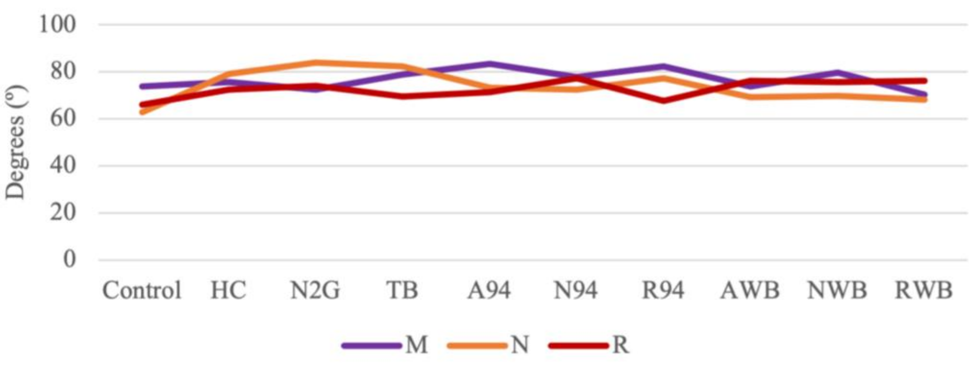

Figure 6. Contact angle measurements of the tested surfaces. The control measurement is indicated, followed by the measurement of the zones after removal of the aerosol HC, N2G, TB, 94 (A, N, and R), and WB (A, N, and R).

Chemical and micromorphological assessment

The chemical characterisation of the supports after the cleaning tests made it possible to analyse the transition between the clean areas and the areas covered with paint, identifying possible graffiti residues that had not been removed. Point and area analyses were carried out both on the surface and in cross-section, and elemental distribution maps were obtained using FESEM-EDX.

In the elemental distribution maps (Figure 7), corresponding to the test areas AWB_M and NWB_N, a clear demarcation between clean and graffitied surfaces can be observed. Elements such as silicon (Si) and magnesium (Mg), characteristic of paint fillers, are only detected in the graffiti areas, corroborating their removal. The images show no evidence of microcracks, erosions, or topographical alterations on the treated surfaces. In some tests, such as in the NWB_R area, paint residues were detected on the perimeters of the cleaned areas, identifying fragments with Si and Mg content.

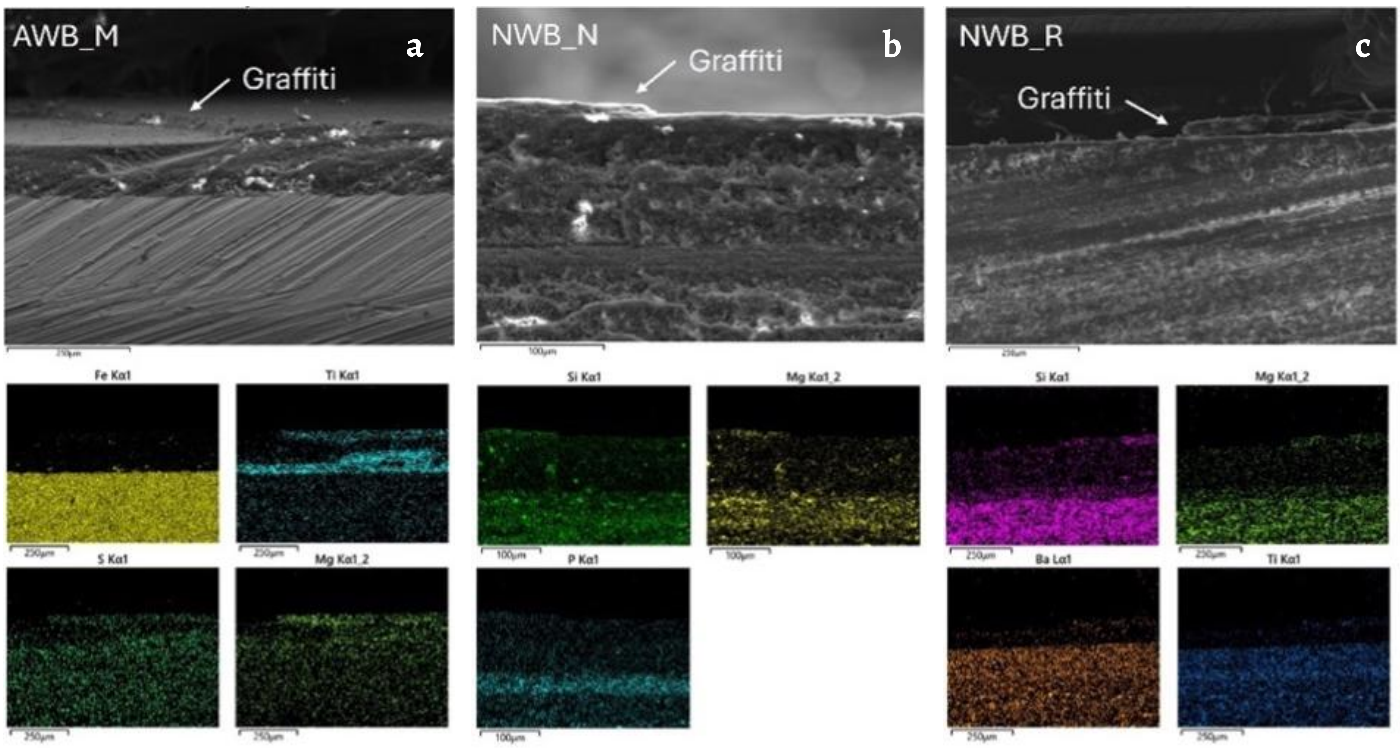

Figure 7. Cross-section element distribution maps: *a)* AWB_M; *b)* NWB_N; *c)* NWB_R.

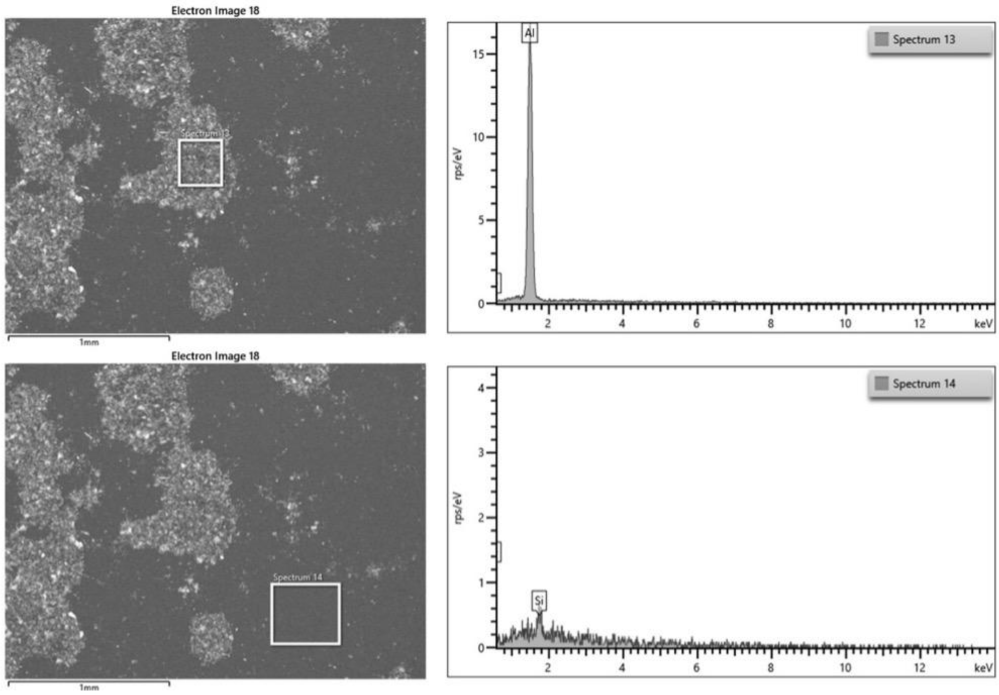

Figure 8. Analysis of area in the waste and clean area on the perimeter of the HC_R projection area.

In the HC zone (Figure 8), the perimeter shows significant residues in the form of scattered fine particles with high aluminium (Al) content, while the cleaned areas are free of this element. The residues are concentrated at the edges of the treated areas, while the central areas reach an optimal degree of cleanliness.

Examination of the coatings revealed smooth, undamaged surfaces on the M and R substrates. However, on the N substrate (Figure 9), spherical aggregates consisting mainly of barium sulphate ($BaSO_4$) and aluminosilicates (kaolinite, $Al_2Si_2O_5(OH)_4$) were observed. These aggregates were also found in the inner layers of the coating, accompanied by microcracks recorded in the coating of control samples.

The analysis by FTIR spectroscopy made it possible to determine the chemical composition of the coatings present on the M, R, and N substrates before and after the dry ice blasting tests. The infrared spectrum of the M substrate identified an acrylic-urethane-type coating, with absorption bands at 1720, 1690, and 1150 cm^{-1}, characteristic of this composition. Bands associated with styrene (1450, 760, and 700 cm^{-1}) and silicates and carbonates (871 and 900-1000 cm^{-1}) were also detected. On the other hand, a similar composition was observed in support R, with bands corresponding to acrylic-urethane (1722, 1682, and 1132 cm^{-1}), styrene (1454, 762, and 701 cm^{-1}), and carbonates (871 cm^{-1}). In addition, isocyanate residues were identified at 2258 cm^{-1}.

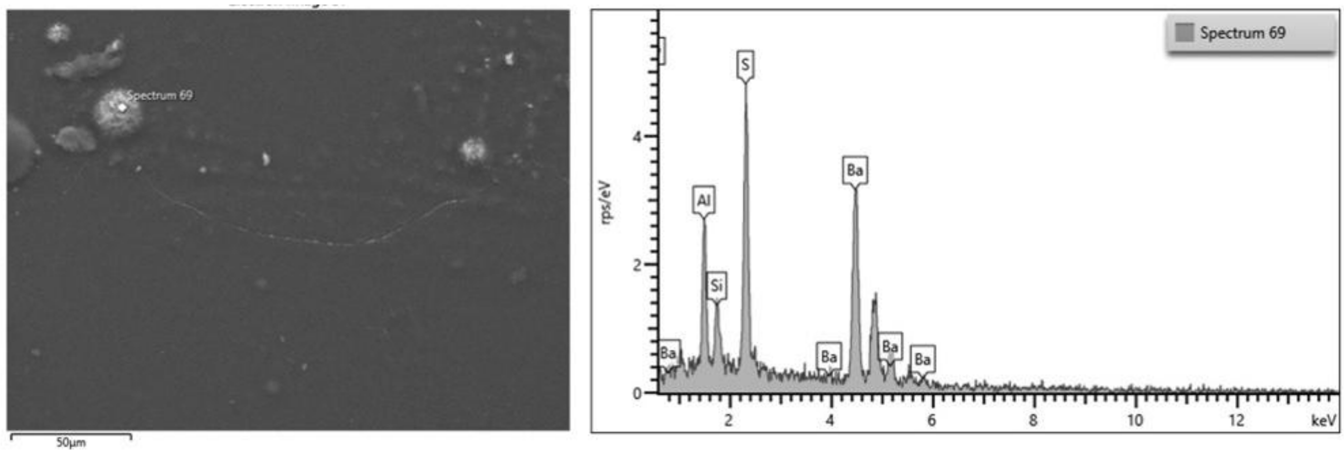

Figure 9. Point analysis of spherical aggregates and microcracks present in the control samples of the N support.

On support N, the analysis confirmed an acrylic-styrene-type coating (1720, 1373, and 1158 cm^{-1}). Bands corresponding to styrene (1460, 761, and 699 cm^{-1}), and minerals such as kaolinite and sulphates (3676, 1016, 669, and 605 cm^{-1}), were also identified. The sulphates are related to spherical aggregates of barium sulphate detected in the FESEM-EDX analysis.

After the cryocleaning trials, the substrates were analysed for evaluating any potential any changes in chemistry or residues that could be associated with the cleaning process (Figure 10). As can be observed in the corresponding spectra, no additional adsorption bands were identified on any of the surfaces that could be associated with neoformation products.

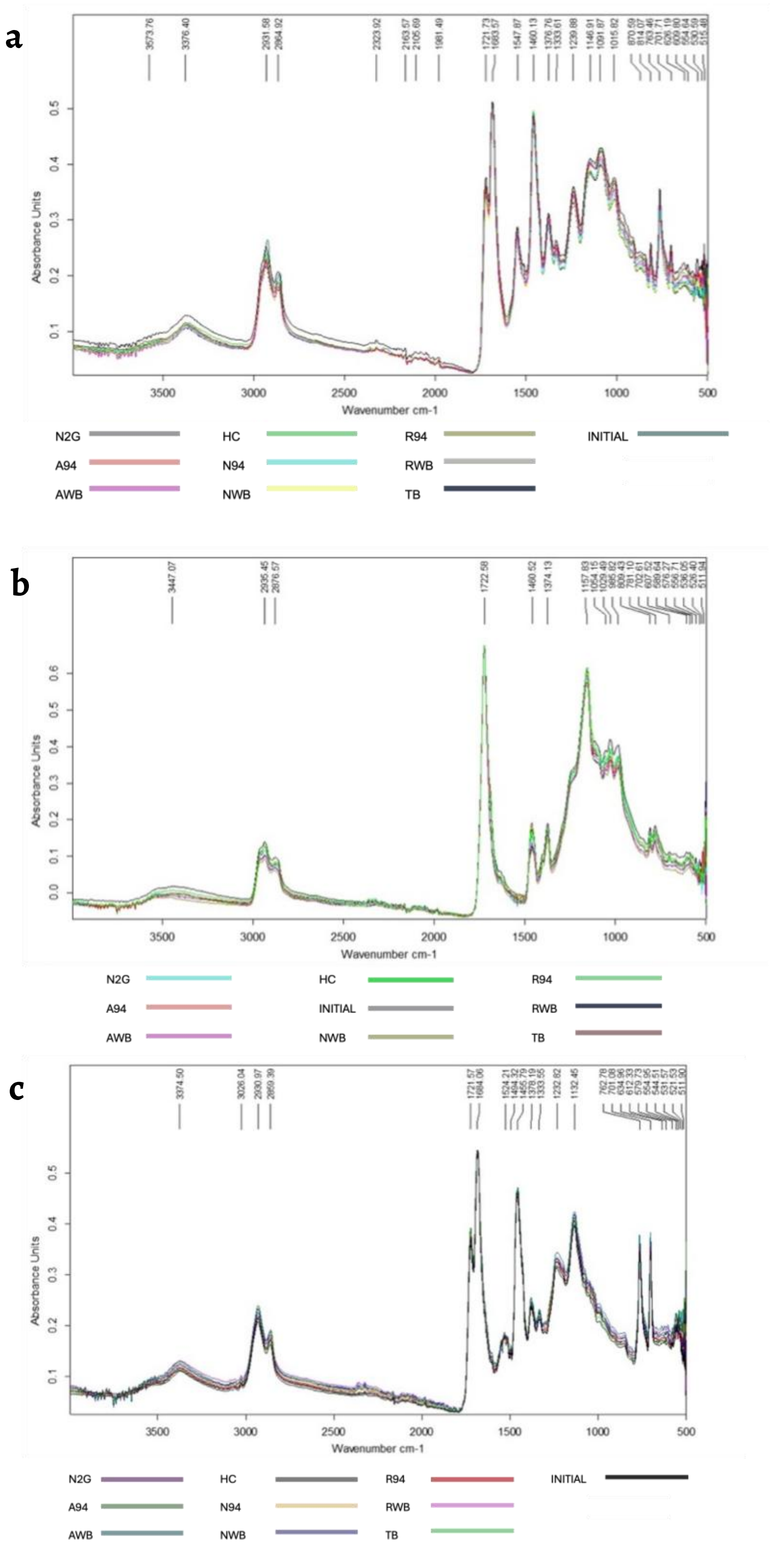

Figure 10. Infrared spectra of the surfaces before and after cryocleaning: *a)* Coat M; *b)* Coat N; *c)* Coat R.

Discussion

Impact on colourimetric and optical properties

The ΔE_M values are less than 1, indicating minimal or imperceptible colour differences after cryocleaning, suggesting that the process was highly effective, with almost complete colour recovery. The only exception was the HC zone, with a ΔE value of 1.244, indicating a slight perceptible variation. This deviation may be associated with the presence of minimal residues or occasional surface disturbance. The ΔE_R values are consistently lower than 1 in all treated areas, indicating effective cleaning with no perceptible differences in chromatic terms. This confirms that the applied procedure succeeded in removing the paints without compromising the chromaticity of the support.

Greater chromatic variations were observed in the N-bracket. In the NWB, 2NG, and AWB areas, ΔE values slightly exceeded the threshold of 1 (1.559, 1.169, and 1.145, respectively), indicating some chromatic differences in these areas. These variations could be due to a lower cleaning efficiency in certain areas or to the inherent characteristics of the support, such as previous alterations or aggregates, which prevent the complete removal of the paints. Nevertheless, in the other areas of substrate N, ΔE_N values of less than 1 support the overall effectiveness of the process.

In general terms, the results of the L*, a*, and b* parameters and ΔE values show that cryocleaning is an effective technique for colour recovery in most of the substrates and areas treated.

However, analysis of the results reveals that the impact of the microprojection on surface gloss varies significantly between the different substrates, depending on both the intrinsic properties of the materials and the specific conditions of the treated areas. In the case of substrate M, the uniformity of the final gloss values and their proximity to the initial levels underline the effectiveness and consistency of the treatment. This indicates that cryocleaning can be safely and effectively applied to this material without compromising its surface integrity. The low variability between treated areas suggests a good ability of the technique to homogeneously restore the original gloss.

Support N showed a more heterogeneous response to treatment. The significant loss of gloss observed in areas such as N94 and R94 could be related to pre-existing changes in the material, such as the presence of spherical aggregates, which may have affected the effectiveness of the cleaning process. On the R support, the areas of higher gloss loss coincide with substrates with smaller clean areas and a significant percentage of residue, as in the case of A94. In certain cases, smaller graffiti removal areas and/or the presence of residue can affect the scatter of the gloss measurements.

In some cases, the measurement area of the photometer (3 cm) may slightly exceed the "clean" area and include peripheral areas more affected by the presence of dirt, resulting in significantly lower gloss values than the reference values. According to the gloss measurements obtained, for the HC, 2NG, and TB test areas, where larger clean area diameters were obtained, the gloss values recorded are similar to reference values for all the substrates tested. This confirms the direct relationship between the achieved cleaning diameter and the gloss deviations from the initial values. Although some areas achieved gloss levels close to the original values, the variability between areas underlines the importance of adjusting the treatment parameters to ensure greater uniformity of results.

Assessment of physical-mechanical properties

The use of CO_2 microprojection as a cleaning method was found to be highly effective in maintaining the integrity of the original strata in multi-layer coatings. Adhesion results (ΔAdherence = 0) indicate that the technique minimises delamination and avoids changes in the cohesion of the treated layers. This behaviour is particularly relevant in surface treatment where the preservation of the mechanical stability of the coatings is crucial.

Compared to conventional abrasive methods, which often result in microcracking or weakening of coatings, dry ice blasting offers a less invasive alternative, as evidenced by the results obtained. The uniformity in the response of coatings treated with different sprays reinforces the versatility of the method for a wide range of applications. Additionally, the high initial adhesion in the M samples can be attributed to a higher density or quality of coating application, although this characteristic was not altered after treatment.

Regarding changes in the wettability of surfaces, in the M-bracket (73.77 °), significant variations were observed in the treated samples. For example, the highest values were recorded for A94 (83.27 °) and R94 (82.25 °), indicating a higher hydrophobicity attributable to possible aerosol residues that were not completely removed. In contrast, the N2G sample showed a lower value (72.45 °), suggesting more efficient cleaning or less residue retention.

In the case of the N support (62.74 °), the contact angle variations reflect different behaviours. The N2G removal zone presented the highest value (83.90 °), followed by TB (82.34 °), which can be interpreted as the presence of residues. On the other hand, AWB and NWB showed lower values, 69.14 ° and 69.74 °, respectively.

Finally, in the R-bracket (65.90 °), the differences were less pronounced but equally informative. The highest values in N94 (77.09 °) and RWB (76.08 °) stood out, which again could be related to lower cleaning effectiveness. In comparison, the HC and AWB samples recorded lower values (72.40 ° and 69.14 °).

The results of the surface hardness tests performed before and after the dry ice blasting treatment indicate that no significant changes have occurred in the hardness values of the coatings.

Impact on chemical composition and microtextural changes

The assessment of the impact on the integrity of the treated surfaces after dry ice blasting confirms that the process does not generate significant chemical alterations to the original coatings. In the elemental distribution maps, the clear delineation between clean and graffiti areas, together with the absence of microcracks or erosion, suggests that the cleaning conditions preserve the morphological properties of the support.

The finding of residues at the perimeters of the treated areas, especially in areas such as NWB_R and HC, points to a heterogeneous distribution of the CO_2 flux that could be optimised. These residues are limited to fine particles and do not alter the core properties of the surfaces.

The spherical aggregates detected on support N, composed of $BaSO_4$ and kaolinite, seem to correspond to migratory processes of materials from internal strata to the surface, possibly due to pre-existing conditions of the coating. Their presence does not imply an alteration attributable to the cleaning method applied.

It should also be noted that the analyses carried out on the underlying layers (basecoat of the coating) revealed the presence of the same constituents (barium sulphate and kaolin-type minerals), confirming that these spherical aggregates originate from the constituents of the internal layers of the coating.

The FTIR analysis confirms the chemical stability of the coatings after cleaning. The slight variations observed, such as an increase in the intensity of specific bands, reflect the exposure of the underlying layers rather than process-induced changes. The slight variations observed in the 2924 and 2856 cm^{-1} bands of the M support correspond to vibrations of C–H bonds and are not associated with structural changes in the coating. In the N substrate, peaks were observed in the 1461 cm^{-1} absorption band (between 0.2-0.3) attributes to the exposure of the underlying components (basecoat) of the acrylic-urethane type, due to the presence of previously identified spherical aggregates.

Conclusions

The results of this study confirm the high effectiveness of cryocleaning as an advanced and sustainable technique for removing graffiti from non-porous substrates. This methodology proved to be safe, respectful of the integrity of the treated materials, and able to minimise changes in key properties such as colour, gloss, hardness, and adhesion. However, the heterogeneous reaction observed on some substrates highlights the need for specific adjustment of the cleaning parameters to allow homogeneous removal of this type of polymer.

Morphological and chemical analyses by FESEM and FTIR confirm the preservation of the intrinsic properties of the coatings, while wettability and hardness tests confirm the viability of the technique for future conservation applications. These results not only reinforce the applicability of cryocleaning in heritage and other technical sectors but also highlight its alignment with sustainability goals by minimising secondary waste and reducing environmental impact.

Despite the positive results, areas for improvement were identified, such as the development of specific parameters according to the support and composition of the graffiti. These recommendations open new opportunities to optimise the technique and ensure greater consistency of results. Overall, this study provides a solid basis for the implementation of dry ice blasting as an efficient and safe method, promoting its use as a key tool in the conservation of heritage materials and challenging surfaces.

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Data availability statement

The raw data supporting the conclusions of this article will be made available by the authors on request.

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