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Nanofluids confined in chemical hydrogels for the selective removal of graffiti from street art

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ABSTRACT

The main challenge in the conservation of street art is the selective removal of graffiti (i.e. tags, writings and overpaintings) from the original artwork. Nowadays, the effective methods available for this intervention involve risking damage to the original. The novel combination of nanofluids with highly retentive pHEMA/PVP chemical hydrogels is proposed as a controllable cleaning method for selective removal of graffiti from street art. Nanofluid-loaded hydrogels were tested on laboratory models simulating street art paintings covered in graffiti. The outcome of cleaning tests was investigated by means of visual, photographic and microscopic observation, and micro-reflectance FTIR spectroscopy. It was shown that the proposed

INTRODUCTION

Today, street art is becoming a mainstream artform and a number of street artists have attracted the attention of art critics and collectors. The economic and artistic value of pieces by Banksy, Blu and many others is rapidly increasing to such an extent that the issue of preserving their works has suddenly become a novel challenge for conservators. The peculiarity is that this is an evanescent, unconventional form of art which is not intended to last more than some months or a few years. Several options have been explored recently for its preservation. Some pieces have been detached and moved to galleries, museums or controlled environments, but that has provoked some controversy because it is viewed as a decontextualisation of the works of art and a misunderstanding of the true nature of the street art culture (Brajer 2015).

Nevertheless, leaving street artworks in their original places creates significant conservation issues due to their broad accessibility and vulnerability to attack, as they are on open display.

It has been observed that signs of ageing on outdoor murals (blanching or desquamation of the paint layer) attracts vandalism (i.e. graffiti), and the appearance of one tag will invite more, which can lead to the ultimate destruction of the artwork by overpainting (Brajer 2015). When street art is vandalised with graffiti, a number of different paint layers can be found on the works. This has led to a completely novel and particularly tough challenge for conservators and conservation scientists: the selective removal of tags, writings and overpaintings from street art.

Performing a selective cleaning in this case is not trivial, since the binder of the undesired paint is likely to have a very similar chemical nature to the artwork, especially if both are of similar age. None of the methods available today for this type of intervention are fully satisfactory. Organic solvents and water-based detergents (Sanmartín et al. 2014) are often too aggressive (particularly because mechanical action is required), poorly controllable and toxic to the user and surrounding ecosystems. Mechanical methods, including sand blasting or high-pressure water spraying (Chapman 2000, Ortiz et al. 2013, Sanmartín et al. 2014), can place the original artwork at risk of damage or destruction. Laser ablation can be selective in some specific cases, but this is mainly due to the different levels of absorpion of radiation

methodology is effective in removing acrylic-, nitrocellulose- and alkyd-based graffiti without damaging the underlying paint. This can be achieved by means of a gradual swelling action performed by the nanofluid, which is limited to the surface layers by the retentive power of the hydrogel.

of the material to be removed with respect to the original material. In the case of tag removal from street art, the low optical absorption and poor thermal conductivity of paints are not suitable for the use of lasers (Brygo et al. 2006a, Brygo et al. 2006b, Sanmartín et al. 2014). Some positive results have been recently obtained in the removal of overpaintings from oil on canvas paintings (Siano et al. 2015), but, at present, laser ablation for the removal of tags (Selva Bonino 2016) from street art is still under investigation. Finally, bioremoval of graffiti opens interesting perspectives, but it is not yet a fully validated approach to thisissue.

Within the framework of the Horizon 2020 EU-funded NANORESTART project (www.nanorestart.eu), the combination of nanofluids, such as micelles and microemulsions, with highly retentive chemical hydrogels was evaluated and is proposed as a selective and controllable cleaning system for the removal of graffiti and overpaintings from street art. This paper presents the first part of this project, and is limited to laboratory experiments aimed at finding the most efficient methods. These will be applied to in-situ cases in upcoming fieldwork and will be documented in a forthcoming publication.

This approach presents a number of advantages compared with traditional methods. The toxicity and environmental impact of the cleaning systems are highly reduced, since these systems are water based and include small amounts (less than 10% by weight) of sustainable organic compounds as solvents and surfactants. Moreover, since these nanofluids are confined in highly retentive hydrogels, the evaporation rate of the organic fraction is further decreased. This is crucial when operators treat large works in poorly controlled environments, as usually happens in the field of conservation of outdoor works of art.

From an application standpoint, nanofluid-loaded retentive chemical hydrogels greatly increase control of the cleaning procedure. Their action can be controlled and limited in space and time due to their low content of organic solvents, the slow penetration rate in the porous substrate and the transparency of these gels, which permits conservators to follow the cleaning process just by looking through them. Using nanofluids, the undesired paint layer is not completely dissolved, as happens using unconfined pure organic solvents, but is swollen. This permits the conservator to perform a gentle mechanical action, for example with a plastic spatula or a moist cotton swab, on the softened paint, which guarantees more control than traditional methods allow. Finally, in contrast to poulticing techniques based on cellulose fibres, there is no problem with clearance when using hydrogels (Brajer et al. 2014).

EXPERIMENTAL

Highly retentive hydrogels

The hydrogels reported in this study are based on a three-dimensional network of poly(hydroxyethyl methacrylate)/N,N'-methylene bisacrylamide (pHEMA/MBA), interpenetrated by a high-molecular-weight poly(vinyl pyrrolidone) (PVP) (Domingues et al. 2013a, 2013b, 2013c). They are chemical gels since their structural network is based on covalent bonds. This

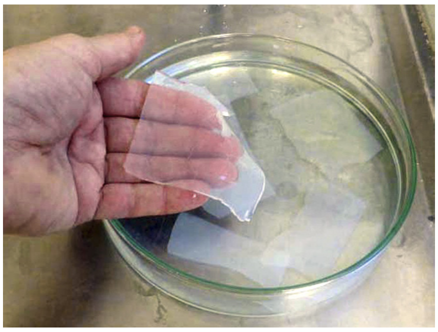

Figure 1. pHEMA/PVP SIPN gel used in the laboratory experiments

makes them completely different from traditional physical gels commonly used in the conservation of cultural heritage (i.e. Klucel, Carbopol, etc.), or from rigid gels (i.e. gellan gum and agarose-based formulations). Physical gels tend to leave some residues on the treated surface after application because cohesion forces inside the gel have similar magnitudes as adhesion forces with the treated substrate. By contrast, chemical gels, in view of their covalently bound structural polymeric network, guarantee a residue-free application, because adhesion forces to external surfaces are highly overcome by cohesion forces, which keep the gel together (Domingues et al. 2013a). As a consequence, chemical gels cannot be spread freely; they keep the shape of the container they were synthesised in. However, they can be easily cut to give them the desired shape for the application (Figure 1).

Nanofluids

Four aqueous nanofluids were used in this study, which are based on a mixture of medium-high polar solvents and three different surfactants.

Nanofluid A contains more than 70% w/w of water, a mixture (~25% w/w) of 1-pentanol, propylene carbonate and ethyl acetate, and an anionic surfactant.

Nanofluid B contains 60% w/w of water, a mixture (~35% w/w) of 2-butanol, propylene carbonate, 2-butanone and ethyl acetate, and a nonionic surfactant.

Nanofluid C contains less than 60% w/w of water, a mixture (~35% w/w) of 2-butanol, propylene carbonate, 2-butanone and ethyl acetate, and a nonionic cleavable surfactant together with an alkyl glucoside hydrotrope (i.e. a chemical that helps hydrophobic compounds to be dissolved in aqueous solutions without forming micelles by itself – in this case it is used as a co-surfactant).

Nanofluid D contains less than 65% w/w of water, a mixture (~25% w/w) of 2-butanol, propylene carbonate and diethyl carbonate, and a nonionic surfactant together with an alkyl glucoside hydrotrope.

The choice of these particular solvents was mainly based on two factors: effectiveness in dissolving the polymeric binders that are typical of spray paints used for graffiti, and toxicity/eco-compatibility. In view of this, alcohols, ketones and esters commonly used in conservation were selected, together with some more unconventional chemicals, such as propylene carbonate and diethyl carbonate. Alkyl carbonates represent an interesting class of 'green', non-toxic, water-compatible solvents, which can be effectively employed for cleaning purposes in the conservation of cultural heritage.

All these cleaning systems were specifically designed for the removal of acrylic or vinyl polymeric coatings from porous surfaces. They are all transparent, isotropic liquids, which can be applied using thickeners or poultices, such as arbocel or sepiolite, or, as in the present case, loaded into suitable hydrogels that act as smart carriers for the cleaning fluids.

Cleaning tests

Nanofluids and nanofluid-loaded hydrogels were tested on laboratory models simulating street art paintings covered by graffiti. The samples were prepared by overlapping different paints in various combinations.

Figure 2. Example of the model substrate (brick tile), with the white background representing street art and the coloured stripes representing the graffiti

The paints considered in this study were selected as those identified most frequently from chemical analyses of graffiti applied to public buildings and cultural heritage since 2000 in Denmark.

Model substrates that were highly representative of street art on porous substrates (brick and concrete walls) were prepared and aged using a light box that delivered sufficient ultraviolet radiation to represent works with 5–10 years of exposure to European weather.

The model artworks were designed to examine the extent of removability of the most frequently found paint combinations applied to painted and untreated porous surfaces. The paints investigated were acrylic (Plastikote), nitrocellulose alkyd (NC alkyd, Montana Black MC) and oxidising alkyd (Ox alkyd, Montana White synthetic gloss). Paints were sourced at a specialist graffiti artists' shop. To ease observation during graffiti removal, the tiles were prepared by applying a white ground layer representing the original artwork on one half, while the unpainted half represented graffiti applied to unpainted porous surfaces (Figure 2). Stripes of all the paints in green, black and red colours were applied across the width of the tiles so that combinations of all the paints and all the colours were achieved.

Four sets of the painted tiles were prepared and are listed in Table 1.

Table 1. Description of the samples prepared for the cleaning tests

Samples set	Purpose – scenario to simulate	Ageing		Use
		White background	Graffiti stripes	
Graffiti Set 0	Reference set	Aged[a]	Unaged	Left untreated at room T in the dark
Graffiti Set 1	Greatest conservation challenge: graffiti applied to freshly painted street art or walls	Unaged	Unaged	Used for cleaning tests
Graffiti Set 2	Graffiti applied to established artwork and cleaned immediately	Aged[a]	Unaged	Used for cleaning tests
Graffiti Set 3	Graffiti applied to established artwork and cleaned after at least one month	Aged[a]	Aged[a]	Used for cleaning tests

[a]Ageing was carried out in a UV/ozone box for 14 days.

Cleaning tests were performed by shaping the nanofluid-loaded gels in small pieces, in order to treat small square areas. Gels were applied for a few seconds (see the following paragraphs for details about application times), then the swollen paint layer was gently removed with a blunt scalpel or plastic spatula, followed by a final cleaning with a cotton swab. Often, more than one application was needed on the same area. The mechanical removal of the swollen paint prior to the final cleaning with a cotton swab was an important step in the cleaning process. Working only with cotton swabs showed that the swollen paint could be 'massaged' into the surface, resulting in a less efficient cleaning. During the cleaning process, the efficiency of graffiti removal was assessed by observing the amount of residual graffiti paint present before reaching the point of damaging the original paint. The residual graffiti paint was often lodged in small indentations or irregularities in the surface profile. Another phenomenon indicating efficiency was the amount of damage inflicted on the original paint during graffiti removal. This could occur when both layers swelled in reaction to the nanofluid-loaded gels.

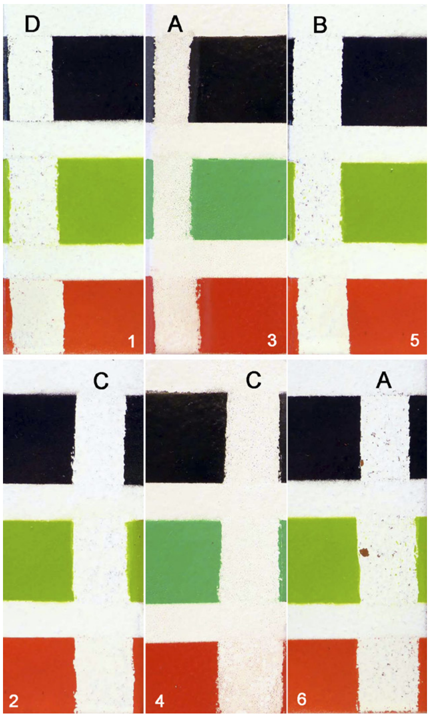

Figure 3. Laboratory test results showing the removal of unaged graffiti over an aged paint layer using nanofluids A–D. 1–2) alkyd graffiti over alkyd painting; 3–4) nitrocellulose graffiti over nitrocellulose painting; 5–6) acrylic graffiti over acrylic painting

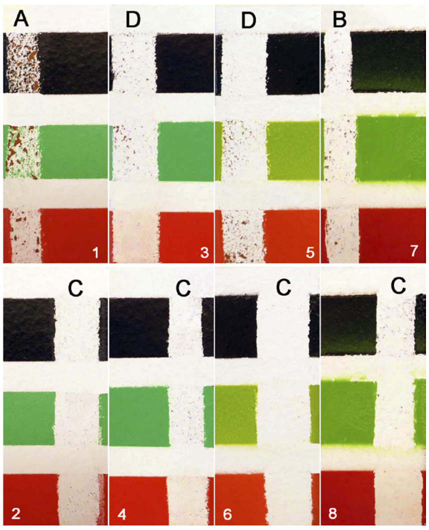

Figure 4. Laboratory test results showing the removal of unaged graffiti over an aged painting using nanofluids A–D. 1–2) nitrocellulose graffiti over acrylic painting; 3–4) nitrocellulose graffiti over alkyd painting; 5–6) alkyd graffiti over acrylic painting; 7–8) acrylic graffiti over alkyd painting

The outcome of cleaning tests was also investigated by means of photographic and microscopic observation. In addition, micro-reflectance Fourier transform infrared (FTIR) spectroscopy was performed on the treated area before and after the application of the nanofluid-loaded gel, in order to gather information about the chemical composition of the surface, in search of possible residues of the removed paint layer.

Micro-reflectance FTIR spectroscopy

Micro-reflectance FTIR spectra were obtained with a Nicolet Nexus Fourier transform infrared spectrometer interfaced with OMNIC software and equipped with a microscope for microanalysis. An MCT detector was used to collect the signal in the 4000–650 cm^{-1} range. A gilded surface was used to collect the background signal. The spectra were collected as single-beam files as the sum of 128 scans with a resolution of 4 cm^{-1}. Then they were divided by the background signal and transformed using the Kubelka-Munk algorithm, which is commonly used to display reflectance spectra, as it applies a scaling factor to the curves in order to obtain data more easily comparable to absorption spectra.

RESULTS AND DISCUSSION

It was quickly observed that removing graffiti from the non-painted porous backgrounds was not a problem. Therefore, the experiments focused on the removal of the coloured stripes on the white backgrounds. As was anticipated, the effectiveness of removal was related to the chemistry of the paint binder. In particular, alkyd paints, as they cross-link with time, are challenging to remove, particularly when painted over acrylic street art. Conversely, when the original paint layer is alkyd based, selective removal is easier. However, some results in the cleaning experiments contradicted these general observations, showing that it was possible to remove graffiti on acrylic paintings in more challenging circumstances.

Setting up application times and performing careful and delicate mechanical actions were found to be key factors when removing graffiti, particularly when the graffiti had the same binder as the original paint layer. However, it was difficult to follow a strict protocol as each particular colour reacted differently. For all binding media, the red colour was the easiest to remove, and the green was the most difficult. Application times could range between several seconds to one minute. The factor influencing ease in graffiti removal most strongly was the age difference between the two layers. Good results were achieved with alkyd graffiti over alkyd paintings and nitrocellulose graffiti over nitrocellulose paintings when fresh graffiti was removed from aged paintings, and slightly poorer results were achieved for removing fresh acrylic from aged acrylic paintings (Figure 3).

It was shown that repeated, short applications on the same area produced better results with less removal of the original underlying paint than one single longer treatment. The longer a gel remained on the surface, the more likely it was for the bottom layer to become swollen and damaged during the graffiti removal process. Thus, the two slow-working nanofluids A and B gave the poorest results, with numerous lacunae occurring in the bottom layer (Figures 4 and 5). Nanofluid D gave slightly better results.

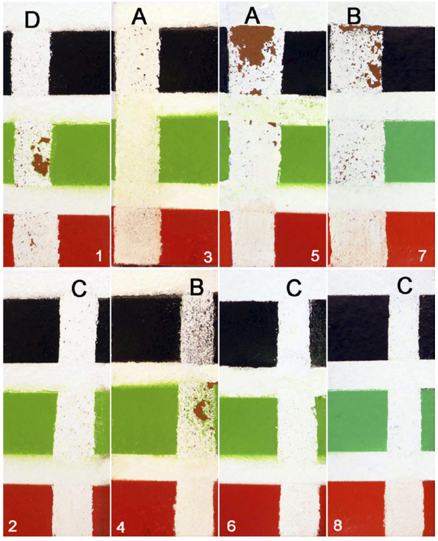

Figure 5. Laboratory test results showing the removal of aged graffiti over an aged painting using nanofluids A–D. 1–2) acrylic graffiti over acrylic painting; 3–4) acrylic graffiti over nitrocellulose painting; 5–6) acrylic graffiti over alkyd painting; 7–8) nitrocellulose graffiti over alkyd painting

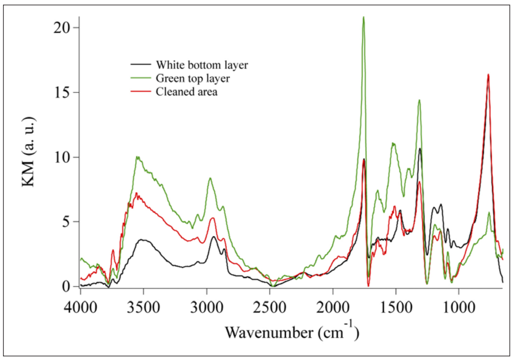

Figure 6. Micro-reflectance FTIR spectra showing the selective removal of unaged acrylic green graffiti from aged nitrocellulose white painting. The spectrum collected in the cleaned area presents the same peaks as that of the white painting, confirming that selective removal was successful

The fastest working Nanofluid C gave consistently better results in all situations, both in configurations testing unaged graffiti over an aged paint layer (Figure 4), and aged graffiti over an aged paint layer (Figure 5). Particularly notable were the good results in the most challenging task of removing nitrocellulose and alkyd graffiti from acrylic paintings, which was only possible when the acrylic paint was aged.

Microscopic observations of the cleaned surface confirmed visual observations regarding the higher performance of Nanofluid C, with minimal or no mechanical damage detected. In Figure 6, some FTIR spectra reported the example of the removal of acrylic green graffiti from nitrocellulose white painting. The three spectra, in particular, show the surface chemical composition of the untreated white paint, of the untreated green graffiti and of the cleaned area. In this area, almost no traces of green paint were visible when observing the sample under the microscope. The analysis of micro-reflectance FTIR spectra confirmed the good result of the selective removal test. As can be observed in the region below 1000 cm^{-1}, the spectrum of the cleaned area almost perfectly superimposes that of the white paint, while it is significantly different from that of the green graffiti. The intense (inverse) peak that both spectra show at 765 cm^{-1} is most likely due to a pigment, which is probably TiO_2, and can be conveniently used as a marker for the white paint.

CONCLUSION

It was shown that the use of microemulsion-loaded pHEMA/PVP hydrogels selectively removes acrylic-, nitrocellulose- and alkyd-based graffiti from paint layers including the same polymers, particularly when there is an age difference between the two layers. Graffiti removal can be achieved by means of a gradual swelling action performed by the nanofluid, which is limited to the surface layer by the retentive power of the hydrogel. By varying the application time and the number of applications on the same area, it is possible to tune the intensity of the cleaning action.

This novel method combines advanced nanostructured materials and offers an innovative alternative to the growing challenge of cleaning contemporary street art spoiled by graffiti.

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