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Cyrene™, a Sustainable Solution for Graffiti Paint Removal

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Abstract: Graffiti can create detrimental aesthetic and environmental damage to city infrastructure and cultural heritage and requires improved removal methods. Incumbent laser, mechanical and chemical removal techniques are often not effective, are expensive or damage the substrate. Solvents are generally hazardous and not always effective because of the insolubility of the graffiti paint. This study proposes a simple strategy for safe and effective graffiti removal, using the bio-based, non-toxic and biodegradable solvent dihydrolevoglucosenone (Cyrene™). The results showed that the type of substrate influenced the cleaning performance; in benchmark studies a non-porous substrate was easy to clean, while porous ceramic showed the presence of residual paint and yellowing when the conventional polar aprotic solvents were used. Cyrene, however, showed good removability of graffiti paint from both glazed and porous substrates, with little paint remaining in the pores of ceramic tiles. The paint suffered a reversible change in colour and a selective solubility of its components when using *N*-methyl-2-pyrrolidone; no changes occurred when Cyrene was used. While *N*-methyl-2-pyrrolidone and *N*,*N*′-dimethylformamide were only effective when neat, a Cyrene–water mixture showed some cleaning results. The performance of Cyrene was validated with Hansen solubility parameters and represents a greener and more sustainable solvent for paint removal.

Keywords: Cyrene; Cyrene–water; paint removal; sustainability; binary solvent system; Hansen solubility parameters

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1. Introduction

Graffiti has existed as long as human society, and has changed throughout time in its visual appearance, type and motivation [1]. Spraying graffiti escalated at the start of 1970s in the wake of hip-hop culture when "graffiti art" became popular in inner cities. Graffiti is sometimes sprayed, without any artistic intention, but as deliberate vandalism [2,3]. The invention of aerosol spray paints encouraged the proliferation of graffiti and it is widely used due to its visual impact, quick application, permanence, availability and low price [4].

Graffiti removal from public spaces and cultural heritage nowadays represents a costly activity for the state, and novel methodologies of graffiti removal are continuously developed to improve the process [4,5]. The choice of the cleaning method mainly depends on two factors: (1) the type of substrate that has been vandalised (including wood, metal, stones with different porosities) and (2) the type of graffiti paint used. Smooth surfaces, such as metals, plastics or glass, are easier to clean, while a porous substrate (e.g., concrete, calcareous stone, building stones, marble) can be irreversibly affected by the application of graffiti paint. Porous substrates can also be affected by the cleaning agents used and even its ageing process [4,6,7]. The historical, architectural and societal importance of many stone and marble buildings and statues makes this problem of widespread concern.

The large variety of graffiti formulations and brands of commercial paints for graffiti has enabled the graffitists to produce longer-lasting work. However, the specific chemical composition of the graffiti paints is not usually disclosed leading to a lack of knowledge of their behaviour when exposed to cleaning media and a real challenge for those who seek to remove it. The main monomers used in acrylic paints are acrylic acid, acrylates (methyl, ethyl or butyl), methacrylates (methyl or butyl) and styrene (Figure 1a–f). Cellulose nitrate monomer from the cellulose-based paint can be seen in Figure 1g.

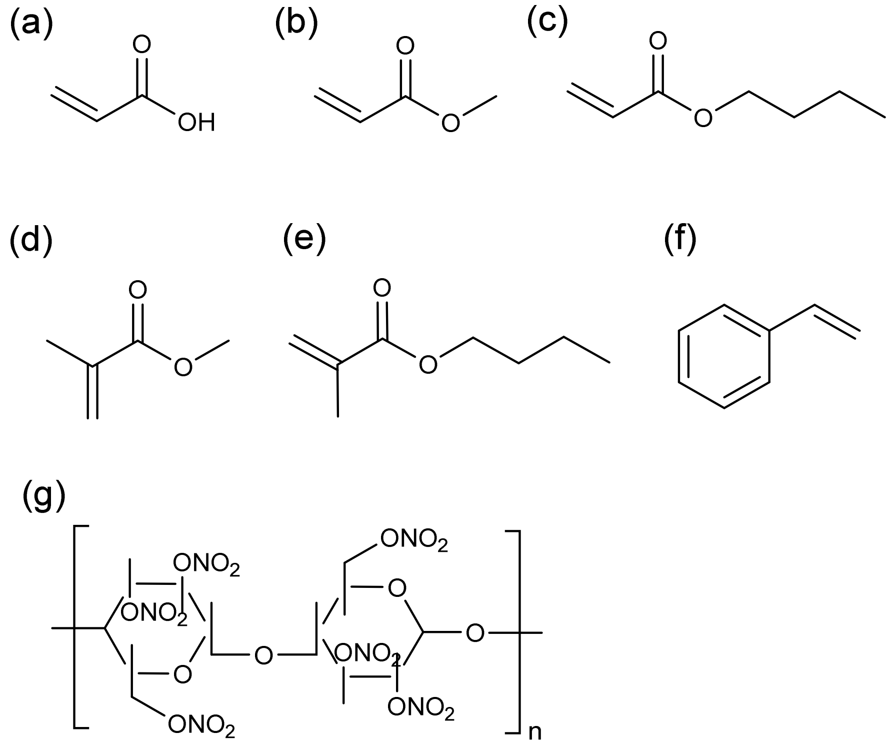

Figure 1. Chemical structures of monomers used in acrylic paints (**a**) acrylic acid, (**b**) methyl acrylate, (**c**) butyl acrylate, (**d**) methyl methacrylate, (**e**) butyl methacrylate and styrene (**f**). Cellulose nitrate monomer is also pictured here (**g**).

Currently graffiti removal methodologies include laser, mechanical methods (water pressure washer, blade scrapping, grit-blasting) and chemical [6,8–10]. However, they are typically expensive, demand high energy, only give temporary results, and generate compounds which are toxic to the public and the environment [4,11–13]. Chemical methods are often the most economical solution and are normally based on neat solvents, mixtures of solvents or solvent-containing compositions such as gels and poultices [2,14–16]. This method of graffiti removal is potentially dangerous due to the toxicity of the solvents involved and the negative environmental impact of the waste generated. Solvent spillage may endanger the environment and require expensive remediation to correct. Moreover, chemical methods using pure solvents may not always be successful because of the insolubility of the graffiti material or chemical contamination and shadows that can occur inducing the ghosting effect, making the removal more difficult [6].

Many commercially available paint strippers incorporate volatile compounds, linked to ozone formation and users' health hazards. They contain aromatics (toluene, xylene), amides (*N*-methyl pyrrolidone (NMP) and other pyrrolidones, *N*,*N*′-dimethylacetamide (DMAc), *N*,*N*′-dimethylformamide (DMF)), ethers (THF, dioxane) and esters (glycol ether-based solvents, carboxylic esters such as γ-butyrolactone (GBL)), halogenated hydrocarbons (dichloromethane (DCM)), alcohols, and ketones (acetone, cyclohexanone), in the pure form or in mixtures [17–23]. The chemical structures of some of the current solvents used in paint stripping formulations can be seen in Figure 2.

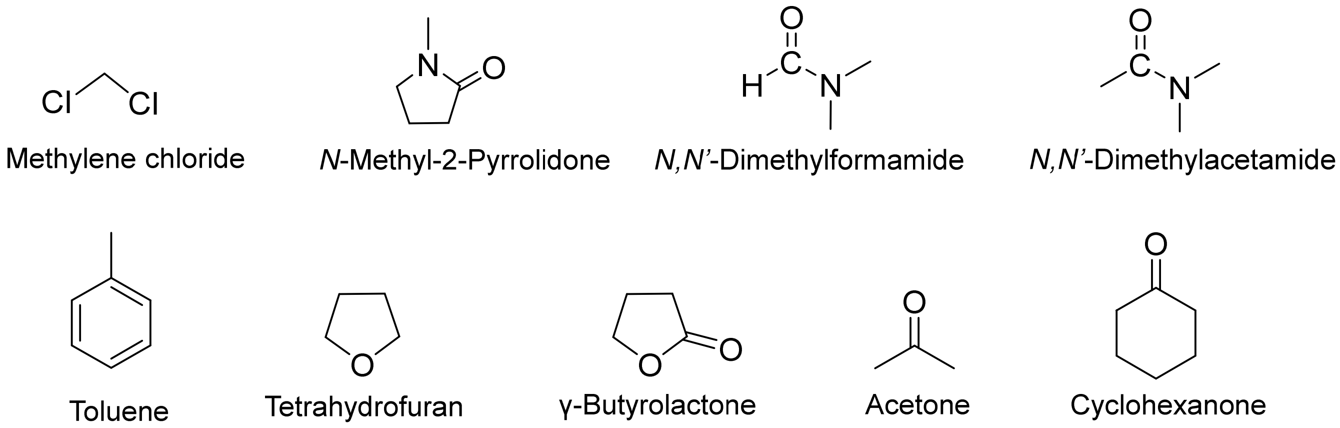

Figure 2. Chemical structures of solvents used in current paint strippers.

In the past, DCM was widely used in this application. DCM was recognised in 1990 as highly toxic and suspected of being a potential carcinogen [24]. The solvent was banned from paint strippers in the European Union (EU) in 2010 by ECHA and added to ANNEX XVII to REACH [25]. NMP replaced DCM in some paint strippers [24], but was suspected of having a teratogenic action in 2007 [26]. However, NMP remained in use until its restriction in 2018 in the EU. In 2017, DCM and NMP from paint stripping products have been associated with deaths and hence prohibited from these products in the USA [27]. DCM is classed as a CLP00 (classification, labelling and packaging regulation) carcinogen category 2. NMP can be mildly irritating to the eyes, skin and mucous membranes with short-term exposure (8 h exposure to 50 mg/m^3) [28,29], but mild to severe after longer times (two-day exposure) [30] and has been shown to be reprotoxic in rats [31,32].

Considering the increasingly stringent environmental and safety regulations which have been and will likely continue to be enacted on the currently use solvents, a major need exists for paint stripping formulations that are significantly more toxicologically and environmentally acceptable. The greener/cleaner products are required to have a low volatility; have fast performance across a wide range of coatings on different substrates; be produced from a cheap raw material; not damage the substrate; and contain safer chemicals for human health and the environment. Greener cleaning formulations under development contain dibasic esters, benzyl alcohol, formic acid, triethyl phosphate, DMSO, MEK, carbonates, γ-valerolactone (GVL), and esters [14,26,33–37]. Some examples of the greener solvents used in paint removal formulations are seen in Figure 3, together with Cyrene, which was used for the first time for the same purpose in this study.

Alternative halogen-free stripping formulations often have the disadvantage that they require relatively long action times, they strip one layer of paint at the time and hence, they require multiple applications for efficient cleaning [38]. In this study, non-porous substrates coated with aerosol paints have been chemically cleaned using either pure solvents or these same solvents as part of poultices. As polar aprotic solvents are widely used to remove paints from various substrates, we proposed the use of an emerging, bio-based, non-toxic and bio-degradable solvent. Cyrene is manufactured using wood waste and has proven to be non-toxic, non-persistent and biodegradable [39]. Cyrene has already been demonstrated as a suitable solvent for a multitude of applications, successfully replacing the traditional and more toxic polar aprotic solvents NMP, DMF and DMAc [40–44]. Herein we use a non-porous aluminium slide and a highly porous ceramic tile to study removing both acrylic and cellulose-based graffiti paints by Cyrene for the first time.

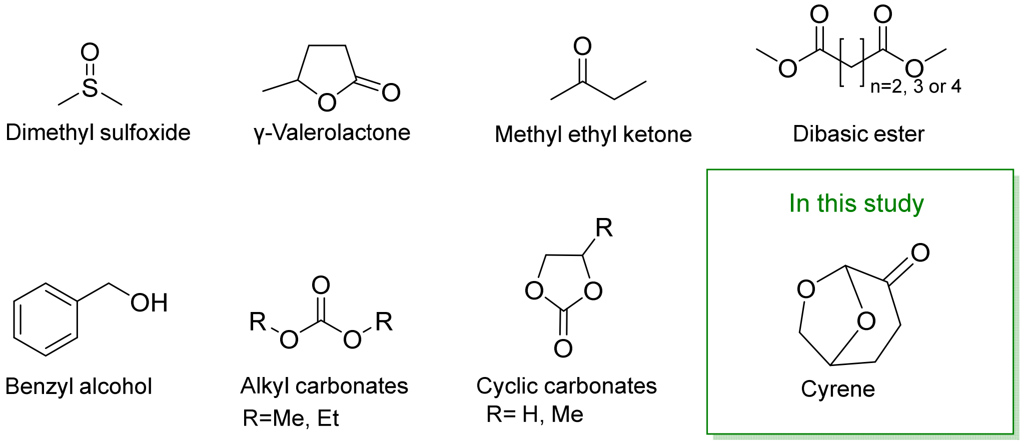

Figure 3. Chemical structures of safer solvents used in the formulation of greener paint strippers. Cyrene was used in this study as a safer, bio-based alternative to conventional paint removal products.

2. Materials and Methods

2.1. Solvents

Cyrene 98.5% was provided by Circa Group SA. *N*-methyl-2-pyrrolidone (NMP) and 99.5% and methylene chloride (DCM) $\geq$ 99%, were purchased from Fisher Scientific Chemicals (Loughborough, UK). *N,N*′-Dimethylacetamide (DMAc) $\geq$ 99.5%, and dimethyl sulfoxide reagent grade 99.9% were sourced from Merck (London, UK). *N,N*′-Dimethylformamide (DMF) technical grade, min. 98% was purchased from VWR Chemicals (Lutterworth, UK). DMF anhydrous 99.8% was sourced from Merck. All the other solvents were purchased from Merck or Fisher Scientific Chemicals.

2.2. Substrates and Spray Paints

Aluminium slides were sourced from Amazon and cut into 5 × 10 cm × 2 mm pieces. Glazed ceramic tiles were purchased from a local store and cut into small pieces of 2 × 3 × 1 cm. Two solvent-based aerosols were used in this study. Fast-drying Kobra HP250 400 mL Aerosol Spray Paint—Red Orange, 100% acrylic formulation (from Kobrapaint.co.uk, accessed on 1 March 2023) with a high "solid" content containing acetone, butyl acetate, 1-methoxy-2-propanol was used as received for "acrylic paint removal tests". Cellulose-based Clostermann Aerosol Honda Repsol Racing Red High Gloss spray paint from Advanced Paints.co.uk (accessed on 1 March 2023) contains butanol and acetone and was used for "cellulose paint removal tests". Two acrylic binders, Viacryl SC 134/50WS165 and SC 166/45BAC, kindly donated by Allnex, Germany, were used for binder dissolution in Cyrene and NMP.

2.3. Samples Preparation

Non-porous aluminium foils were one-coat painted (one side only) in a fume-hood with the commercially available red aerosol paints described above and left to dry for a week (Figure S1a,b). The porous ceramic tiles were coated on the glazed side up and left to air-dry under laboratory conditions for one week (Figure S1c,d). The tiles were then rotated to the glazed side down and the porous surface coated and left to dry for one week.

2.4. Immersion Tests

Direct interaction between pure solvents and polymer films was used to assess the dissolution of polymeric coatings in different individual solvents. In a simple test, the coated aluminium slides were partly immersed in beakers containing 20 mL of the selected pure solvents (Figure S2a). The painted ceramic tiles were immersed in vials containing 20 mL of different solvents and rolled for a dwelling time of 3 days to ensure uniform contact with the solvents. Stuart analogue tube rollers were used for complete mixing (Figure S2b). After three days, the tiles were removed from the solvent and a gentle mechanical action was performed using tissue paper to remove any residues; no rinsing was performed afterwards.

2.5. Poultice Test

This test represents and more equivalent method to current cleaning materials, using a paste formed of talc and solvent, followed by scraping this off after one day of contact. Small spots of polymeric coatings were applied to the substrate and left to dry overnight (Figure S3a). Poultices were prepared from 2 g of talc and 5 mL of neat solvent (Figure S3b). The obtained poultices were applied on the painted spots and covered with a plastic film to prevent the solvent from evaporating (Figure S3c). The next day, the plastic film was removed from the treated spots and the residues were removed from the surface using a soft toothbrush and tissue paper.

2.6. Paint Characterisation

Chemical functional groups present in samples were investigated using a PerkinElmer Spectrum 400 FT-IR/FT-NIR spectrometer with transmittance peaks in the 4000–650 cm^{-1} region, with rapid scanning (four scans) and a resolution of 4 cm^{-1} at room temperature. Prior to this test, dried, hardened paint was carefully scrapped off the glazed side of the tile, avoiding removal of the substrate.

2.7. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) Analysis

ICP-MS was used to quantify the chemical elements found in the acrylic paint and ceramic tiles using an Agilent 7700 series ICP-MS fitted with a standard Ni sample, skimmer cones and 64 coupled to a mass spectrometer. The digestion vessels containing the samples were sealed and placed in a microwave (Milestone Ethos Up SK-15) and heated to 200 °C for 15 min. The digested samples were each diluted with ultrapure deionized water (15 mL), filtered and the filtrate was subjected to ICP analysis. The results for each element were fitted onto the calibration curve and multiplied by the dilution factor to produce the concentration for each element in the samples.

2.8. Hansen Solubility Parameters and Laboratory Cleaning Tests

Hansen solubility parameters (HSP) were used to predict the dissolution and extraction of acrylic and cellulose paint from the porous ceramic substrate. The three parameters can predict, when mapped in a 3D Hansen space, the solubility of molecules in different solvents. Solubility was assessed based on visual inspection and ranking scores were given from 1 to 5, 1 meaning fully dissolved, 4 only the glazed side was cleaned and 5 where the solvent did not clean the painted ceramic tiles in any way (Figure S4). The obtained solubility scores were inserted into the HSPiP software, 5th edition, version 5.0.03, to generate an empirical Hansen solubility parameters sphere for each commercial paint, and their RED, δ_D, δ_P and δ_H were calculated. This was based on a spherical model (Hansen solubility sphere) where good solvents are inside and bad ones are outside the computed sphere within the Hansen space. The RED values determine the ability of a solvent to dissolve a solute. A RED ≤ 1 suggests a high solvent–solute affinity; a RED > 1 suggests a low affinity.

2.9. Water Content

Water content analyses were carried via volumetric Karl Fisher titrations using a 907 Titrando unit (Metrohm, Herisau, Switzerland). The titrant used to analyse the samples was Hydranal Composite 5 K and the working medium used was Hydranal Composite 5. All titrations were carried out in triplicate at 22 °C with a minimal duration of 90 s and sample sizes of approximately 0.2–0.8 g.

2.10. Viscosity Measurements

The dynamic viscosity of Cyrene and Cyrene–water mixtures was realised by using a Brookfield RVDV-E rotational viscometer, at 20 °C and 100 rpm. Apparent viscosity of the samples was determined at 20 °C using a Malvern Kinexus pro+ rotational rheometer, using 0.1448 mm distance between the plates and shear rate from 0 to 100 Pa.

3. Results

In this study, 33 solvents were trialled for graffiti paint removal from aluminium foil and ceramic tiles (glazed and porous side) (Table 1):

Table 1. The types of graffiti paint, the substrates, cleaning methods and the solvents used in this study.

Solvent	Graffiti Paint	Substrate	Cleaning Method
Cyrene	acryl, cellulose nitrate	aluminium foil, ceramic tile (both sides)	immersion, poultice
N-Methyl-2-Pyrrolidone	acryl, cellulose nitrate	aluminium foil, ceramic tile (both sides)	immersion, poultice
N,N′-Dimethylformamide	acryl, cellulose nitrate	aluminium foil, ceramic tile (both sides)	immersion, poultice
N,N′-Dimethylacetamide	acryl, cellulose nitrate	ceramic tile (both sides)	immersion, poultice
Dimethyl Sulfoxide	acryl, cellulose nitrate	ceramic tile (both sides)	immersion, poultice
Methylene Chloride	acryl, cellulose nitrate	ceramic tile (both sides)	immersion
Acetone	acryl, cellulose nitrate	ceramic tile (both sides)	immersion, poultice
Acetonitrile	acryl, cellulose nitrate	ceramic tile (both sides)	immersion
Dimethyl Carbonate	acryl, cellulose nitrate	ceramic tile (both sides)	immersion
Propylene Carbonate	acryl, cellulose nitrate	ceramic tile (both sides)	immersion
Tetrahydrofuran	acryl, cellulose nitrate	ceramic tile (both sides)	immersion
2,2,5,5,-Tetramethyloxolane	acryl, cellulose nitrate	ceramic tile (both sides)	immersion
Oxymethylene Dimethyl Ethers	acryl, cellulose nitrate	ceramic tile (both sides)	immersion
Ethyl Acetate	acryl, cellulose nitrate	ceramic tile (both sides)	immersion
Acetic Acid	acryl, cellulose nitrate	ceramic tile (both sides)	immersion
Ethanol	acryl, cellulose nitrate	ceramic tile (both sides)	immersion
Methanol	acryl, cellulose nitrate	ceramic tile (both sides)	immersion
1-Butanol	acryl, cellulose nitrate	ceramic tile (both sides)	immersion
1-Propanol	acryl, cellulose nitrate	ceramic tile (both sides)	immersion
2-Propanol	acryl, cellulose nitrate	ceramic tile (both sides)	immersion
Water	acryl, cellulose nitrate	ceramic tile (both sides)	immersion, poultice
Lactic Acid	acryl, cellulose nitrate	ceramic tile (both sides)	immersion
Toluene	acryl, cellulose nitrate	ceramic tile (both sides)	immersion
Cyclohexene	acryl, cellulose nitrate	ceramic tile (both sides)	immersion
Hexane	acryl, cellulose nitrate	ceramic tile (both sides)	immersion
Heptane	acryl, cellulose nitrate	ceramic tile (both sides)	immersion
Chlorobenzene	acryl, cellulose nitrate	ceramic tile (both sides)	immersion
Diethyl Ether	acryl, cellulose nitrate	ceramic tile (both sides)	immersion
2-Methylfuran	acryl, cellulose nitrate	ceramic tile (both sides)	immersion
Propionic Acid	acryl, cellulose nitrate	ceramic tile (both sides)	immersion
β-Pinene	acryl, cellulose nitrate	ceramic tile (both sides)	immersion
Benzyl Alcohol	acryl, cellulose nitrate	ceramic tile (both sides)	immersion
Dichloroethane	acryl, cellulose nitrate	ceramic tile (both sides)	immersion

3.1. Paint Removal by Immersion

The removal of red paints was chosen because it is a colour widely used (i.e., by graffitists) and it is typically more difficult to remove than other colours, attracting the attention of researchers in previously reported attempts at paint removal from different substrates [4,45–47].

The interaction between the solvent and either acrylic or cellulose nitrate paint was initially investigated by immersing painted non-porous aluminium slides and porous ceramic tiles in Cyrene, NMP and DMF. The effectiveness of each solvent was ranked by visual observation.

In the immersion tests of a non-porous aluminium slide, NMP and Cyrene demonstrated efficient paint removal (Figure 4). Removal of both cellulose nitrate and acrylic paints occurred in a matter of minutes in NMP, with complete dissolution observed. Conversely, Cyrene penetrated the paint and caused it to swell, taking longer to remove the paint.

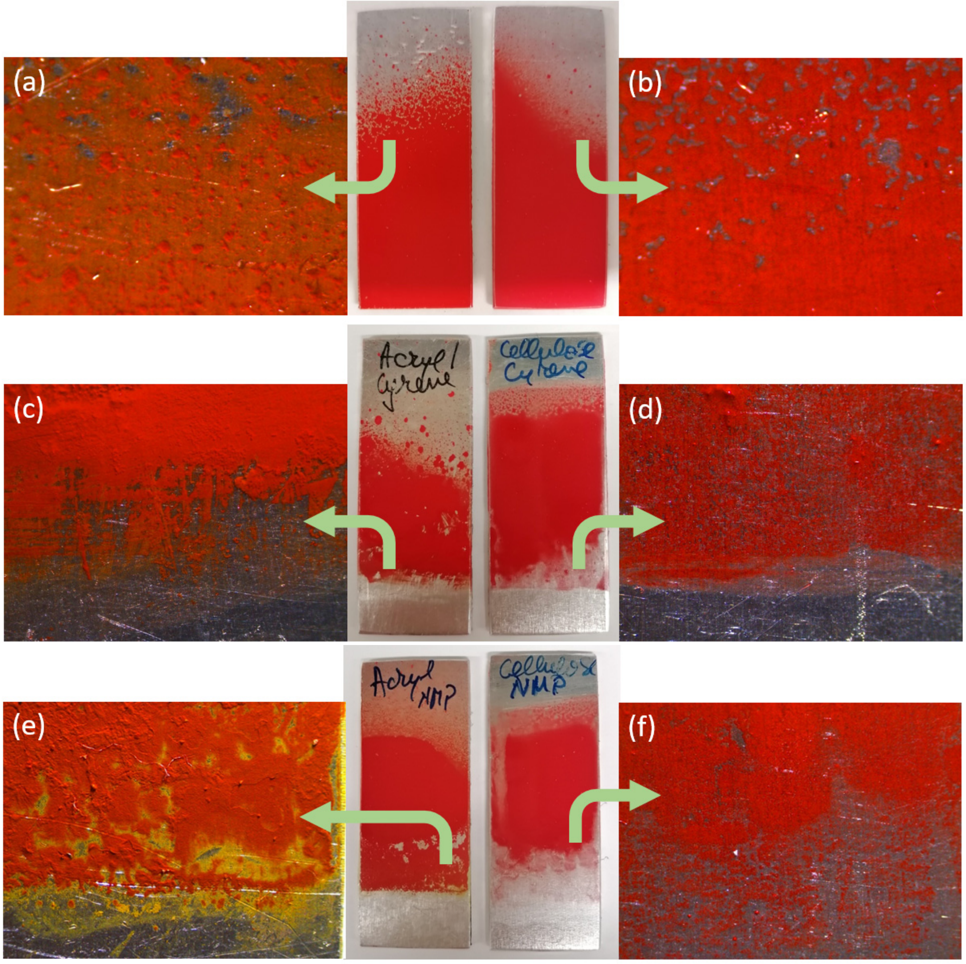

Figure 4. Acrylic (**c**,**e**) and cellulose (**d**,**f**) paint removal images from aluminium slides using Cyrene (**c**,**d**) and NMP (**e**,**f**). Painted aluminium foils with acrylic (**a**) and cellulose-based paints (**b**) are shown for comparison.

A yellow layer was observed on the substrate when the paint was removed by NMP (Figure 4b,g), whilst this yellow layer was seen to a lesser extent in case of Cyrene (Figure 4a,e,f). As the acrylic paint used in this study was of a red-orange shade, the pigments contain red, orange, and yellow components (see the ICP-MS data). The yellow layer is believed to be the insoluble yellow pigment in the solvent.

The water content of the solvent played an important role in paint dissolution. As seen in Figure S5, DMF was only efficient when of 99.8% purity and a low water content (0.12%). When the solvent had a higher water content (approx. 2%), DMF did not dissolve the paint. The water content was determined for the main polar aprotic solvents used, including Cyrene (Table S1).

In the case of a highly porous ceramic substrate, the paint was more difficult to remove with neat solvents. The paint residues enter the pores, contaminating the substrate and reducing the cleaning efficiency. This causes a “ghosting” effect as cleaning is only partially effective (Figure 5):

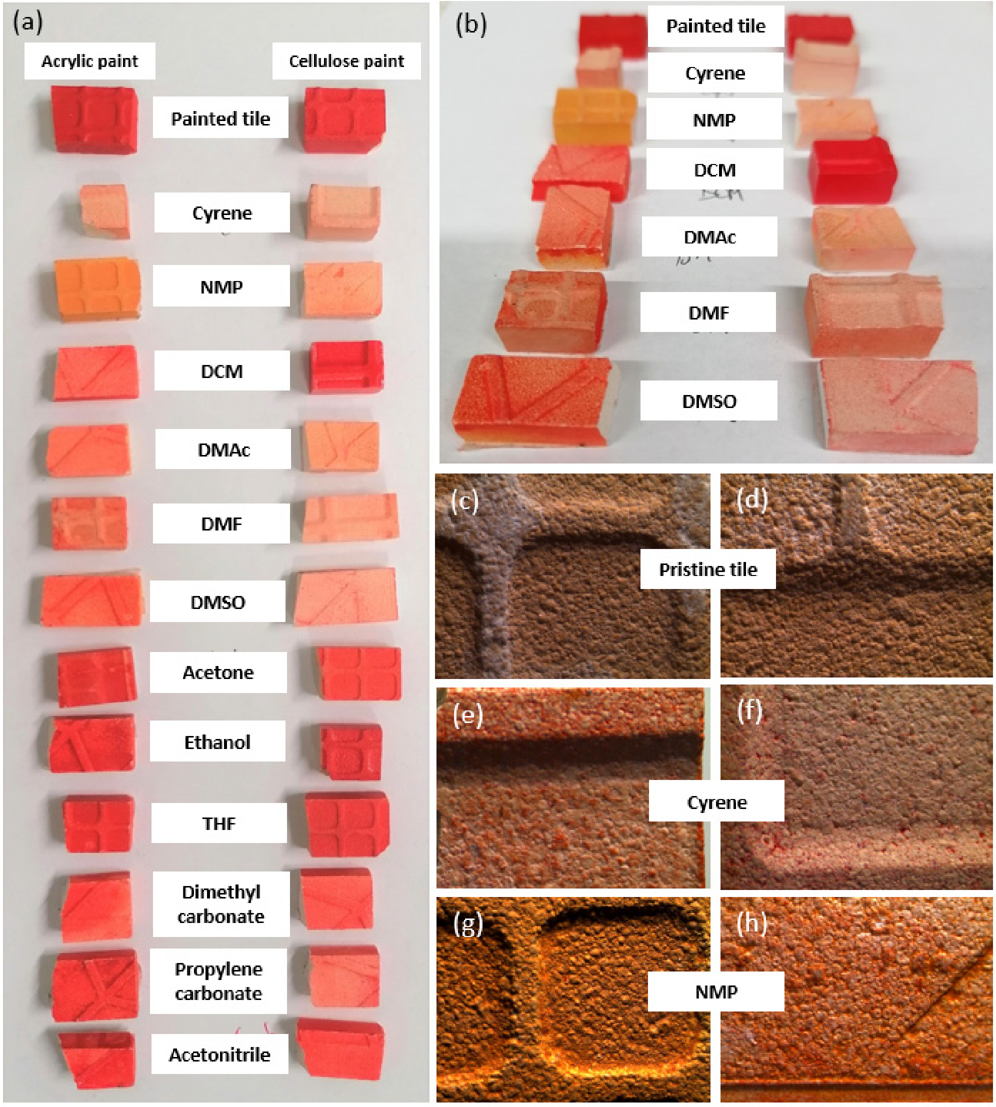

Figure 5. Acrylic and cellulose-based paint removal from ceramic tiles with Cyrene, *N*-methyl-2-pyrrolidone (NMP), methylene chloride (DCM), *N*,*N*′-dimethylacetamide (DMAc), *N*,*N*′-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetone, ethanol, tetrahydrofuran (THF), dimethyl carbonate, propylene carbonate and acetonitrile (**a**). Untreated painted tiles are shown on top for comparison. A closer look at the tiles cleaned with polar aprotic solvents (**b**). Higher magnification pictures of the Cyrene (**e**,**f**) and NMP (**g**,**h**) removal efficiency of acrylic (**e**,**g**) and cellulose-based paints (**f**,**h**). Pristine tiles are shown for comparison (**c**,**d**).

Interestingly, in our investigation, the acrylic paint was mostly detached from the porous substrate by Cyrene (Figure 5a,b,e,f). However, traces of red pigments can still be seen. When using NMP, a yellow residue can be observed on the entire surface of the porous substrate (Figure 5a,b,g,h). Yellowing can also be seen in the case of other polar aprotics, such as DMAc and DMSO (Figure 5b).

When cleaning the cellulose-based aerosol paint, NMP, DMF and DMAc left the porous substrate partly coloured in yellow (Figure 5b). At a higher magnification, the picture of the tile cleaned by NMP (Figure 5f) showed large areas of yellow residue present of the porous substrate painted with cellulose-based paint. The yellow effect was not present in the case of Cyrene (Figure 5e). This residue is believed to be inorganic substrates including pigment washes and coatings. DCM did not dissolve the cellulose paint and only partially removed the acrylic paint, despite it being widely used in the past (Figure 5a). The poor performance of DCM may be attributed to fast evaporation of the solvent.

The solvents used for paint removal were further analysed. The tiles were removed from vials containing different neat solvents for both acrylic (Figure 6a) and cellulose nitrate (Figure 6b)-based paint formulations. A clear solution and a yellow solid residue were observed after chemical cleaning of the acrylic aerosol by NMP, DMAc and THF; this effect is also partially seen in DMSO. For chemical cleaning of a cellulose-based paint (Figure 6b), yellow solutions were observed after cleaning by NMP and THF (THF evaporates over time; hence in small amount in the picture); this effect was partially seen in DMAc and DMSO. For all the other solvents screened and for both paint types the residue recovered was much more orange-red in colour.

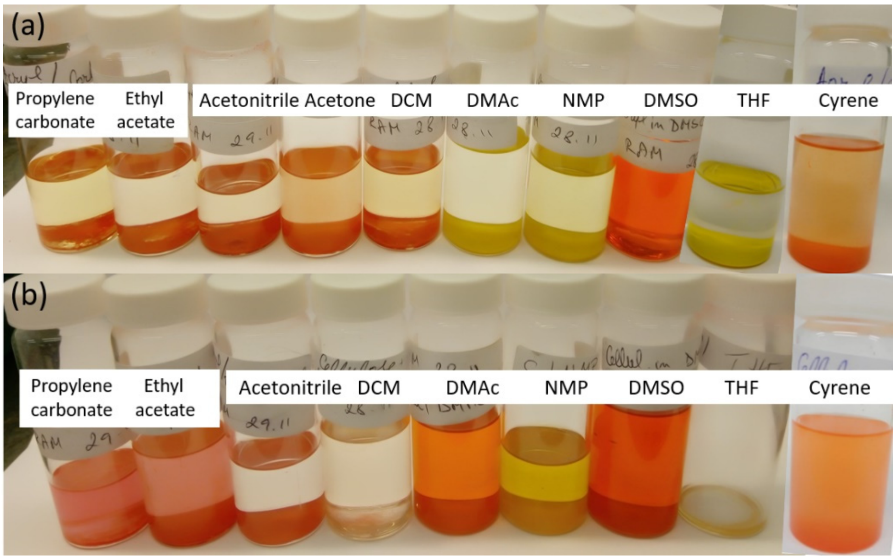

Figure 6. The solvent and paint residues after removal of acrylic (**a**) and cellulose nitrate (**b**) paints using various neat solvents, including Cyrene.

3.2. Paint Removal by Poultices

In many cases, commercially available cleaning compositions are not able to penetrate micrometre-sized pores of fine-pored stone tiles to remove paint residues. Hydrogels and nanofluids, such as micelles or microemulsions, have been used in selective removals and to minimise the diffusion of paint inside the substrate carried by the solvent [2,5,48]. This type of paint removal is generally performed in the conservation of cultural heritage, where a controlled, layer-by-layer paint removal is necessary. Hence, if the removal is not correctly performed, it can irreversibly damage valuable heritage assets. In our study, we used neat solvents as part of poultices, to test their efficiency in paint removal which would draw the paint off from the substrate by capillary action [5,14].

Both glazed (Figure 7a,b) and porous sides (Figure 7c,d) of the ceramic tiles were stained using small spots of paint. After the paints dried out, poultices of talc and neat solvents were applied to the spots to remove the coating. The paint residues were scraped off a non-porous substrate easily with the poultice when using both Cyrene and NMP (Figure 7a,b). However, a porous substrate is more difficult to clean due to its porosity and void connectivity which determine the extension and depth of this shadowing generated by the use of solvents (Figure 7c,d) [49]. As seen in Figure 7c, all solvents left a shadow after the acrylic paint removal. NMP, DMF, DMAc and DMSO (lesser effect) left behind a yellow layer, while Cyrene removed the paint slightly better with no yellowing effect. This is likely because the first group of solvents dissolves the red pigment and extracts it from the pores but does not dissolve the yellow pigment, leaving this as a residue. DMSO left a wet spot for longer due to its high boiling point (B.P. of 189 °C), the opposite is true of acetone, which evaporates rapidly (B.P. of 56 °C).

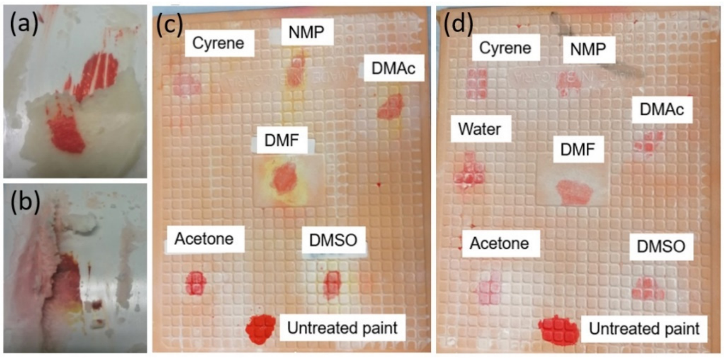

Figure 7. Paint removal from a non-porous substrate using a poultice and Cyrene (**a**) or NMP (**b**). The removal of the acrylic (**c**) and cellulose-based paint (**d**) from the porous side of the ceramic tiles after cleaning by several solvents, including Cyrene and NMP. Small untreated paint spots were applied for visual comparison.

3.3. The Effect of the Solvent on the Paint

To study the effect of the solvent on the paint, dried acrylic paint was dissolved in NMP and Cyrene. The solution was decanted the next day and the solid washed with the same solvent. This process was repeated nine times. The final samples in Figure 7a, b were left to sit for a week.

Cyrene dissolved some of the yellow pigments in the first stage, as seen in vials C/1 to C/3 in Figure 8a, where the solution appears to be orange, which persisted for months. On the other hand, Figure 8b,c show how NMP and acrylic paint solution exhibits a reversible change in colour, from bright red to dark red (Figure 8c), and back to red, then to orange and ultimately to yellow after five washes (Figure 8b). This reversible change occurred overnight. This could indicate NMP selectively dissolving the red pigments while the yellow pigments remain unaffected at the end of the process. At the end of the dissolution process, the residue of cleaning acrylic paint using NMP was yellow, while after cleaning the same aerosol paint with Cyrene, the residue remained red. These solid residues were further analysed by ATR-FTIR and ICP-MS.

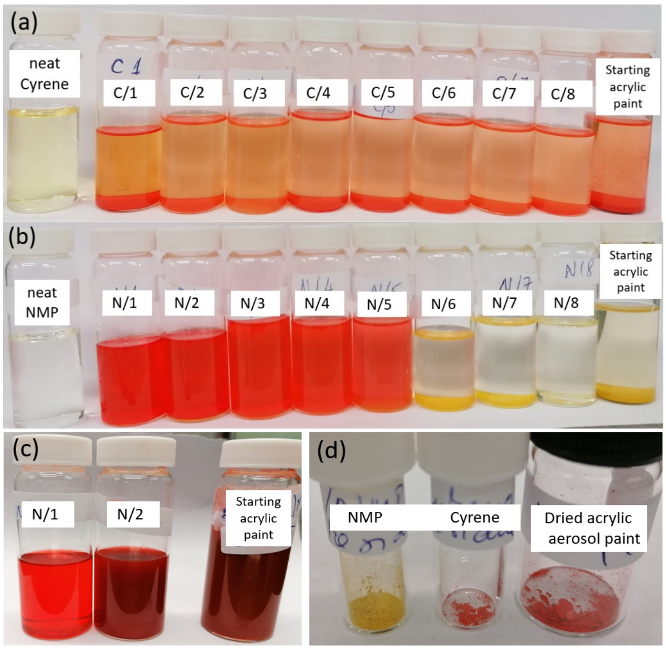

Figure 8. The sequential stages of the acrylic paint dissolution in Cyrene (**a**), NMP (**b**,**c**) and the remaining residue compared to a sample of the dry paint (**d**).

3.4. Infrared Spectroscopy

The infrared spectra of the acrylic paint has previously been reported in the literature [46]. The paint compositions are complex, consisting of binders (to hold all the ingredients together), pigments (for colour and opacity), solvents (that allows the mixture to flow) and additives (to improve wetting, plasticity, fluidity, thickness, UV stability, etc.) [4,50]. Acrylic resins are based on the esters of acrylic and methacrylic acids, while cellulose resins are composed of cellulose nitrate and a second resin (usually alkyd) [51]. Two commercial acrylic binders were studied in this work: Viacryl SC134 and SC166. Viacryl SC134 is a methacrylate resin with rapid drying, is resistant to water and alkali and is used for paints or resin-modified plasters. Viacryl SC166 is a fast-drying acrylic co-polymer with good adhesion to metals, and good compatibility with aerosols. Observed signals from the acrylic resin (Figure S6) indicate the presence of C-H asymmetric stretching vibrations (2960–2870 cm^{-1}) [15]. The broad band at 2960–2865 cm^{-1} and the peak at 1726 cm^{-1} can be attributed to C=O stretching in ester vibration. The peaks in these regions are present in both acrylic binders and in the pristine acrylic paint used. However, they faded in the residue after dissolving in Cyrene and completely disappeared in the case of NMP. This means that the binder was dissolved and washed out when NMP was employed. However, when Cyrene was used to dissolve the acrylic paint, the binder only dissolved partially, with some resin still present after the nine washes, suggesting a layer-by-layer paint removal.

3.5. ICP-MS Analysis

The solid residue left by the chemical cleaning of the acrylic aerosol paint was further analysed by ICP-MS (Table S2). The acrylic paint used in this study was of a red-orange shade. Red pigments typically contain cadmium (Cd), mercury (Hg), arsenic (As), iron (Fe), silicon (Si), aluminium (Al), zinc (Zn), bromine (Br, titanium (Ti), calcium (Ca), and chlorine (Cl) and have been reported previously [46,52]. Additionally, the yellow and orange pigments contained in the aerosol possibly contain Mg, Cd, Ca, Ba, K, Cr and Sn. Magnesium (Mg) pigments are yellow-green and are mainly used in paint for corrosion protection, similar to Zn and Cr [53]. Orange pigments contain elements such as Cd, Se or Cr. Arsenic (As) and mercury (Hg) are poisonous and are not used nowadays [54]; however, As was present in small amounts in the acrylic aerosol used in this work. After repeated dissolution cycles of the acrylic paint in Cyrene, the amount of inorganic material in the residue (Figure 8d) showed a decrease in the concentration of elements such as Ca, P, Na, Pb, Cd and Se. This could indicate the solubility of the yellow/orange pigments (Ca, Cd and Se) in Cyrene generating a stable yellow/orange solution (vials C1–C3 in Figure 8a). The percentage of yellow and orange pigments containing Mg, Cd, Ca, Ba, K, and Cr were visibly higher in the residue from an NMP-based dissolution than after Cyrene dissolution, hence the bright yellow colour residue.

3.6. Paint Removal Mechanism

In chemical cleaning, the solvent swells the paint and disrupts the adhesive force between the layers of paint and between the paint and substrate, ultimately leading to both lifting and dissolving the paint film. The cleaning of acrylic and cellulose-based paints by Cyrene and NMP differed in the process by which dissolution occurred. The mechanism of paint removal by Cyrene is described in Figure 9.

Cyrene removed both acrylic and cellulose-based paints from a non-porous substrate, when used as neat solvents or as part of a poultice. Cyrene was also able to remove both paints from a porous substrate when used on its own. However, in the case of a porous ceramic substrate, Cyrene partially removed the paint after a single use and no yellowing was observed. That is considered an advantage in controlled paint removals from paintings and other objects (e.g., artwork), where thin layers of coatings need to be removed without affecting the layers underneath. Generally, Cyrene required a longer time (over an hour) to remove the paint coating compared to NMP (bellow 5 min), suggesting Cyrene removed the acrylic paint layer by layer (Figure S7a).

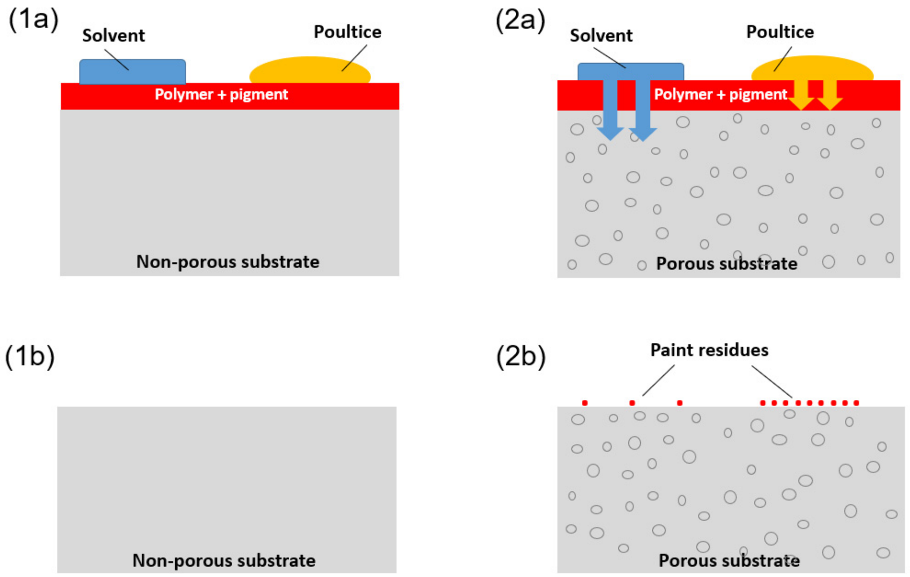

Figure 9. The mechanism of paint removal from non-porous (**1a**) and porous (**2a**) substrates, using neat Cyrene and as part of a poultice. The results of paint removal from a non-porous (**1b**) and porous (**2b**) substrates.

In the case of the cellulose-based paint, the removal of the paint layers occurred in larger pieces prior to dissolving in the solvent (Figure S7b). In some cases, this phenomenon of lifting off is desirable in order to avoid chemical contamination of the substrate (e.g., wood, art objects) and using Cyrene in these applications could represent a simple method of controlled cleaning [16]. NMP swelled and detached both paints from the substrate, dissolving it relatively fast, but leaving behind a yellow layer. NMP migrated through the coating, detaching the polymeric paint resins but causing chemical contamination of the substrate by migrating some insoluble paint components into the pores of the substrate.

Cyrene has a higher viscosity than of NMP at 20 °C (Table S3), and this could explain why it takes longer to Cyrene to swell and detach the paint from the substrate. Smaller solvent molecules often penetrate rapidly into the coating, but in most cases also evaporate again rapidly. This possibly explains why NMP poultice coloured red during the process (NMP evaporates faster) (Figure 7b) whereas Cyrene-based poultice appeared colourless (Figure 7a). Larger solvent molecules often require considerably more application time and often lead to swelling of the paint/coating; these can then be rubbed off mechanically from the substrate more easily.

3.7. Solvent–Polymer Interactions Predicted by Solubility Parameters

Hansen solubility parameters (HSPs) were used to rationalise the thermodynamics of dissolving the paints [55,56]. The effectiveness of each solvent was ranked by visual observation and the scores for each solvent can be seen in Tables S4 and S5. The representation of solvents capable of dissolving the intended paint takes the form of a sphere defined by three axes corresponding to the dispersion, polarity, and hydrogen bonding parameters. Based on the three Hansen parameters and scores given, for the acrylic paint the optimal solvents have strong dispersion forces (Figure 10).

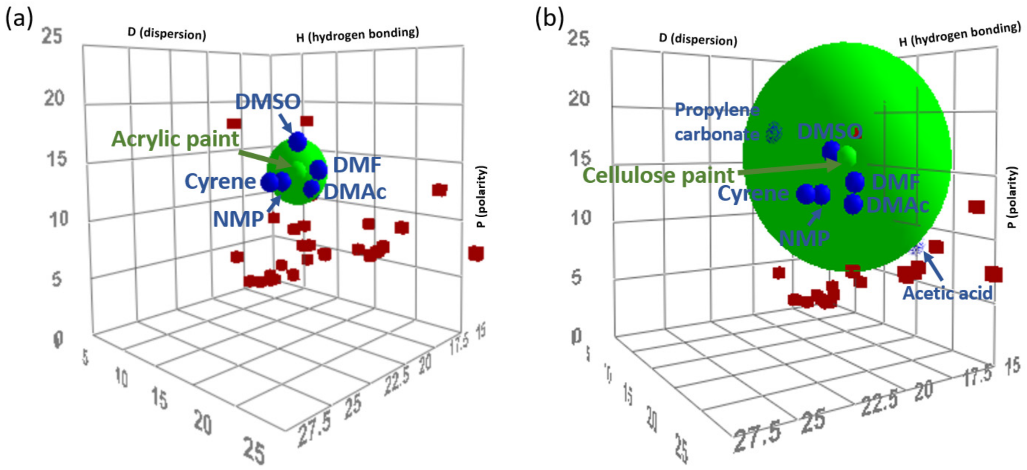

Figure 10. The Hansen spheres of the acrylic paint (**a**) and cellulose (**b**)-based paint indicating good solvents (blue), poor solvents (red), and the boundary defining good solvents (green sphere cage) centred on the calculated position of the substrate.

As seen in Figure 10a, the Hansen sphere only contains polar aprotic solvents, because they were the only solvents effective in acrylic paint removal. NMP was calculated as the most suitable solvent for acrylic paint dissolution, occupying the position closest to the centre of the sphere, followed by DMF, Cyrene, DMAc and DMSO, all with RED < 1 (Table S4). However, when tested, DMF only removed the paint when dry, while NMP left a yellow layer on the substrate.

The cellulose-based paint was best dissolved by solvents with high dispersion forces and high dipolarity (Figure 10b). This makes polar aprotics most effective for this type of paint, including Cyrene and NMP (Table S5). The similar HSPs of NMP and Cyrene mean that they would expectedly exhibit similar performances in dissolving any given substrate (i.e., the resin component of a paint formulation). However, this is a thermodynamic theory of solubility.

In practice, a difference between the action of NMP and Cyrene in paint removal is evident and can be attributed to a kinetic phenomenon. The higher viscosity of Cyrene compared to NMP reduces the rate of mass transfer in solution. This resulted in the observed swelling and subsequent flaking of the paints in Cyrene before dissolution, whereas in NMP the transition from swollen resin to dissolved resin is rapid enough so not to be distinguishable as separate stages. The high viscosity of Cyrene has previously been attributed to improving the stability of dispersions by reducing settling velocity [57]. Within the scope of this work, the lifting of paint from a surface remains beneficial even without achieving complete solubility as in many instances manual removal (i.e., wiping with a cloth) will follow the application of solvent as part of the cleaning process.

Another distinction between the performance of NMP and Cyrene is the intensity and colour of the residual staining of the substrate (ghosting). NMP appears to selectively dissolve paint components, leaving behind a yellow pigment. The slower action of Cyrene is less disruptive to the formulation, hence no visible paint fractionation in components was observed.

3.8. The Efficiency of Cyrene-Water Mixture in the Paint Removal

As Cyrene cleaned the graffiti paint from both porous and non-porous substrates but water proved to be inefficient in paint removal, a mixture of 75% Cyrene–25% H_2O (%v/v) was tested in this work. For comparison, a mixture 75% NMP–25% H_2O was also tested (Figure S8). The Cyrene–water mixture removed the acrylic aerosol better (Figure S8a,c) than the cellulose-based paint (Figure S8a,d). However, the new NMP-based binary system did not dissolve the acrylic or cellulose-based paint (Figure S8b,e,f).

The viscosity of Cyrene and its mixtures with water were measured in this study and complete data can be found in Table S5. The dynamic viscosity of Cyrene at 20 °C was determined to be 46 cP using a rotational viscometer and 11.67 when a rheometer was employed. When water was added to Cyrene, the viscosity changed. The mixture of 75% Cyrene and water showed higher viscosity than of neat Cyrene, due to the presence of Cyrene/diol/water. As the amount of Cyrene in the water decreased, the viscosity of the blend also decreased. A mixture of 50% Cyrene in water showed a similar viscosity to neat Cyrene, while the viscosity of a 25% Cyrene in water dropped dramatically due to the high amount of water present in the system. Interestingly, the temperature increased during the blending of the two solvents, with increases from 20 °C (neat Cyrene) to 32 °C, 34 °C and 38 °C for 25%, 75% and 50% Cyrene in water, respectively. This indicates that the addition of water to Cyrene is an exothermic process that generates heat.

3.9. Other Greener Solvent Systems Proposed for Paint Removal

Other mixtures of Cyrene with greener solvents have been proposed for future work. GVL and 2-MeTHF mixtures with Cyrene are already on the market and various ratios have been proposed in this work [58]. Full data can be seen in Tables S6 and S7. For acrylic paint dissolution, when plotting the new mixtures of Cyrene with GVL and 2-MeTHF, the new mixtures were calculated as effective at 50% Cyrene–50% GVL and 75% Cyrene–25% GVL, with RED < 1 (Table S6). The blend of 75% Cyrene–25% water was calculated by HSPiP as likely to dissolve the cellulose-based paint, as well as all Cyrene–GVL mixtures and neat GVL, all with RED < 1 (Table S7).

3.10. Cost and Renewability Considerations

The chemical paint removal method is often regarded as a cost-effective approach to stripping paint from a variety of substrates and is commonly used by city councils. However, the type of solvent used in the process plays a crucial role in achieving efficient cleaning results. The cost of the solvent/cleaning formulation becomes increasingly significant when large quantities are required. Cyrene, while more expensive than its toxic counterparts NMP or DMF, is expected to become more affordable with increased production. In the meantime, a simpler alternative to lower its cost is to mix Cyrene with other solvents. Currently, 50-50 mixtures of Cyrene with GVL and 2-MeTHF are being sold, but this has not significantly lowered the price. Water can be added to the cleaning formulation to reduce the cost of the solvent and still achieve decent paint removal quality. Furthermore, Cyrene can be easily separated from a mixture with water by evaporating water first, allowing for the solvent to be reused. In a more intricate cleaning formulation, Cyrene can be recovered by vacuum distillation. However, this method is energy-intensive and requires a reduced pressure environment.

4. Conclusions

Cyrene has been shown to be advantageous for paint removal applications including cleaning graffiti, removing layers of paint from surfaces and minimising stains and residues. The bio-based solvent completely detached the paint from non-porous substrates. The higher viscosity Cyrene promoted a more controlled cleaning process than other commercial solvents, where the solvent lifts off the paint, avoiding chemical contamination of the porous substrate. A Cyrene–water mixture showed some paint removal whereas NMP–water was completely ineffective. Chemical cleaning by neat NMP was achievable with fast dissolution; however, ghosting results from use of the solvent and undissolved paint components remain in the substrate. The low human and environmental toxicity of Cyrene makes it a more sustainable alternative to conventional paint removal products, including for outdoor use on graffiti.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/suschem4020012/s1. Figure S1. Pristine aluminium foil (a) and ceramic tile (c) and painted substrates (b,d). Figure S2. Immersion tests by dip-in (a) and immersion using Stuart rollers (b). Figure S3. Poultice test: (a) the stained surface was covered by (b) poultices made of solvent and talc and covered using plastic foil. After 24 h, (c) the plastic foil was removed, and results were assessed. Figure S4. Scores from 1 (good cleaning) to 5 (no change) given to the cleaned tiles. Figure S5. DMF technical grade (a,b) and anhydrous (c) used as paint stripper of acrylic and cellulose-based paints from aluminium foil (a) and ceramic tiles (b,c). Table S1. Water content determination *via* volumetric Karl Fisher titration. Figure S6. The infrared spectra for the dry acrylic red paint (black line) and residues after removal with Cyrene (red line) and NMP (blue line). Two acrylic resins (green and purple lines) are shown here for comparison. Table S2. The inorganic content of the acrylic paint residues remaining after dissolution in Cyrene and NMP. Figure S7. The removal process of acrylic (a,c) and cellulose-based (b,d) paint using Cyrene (a,b) and NMP (c,d) from a tile. Table S3. Dynamic and apparent viscosities of Cyrene and Cyrene-water mixtures using different methods and the final temperatures after mixing Cyrene and water at different ratios. Table S4. Hansen Solubility Parameters, the scores given and relative energy distance (RED) of the neat solvents for acrylic paint removal. Table S5. Hansen Solubility Parameters, the scores given and relative energy distance (RED) of the neat solvents for cellulose-based paint removal. Figure S8. The use of binary solvent systems 75% Cyrene-25% water (a) and 75% NMP-25% water (b) as paint strippers for the acrylic (c,e) and cellulose paints (d,f). Table S6. Hansen Solubility Parameters, the scores given and relative energy distance (RED) of the neat solvents and mixtures of Cyrene with greener solvents for acrylic paint removal. Table S7. Hansen Solubility Parameters, the scores given and relative energy distance (RED) of the neat solvents and mixtures of Cyrene with greener solvents for cellulose-based paint removal.

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