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# Evaluation of novel cleaning systems on mock-ups of unvarnished oil paint and chalk-glue ground within the Munch Aula Paintings Project

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## Abstract

Low-risk removal of embedded surface soiling on delicate heritage objects can require novel alternatives to traditional cleaning systems. Edvard Munch's monumental Aula paintings (1911–16) have a long history of exposure to atmospheric pollution and cleaning campaigns that have compromised the appearance and the condition of these important artworks. Soiling removal from porous and water-sensitive, unvarnished oil paintings continues to be a major conservation challenge. This paper presents the approach and results of research into the effect and efficiency of three novel systems used for soiling removal: soft particle blasting, CO<sub>2</sub>-snow blasting, and Nanorestore Gel<sup>®</sup> Dry and Peggy series hydrogels. Cleaning tests were performed on accelerated-aged and artificially soiled mock-ups consisting of unvarnished oil paint and chalk-glue grounds. Visual and analytical assessment (magnification using a light microscope and scanning electron microscope, as well as colour- and gloss measurement) was carried out before and after mock-up cleaning tests and the results were compared to those obtained using the dry polyurethane sponges employed in the most recent Aula surface cleaning campaign (2009–11). Although the results varied, the Nanorestore Gel<sup>®</sup> series proved promising with respect to improved soiling removal efficiency, and reduced pigment loss for the water-sensitive surfaces evaluated, compared to dry sponges.

**Keywords:** Conservation, Cleaning, Evaluation, Mock-ups, Unvarnished oil paintings, Edvard Munch

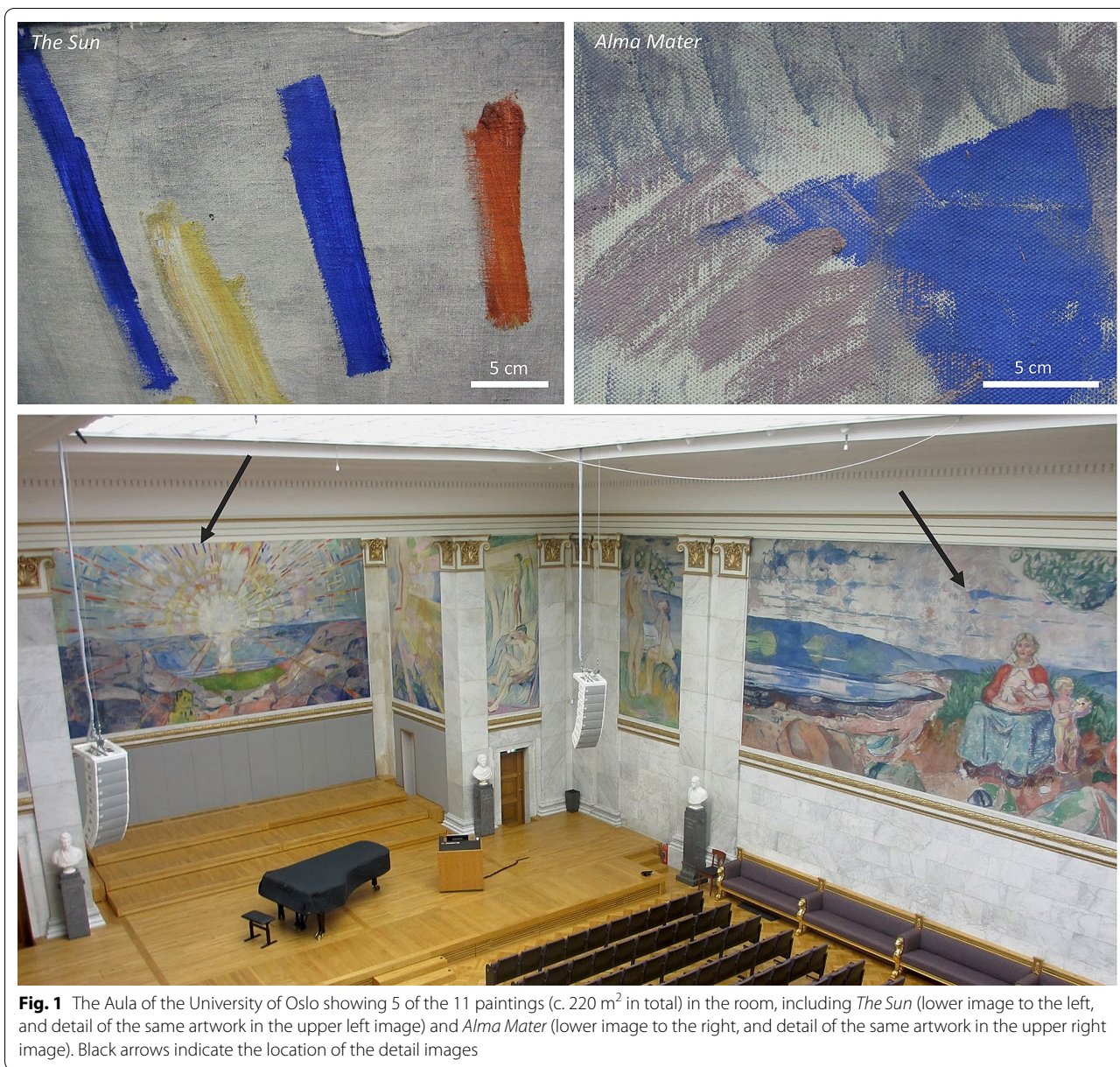
## Introduction

The challenges of removing embedded deposited particulate soiling from historic, vulnerable works of art are well known [1]. Similar to many late-19th, early-20th century oil paintings, Edvard Munch's monumental artworks (1911–16) in the University of Oslo's Aula were intentionally left largely unvarnished by the artist to achieve subtle variations in gloss, saturation, and texture [2–4] (Fig. 1). Unvarnished and unglazed paint surfaces are especially susceptible to physicochemical changes caused

by environmental soiling deposition, pollutants, humidity, and temperature (T). The associated risk and soiling removal efficiency of traditional dry and wet surface-cleaning techniques (i.e., erasers, sponges, brushes, and moistened cotton swabs) on such surfaces are often poor, as the mechanical and solvent action can remove pigment, roughen the surface, remove soiling unevenly, and unacceptably change the gloss and saturation of colours [5, 6]. Several publications from the Munch Aula Paintings Project (MAP) [7] outline concerns about the effects of soiling on these paintings, including the limitations of common aqueous and mechanical cleaning methods in this context. The current consensus is that for the Aula paintings to benefit from further surface cleaning, a safe

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**Fig. 1** The Aula of the University of Oslo showing 5 of the 11 paintings (c. 220 m<sup>2</sup> in total) in the room, including *The Sun* (lower image to the left, and detail of the same artwork in the upper left image) and *Alma Mater* (lower image to the right, and detail of the same artwork in the upper right image). Black arrows indicate the location of the detail images

and effective cleaning strategy should be identified [3, 8, 9]. The most recent foci of the MAP have been to monitor the slow soiling deposition, explore options for more efficient, lower-risk surface cleaning, and to improve in-situ treatment and documentation [9–11].

**Advances in cleaning technology**

Soiling removal using lasers [12, 13], carbon dioxide (CO<sub>2</sub>) snow [14, 15], supercritical CO<sub>2</sub> (SCCO<sub>2</sub>) [16, 17], atomic oxygen [18, 19], micro-aspiration [20–22], improved air abrasive methods [23, 24], and nano-gels [25, 26] have received increased attention in cultural

heritage. A few multidisciplinary studies have explored the application of these novel cleaning systems to unvarnished oil paint [19, 27–30].

This paper contributes to this research by investigating three potential cleaning systems: soft particle blasting, CO<sub>2</sub>-snow blasting, and the Nanorestore Gel<sup>®</sup> Dry and Peggy series hydrogels, described in more detail later. These systems were evaluated using artificially aged and artificially soiled mock-ups comprising an unvarnished cobalt blue oil paint applied to a ground layer of chalk bound in animal glue [31, 32]. Cleaning performance was

**Table 1** Raw materials and ratios used for the preparation of mock-ups

Manufacturer	No.	Material	Composition	Component
Kremer Pigmente	45,710	Cobalt blue medium (PB28)	CoAl <sub>2</sub> O <sub>4</sub> (Blue Spinel)	Paint pigment
	73,600	Poppyseed oil (refined)	Fatty acids	Paint binder
Amertek	n/a	Barium sulfate	BaSO <sub>4</sub>	Paint extender
Ottoson Färgmakeri	n/a	Balsam turpentine	Terpenes (Pine)	Paint thinner
Kremer Pigmente	58,000	Chalk from Champagne	CaCO <sub>3</sub>	Ground pigment
	63,025	Rabbit skin glue	Collagen (hydrolysed)	Canvas sizing and binder for ground
Claessens	068	Linen canvas (395 g/m <sup>2</sup> )	Flax fibres	Canvas substrate
Ratios by mass (%) (wet film)	Glue size	Chalk-glue ground	Undiluted cobalt blue oil paint	Diluted cobalt blue oil paint
Water	93.5	41.6	–	–
Rabbit skin glue	6.5	2.9	–	–
Chalk	–	55.5	–	–
Pigment blue 28	–	–	44.0	26.4
Barium sulfate	–	–	22.0	13.2
Poppyseed oil	–	–	34.0	20.4
Balsam turpentine	–	–	–	40.0

evaluated against dry polyurethane sponges (PU) similar to those used in the most recent Aula cleaning campaign in 2009–11 [8]. The objective was to improve upon the results achievable using PU sponges through developing a new cleaning strategy. This paper therefore describes comparative research into three novel cleaning strategies that were applied to painted mock-ups that simulate unvarnished oil paintings such as Munch's Aula series. Key results are presented as star diagrams which illustrate the advantages and disadvantages of each cleaning system as observed on the mock-ups [26, 29, 33–36].

## Materials and methods

### Mock-up preparation

Mock-ups were designed that approximately mimic the relatively large surface irregularities and wettability observed on two Aula paintings such as the exposed chalk-glue ground of *Alma Mater* and the cobalt blue paint in *The Sun* (see Additional file 1: Figure S1a, b), which exhibit chalking<sup>1</sup> and are sensitive to water.<sup>2</sup> These properties contribute to soiling adhesion and poor

cleanability.<sup>3</sup> Both paintings have previously been cleaned with soft bread and PU sponges, which also influenced the design of the mock-ups.

### Composition

The mock-ups were made using contemporary raw materials (Table 1) [31, 32].<sup>4</sup>

Two mock-up sets (M1 and M2) were prepared. Each set comprised three types, referred to as chalk-glue ground (G), undiluted cobalt blue oil paint (Pu), and diluted cobalt blue oil paint (Pd) representing abrasion- and water-sensitive unvarnished surfaces (Table 2).<sup>5</sup> The first mock-up set (M1) was used for the initial optimising of working parameters. Mock-up set (M2) was used to comparatively evaluate the three novel cleaning systems and PU sponges. M2 also included a control set of soiled, unsoiled, and unaged mock-ups.

Footnote 3 (continued)

40]. Removal efficiency (cleanability) may decrease with increasing surface material roughness, wettability/water-sensitivity, softness, porosity, chalking and elasticity [40], and with wet deposition and decreasing soiling particle size [41]. Rough and textured surfaces can also affect the evenness of soiling removal. The mock-ups were constructed to have at least three of these properties that are associated with low cleanability.

<sup>4</sup> The construction of these purposely simplified mock-ups for cleaning experiments did not follow the standard set by the Historically Accurate Reconstruction Techniques (HART) project [42] because of practical limitations and time constraints.

<sup>5</sup> Similar responses of the cleaning systems may be expected on other artists' colours that share these condition issues and have similarly adhering surface soiling.

<sup>1</sup> 'Chalking' is defined as 'the appearance of loosely adherent fine powder on the surface of a paint film, arising from the degradation of one or more of its constituents' [37].

<sup>2</sup> In the context of the conservation of modern oil paint, water-sensitivity has been defined as 'the removal of pigment and/or binding medium as a result of gentle rolling of a cotton swab dampened with water, over the surface' [38].

<sup>3</sup> Soiling adhesion and surface cleaning are influenced by the surface properties (i.e., texture, wettability, porosity, softness and elasticity) of the material to be cleaned in relation to particle deposition (wet or dry) and the properties of the soiling (i.e., tackiness, particle size and shape) [39,

**Table 2** Overview of mock-up sets before cleaning and cleaning systems tested per mock-up type

Mock-up sets	Type <sup>a</sup>	Ageing <sup>b</sup>	'Pre' cleaning	Layer thickness <sup>c</sup>	Chalking <sup>d</sup> rating	Water-sensitivity <sup>e</sup> rating	Cleaning systems tested
Stage one: cleaning trials							
M1 33 in total	G	1 week 30,719 kJ/m <sup>2</sup>	n/a	n/a	2	4	Options tested—SPB: wheat starch, Arbobcel <sup>®</sup> A and Arbobcel <sup>®</sup> B. Free liquid trials: DI water, pH and conductivity adjusted waters, buffered waters, chelating agents, surfactants. Nanorestore Gel <sup>®</sup> Peggy and Dry series: HWR, MWR, Peggy 5 and Peggy 6
	Pu	1 week 30,719 kJ/m <sup>2</sup>	n/a	n/a	1	3	
	Pd	1 week 30,719 kJ/m <sup>2</sup>	n/a	n/a	2	4	
Stage two: comparative cleaning tests							
M2 72 in total <sup>f</sup>	G	4 weeks 143,349 kJ/m <sup>2</sup>	Bread loaf <sup>g</sup>	Ave. 136 µm Min 44 Max 338 SD: 76	2	4	SPB: Arbobcel <sup>®</sup> A CO <sub>2</sub> -snow: gas source Nanorestore <sup>®</sup> MWR gel, 0.5% w/v citric acid/ NaOH pH 6.5, 4.4 mS/cm. Clearance: MWR with water adjusted to pH 6.5 PU sponge: white, latex free
	Pu	5 weeks 159,521 kJ/m <sup>2</sup>	Bread loaf <sup>g</sup>	Ave. 239 µm Min 176 Max 320 SD: 38	1	3	SPB: Arbobcel <sup>®</sup> A CO <sub>2</sub> -snow: gas source Nanorestore <sup>®</sup> Peggy 6 gel, 1% w/v citric acid/ NaOH pH 6.5, 9.2 mS/cm. Clearance: Peggy 6 with water adjusted to pH 6.0 PU sponge: white, latex free
	Pd	5 weeks 159,521 kJ/m <sup>2</sup>	Bread loaf <sup>g</sup>	Ave. 29 µm Min 11 Max 56 SD: 13	2	4	SPB: Arbobcel <sup>®</sup> A CO <sub>2</sub> -snow: gas source Nanorestore <sup>®</sup> MWR gel, water adjusted to pH 6.0, 1000 µS/cm. Clearance: not required PU sponge: white, latex free

<sup>a</sup> G = chalk-glue ground, Pu = undiluted cobalt blue oil paint, Pd = turpentine diluted cobalt blue oil paint. All mock-ups were composed of the following: linen canvas, hide glue size, chalk-glue ground. Pu and Pd had an additional upper layer of oil paint

<sup>b</sup> Artificial ageing: Xenon-arc lamps indoor window glass filters, irradiance of 30–50 W/m<sup>2</sup> (300–400 nm), Black standard temperature (BST) 45 °C, chamber temperature (CHT) of 30 °C, and RH 65%

<sup>c</sup> Average of 300 measurements from 6 samples of each type. The layer thickness influences the vulnerability of the surface to dry mechanical and aqueous cleaning action

<sup>d</sup> UNI EN ISO 4628-6 (2011)—part 6: assessment of degree of chalking by tape method. The rating from 0 to 5 (5 = most chalking) is based on the amount of pigment particles noted on an adhesive tape after peeling it off the painted surface and comparing it to a visual reference scale in the standard. See also Additional file 2: Table S1

<sup>e</sup> Mills et al. [46]. DI moistened swab rolls. Rating from 1 to 5 (5 = most water-sensitive)

<sup>f</sup> 12 for cleaning tests and 12 controls (3 unsoiled, accelerated aged; 3 soiled, accelerated aged; 3 unsoiled, naturally aged; 3 soiled, naturally aged)

<sup>g</sup> Unsoiled, naturally aged controls were not bread cleaned

### Accelerated ageing and artificial soiling

Painted mock-ups were left to dry for 21 (M2) and 28 (M1) weeks under ambient conditions (19–29 °C and c. 20–80% RH) and light, followed by accelerated ageing and application of artificial soil according to the schemes presented in Table 3.

Accelerated ageing was carried out in a Xenotest 440 weathering instrument (Atlas, Linsengericht, Germany) fitted with a Xenochrome 320 filter with 320 nm UV cut-off to simulate exposure behind window glass and set at 30 °C chamber temperature (CHT), 45 °C black standard temperature (BST), 65% RH, and irradiance 30–50 W/m<sup>2</sup>. Accelerated ageing was used to promote surface chalking and water-sensitivity (by oxidation and/or hydrolysis), and to embed applied surface dirt into the paint surfaces.

An artificial soil mixture based on a system used by Ormsby et al. [43], was slightly amended to better approximate the particulates likely to be present on the Aula paintings [9], with the aim of integrating the soiling and rendering it difficult to remove from the mock-up surfaces. Artificial soiling was sprayed (wet) onto the mock-ups using a top-fed Dual-Action Airbrush (Sparmax, Taipei, Taiwan). The soil mixture contained polar and nonpolar inorganic and organic compounds along with elemental- and organic carbon, suspended in Shell-sol D40 (Kremer Pigmente, Aichstetten, Germany) (see Additional file 2: Table S1).<sup>6</sup> The proportion of mineral oil and olive oil was reduced from the 2013 recipe by

<sup>6</sup> Soiling particles ranged from tarry, sub-micron sized (i.e., Lamp black, 0.095 µm) to non-tacky, larger sized particles (> 10 µm).

**Table 3** Mock-up sets and exposure procedure

Mock-up set 1 (M1)	Mock-up set 2 (M2)
<i>Composition</i>	
Type 1. Stretched linen canvas, glue size, chalk-glue ground (G)	
Type 2. Type 1 + undiluted cobalt blue oil paint (Pu)	
Type 3. Type 1 + turpentine diluted cobalt blue oil paint (Pd)	
<i>Exposure sequence</i>	
Natural ageing: c. 28 weeks	Natural ageing: c. 21 weeks
↓	↓
Artificial soiling: 40 applications	Artificial ageing c. 2–3 weeks 45 °C (BST), 30 °C (CHT), 65% RH, 50 W/m <sup>2</sup>
↓	↓
Artificial ageing: c. 1 week 45 °C (BST), 30 °C (CHT), 65% RH, 50 W/m <sup>2</sup>	Artificial soiling: 40 applications
↓	↓
Natural ageing: c. 18 weeks	Artificial ageing: c. 1 week 45 °C (BST), 30 °C (CHT), 65% RH, 50 W/m <sup>2</sup>
↓	↓
Artificial soiling: 20 applications	Natural ageing: c. 16 weeks
	↓
	'Pre' cleaning with soft bread
	↓
	Artificial soiling: 20 applications
	↓
	Artificial ageing 1 week 45 °C (BST), 30 °C (CHT), 65% RH, 30 W/m <sup>2</sup>
	↓
	Artificial soiling: 20 applications
<i>Total</i>	
Artificial ageing: c. 1 week	Artificial ageing: 4–5 weeks
Light energy dosage for samples: 30,719 kJ/m <sup>2</sup>	Light energy dosage for chalk-glue ground mock-ups: 143,349 kJ/m <sup>2</sup>
	Light energy dosage for oil paint mock- ups: 159,521 kJ/m <sup>2</sup>

50%, and the carbon black from 2 to 1.2 g to buildup soiling more gradually. Sodium nitrate (NaNO<sub>3</sub>) is an additional indoor pollutant found in Oslo owing to the city's close proximity to the sea [9, 44]; 2.5 g of sodium nitrate (Merck, Darmstadt, Germany) was therefore added to the recipe.<sup>7</sup> The artificial soil was applied in multiple (wet) spray-applications (see Table 3). Excess soil was removed in between each application using a soft brush.

To mimic some of the cumulative effects of soiling, ageing, and the twentieth century campaigns of bread-cleaning carried out on the Aula paintings, M2 was cleaned using handmade bread (Table 3).<sup>8</sup> Pieces of freshly-made bread, retrieved from the core of the loaf, were manually

rolled back and forth for approximately 5 s over the surface of each mock-up with gentle, consistent pressure. Together with artificial ageing, this resulted in a visual appearance similar to that of the *Alma Mater* ground.

#### Characterisation of aged mock-ups

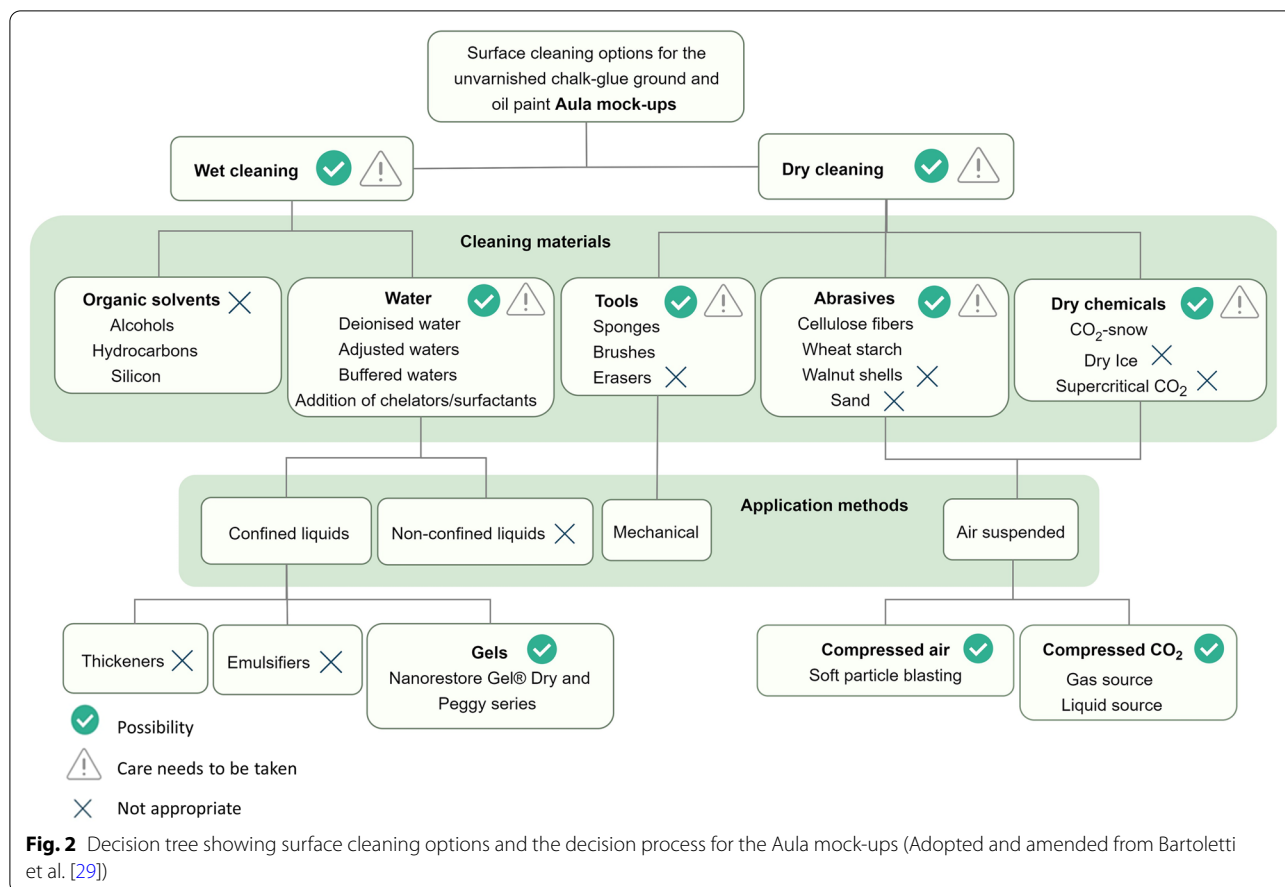
A standardised chalking test (UNI EN ISO 4628-6 (2011)) and water-sensitivity test [46] were used to measure the condition of Mock-ups G, Pu and Pd after accelerated ageing, artificial soiling, and bread cleaning. The degree of chalking of M1 and M2 was determined by visual comparison of pigment loss/removal on adhesive tape strips to a standard visual reference with a rating from 0 (no chalking) to 5 (severe chalking) (Additional

<sup>7</sup> The amount of NaNO<sub>3</sub> was approximated from concentration data [45] from Oslo and amended for the artificial soiling mixture through trials.

<sup>8</sup> The loaf was prepared by hand using wheat flour, yeast, and water only. While the Aula paintings were bread-cleaned at least six times in the twen-

Footnote 8 (continued)

tieth century and once with PU sponges in 2011, the pre-cleaning of the mock-ups were limited to one bread cleaning.



file 2: Table S2).<sup>9</sup> The degree of water-sensitivity of M1 and M2 and of selected areas of the Aula paintings was determined by recording the number of moistened (DI water) standard-size swab rolls before visible pigment loss/removal, according to the criteria developed by Mills et al. [46], with ratings from 1 (not sensitive) to 4 (very sensitive) (Additional file 2: Table S2).

**Selection of cleaning materials and application methods**

Figure 2 illustrates the selection process of the surface cleaning methods tested in this research. Bartoletti et al. [29] identified the following requirements for the cleaning of unvarnished modern paint surfaces: ‘...even and consistent removal of soiling layer(s)...; the ability to be tailored... [to] differences in paint texture, sensitivity, and soiling adhesion; the ability to minimise mechanical action and achieve effective cleaning action; [and] not pose undue risk to paint and ground through swelling,

pigment pickup [loss], gloss change or cleaning system residues.’

These requirements align with those expressed by various conservators involved in the treatment of the Aula paintings [8, 9, 47, 48]. Based on the risks described above, soft particle blasting, CO<sub>2</sub>-snow blasting and Nanorestore Gel® Dry and Peggy gel series hydrogels were chosen for evaluation.<sup>10</sup>

**Polyurethane sponges (PU) (control treatment)**

The blasting and hydrogel systems were compared to treatment with white latex-free PU sponges (Arkivprodukter, Ridabu, Norway) similar to those used in the most recent Aula painting cleaning campaign [49] (Additional file 1: Figure S2). The PU sponges were swiped vertically, horizontally and diagonally over the

<sup>9</sup> The chalking test was created to evaluate commercial outdoor paints and varnishes, and usually is not suitable for use on cultural heritage because it can cause severe pigment loss. Nevertheless, it is useful for testing mock-ups.

<sup>10</sup> In preparation for the 2009–11 Aula painting surface cleaning campaign, cleaning tests included natural saliva, gelled surfactants Marlipal® 1618/25, Brij® 700 gel, and Triton X™-100, the chelating agent triammonium citrate (TAC), vulcanised rubber gum, and bread dough [8]. These options were ruled out because of pigment loss/removal, low soiling-removal efficiency, or risk of metal-soap formation.

mock-up surfaces using gentle pressure as described in the MAP treatment reports [48].

### Soft particle blast cleaning (SPB)

Soft particle blasting (SPB) (Weichpartikelstrahlen) was selected as it offers a gentle and dry ‘non-contact’ alternative to traditional mechanical cleaning with sponges, erasers and brushes [23]. SPB was developed to address challenges associated with mechanical cleaning of delicate historic paper and parchment [23, 50]. In contrast to commercial air blasting technologies, which apply abrasive materials at high pressures, SPB utilises ‘soft’ powdered materials together with low pressure air blasters (Resko Airblaster series) [23]. The SPB system can be tailored to different surfaces by varying the air pressure, the distance, and the angle of the stream to the surface, as well as the type of nozzle [23, 51].

In preliminary tests, three soft powders (see Additional file 1: Figure S3), cellulose-based Arbocel<sup>®</sup> A (40 µm), Arbocel<sup>®</sup> B (120 µm) (all Deffner & Johann, Rötlein, Germany), and wheat starch (20 µm average particle diameter), were selected based on their prior use for cleaning cultural heritage objects [50, 51].<sup>11</sup> Wheat starch consists of small spherical shaped particles composed of ~98% carbohydrates (starch), 0.8–1.0% lipids, 0.2–0.5% proteins, and 0.2–0.3% ash [52]. Arbocel<sup>®</sup> was developed by J. Rettenmaier & Söhne (JRS) and is composed of water- and solvent-insoluble cellulose fibres, are chemically inert, and have low residual moisture content [24].

SPB cleaning tests were performed with a Resko Airblaster II WPS (2018 version) (Deffner & Johann)<sup>12</sup> connected to a Super Fox 3 T 240-5L oil-free compressor (Nardi, Vicenza, Italy) inside a sandblasting cabinet (KC Silkeborg, Denmark) with a HEPA-filtered, environmental vacuum, and dust collector (Additional file 1: Figure S4). The air hose was divided by a Y-connector for simultaneous use of an air blowgun to direct particles away from the cleaned surfaces.<sup>13</sup> The air pressure was set to 1.8 bar (26.1 psi).

### Carbon dioxide snow (CO<sub>2</sub>-snow)

CO<sub>2</sub>-snow blasting promotes removal of organic and inorganic surface contamination, leaves behind no

blasting-media residue, and is considered in industrial processing to be non-abrasive [54]. CO<sub>2</sub>-snow blasting is an established method in industrial and in research institutions for cleaning delicate surfaces, such as lenses and electronic components that are sensitive to scratching [55–57]. For these reasons, CO<sub>2</sub>-snow cleaning has also been explored on cultural heritage objects [14, 58, 59]. The successful removal of surface soil from delicate pigmented basketry [59] was influential in exploring its use on the Aula mock-ups.

CO<sub>2</sub>-snow blasting consists of a stream of fine, not fully dense, dry-ice particles that form when compressed liquid or gaseous CO<sub>2</sub> is released quickly from a pressurized cylinder [57].<sup>14</sup> The accelerating stream of frozen CO<sub>2</sub> particles collides with the target surface, in this case a painting mock-up, and removes surface soiling by momentum transfer, solvation, and freeze-fracture interactions [54]. On impact, the frozen CO<sub>2</sub> particles sublimate, leaving no blasting-media residue behind. The release of liquid or gaseous CO<sub>2</sub> from the pressurized cylinder affects the CO<sub>2</sub> particle size, which in turn affects the likelihood of the frozen CO<sub>2</sub> to cause ambient moisture to condense on the target surface.<sup>15</sup> Studies have shown that simultaneous use of a warm, dry *cover gas* such as nitrogen or air can alleviate the condensation effect and reduce cooling of the painting surface [14]. Delivery of the CO<sub>2</sub>-snow can be adapted by adjusting the shape of the stream with different nozzle geometries, and the impact force with distance and angle of the nozzle relative to the target surface.

Cleaning tests were performed with a K6-10DG-B dual gas unit equipped with a Venturi nozzle suitable for either a gaseous or liquid CO<sub>2</sub>, foot-switch operation, and heated cover gas line (Applied Surface Technologies, NJ, USA) (Additional file 1: Figure S5). Cleaning tests were carried out inside a fume hood, and with a XT-10 carbon dioxide alarm set at 1000 ppm placed nearby to monitor potentially hazardous CO<sub>2</sub> concentrations in the air. Heated nitrogen was used as a cover gas to counteract the condensation and cooling of mock-up surfaces during the cleaning tests [54, 60]. Both a gas (Gilmore, CA,

<sup>11</sup> Arbocel<sup>®</sup> ‘A’ and ‘B’, were produced through a collaboration between JRS and Deffner & Johann. They were designed especially for treating vulnerable cultural heritage surfaces with potential for almost all types of sensitive surfaces (Y. Magnusson. Pers. Comm. 7 August 2020).

<sup>12</sup> The WPS II (2018) version differs from the standard Resko Airblaster II unit in that it has a material bypass (a thin hose) and a recoil valve with a sieve that is optimised for the Arbocel<sup>®</sup> abrasives (R-U. Johann. Pers. Comm. 12 April 2021).

<sup>13</sup> See Deffner & Johann presents: Soft Particle Blasting—setup and implementation [53] for detailed view of setup and accessories.

<sup>14</sup> Used improperly, CO<sub>2</sub>-snow blasting carries significant health risks. Sublimed CO<sub>2</sub> can displace oxygen from the work area and cause suffocation, or potentially fatal blood acidification as inhaled CO<sub>2</sub> converts to carbonic acid (H<sub>2</sub>CO<sub>3</sub>) in the body. For these reasons, training and proper safety controls are critical.

<sup>15</sup> Liquid and gaseous CO<sub>2</sub> can coexist in the same cylinder, with the denser liquid fraction at the bottom and the gas above. A typical pressurized cylinder has its valve at the top, which will favour release of the gas fraction when the cylinder is upright. Supply of liquid CO<sub>2</sub> can be favoured by lying the cylinder on its side or by using a cylinder fitted with a dip tube that pulls material from the bottom.

USA) and liquid (unknown supplier) CO<sub>2</sub> sources were trialled.

#### **Nanorestore Gel<sup>®</sup> Dry and Peggy series hydrogels**

Soiling on the Aula paintings is at least partially removable using water, however the paint and ground layers remain sensitive to water. Despite these inherent sensitivities, aqueous gel systems were considered to deliver water to the surface in a highly controlled way. Nanorestore Gels<sup>®</sup>, developed by the Centre for Colloid and Surface Science (CSGI, Florence, Italy), are designed for optimal water retention, cleaning efficacy, and flexibility [25, 30, 61–64]. They have been used to successfully clean unvarnished and moderately water-sensitive paint surfaces [26, 29, 30, 65–69]. Their properties, and ability to be loaded with tailored cleaning solutions, make these hydrogels attractive potential alternatives to dry mechanical and air-abrasive cleaning systems.

Nanorestore Gel<sup>®</sup> Medium- and High-Water Retention (MWR and HWR respectively; formerly known as ‘Extra Dry’ and ‘Max Dry’) are transparent, rigid hydrogels consisting of an intermolecular network of poly (2-hydroxyethyl methacrylate) and polyvinylpyrrolidone (PVP) [29, 63, 65–67, 69–71]. Nanorestore Gel<sup>®</sup> HWR and MWR are considered especially suitable for cleaning water-sensitive (painted) surfaces due to their rigidity and water retention capacity. The Nanorestore Gel<sup>®</sup> Peggy series is thinner, less retentive and more flexible than the Dry series, which improves cleaning of textured or irregular surfaces [26, 29, 67]. Nanorestore Gel<sup>®</sup> Peggy 5 consists of a blend of polyvinyl alcohol (PVA) and PVP. The more flexible and elastic Nanorestore Gel<sup>®</sup> Peggy 6 is made from PVA alone and conforms better to moderately textured surfaces [29, 30, 67].

In this study, double layers of Evolon<sup>®</sup> tissue were used to remove excess moisture from the nano-gels prior to application. The Nanorestore Gels<sup>®</sup> were applied dry and cool to the touch, as recommended in the CSGI technical sheets [72, 73]. The nano-gels were covered with Melinex<sup>®</sup> sheets after application, and slight pressure was applied to avoid evaporation and to ensure even contact with the sample surfaces.

The Nanorestore Gel<sup>®</sup> Dry and Peggy gels were tested as hydrogels alone using deionised water (DI) and with pH- and conductivity-adjusted waters (AW), chelating agents, and non-ionic surfactants selected from the Modular Cleaning Program (MCP) [74] to explore tailored options (see Table 4 and Additional file 1: Figure S6). Adjusting the cleaning-solution pH and conductivity to a level close to that of the surface to be cleaned can decrease the risk of swelling and pigment loss. Increasing the pH of a cleaning solution tends to enhance soiling removal, however this may also increase the risk of

undesirable surface changes on highly-oxidised and water-sensitive oil (and other) paints [35].

Chelating agents, such as citric acid, increase the removal of metal cations present in surface-soil, which consequently helps promote de-flocculation and dispersion of oily components [75–77]. Surfactants, which are amphiphilic compounds, can enhance soiling removal by lowering the interfacial tension between cleaning solution and soiled surface [78] and aid the dispersal of soiling material within micelles [79]. Cleaning solutions that contain buffering agents, chelating agents, or surfactants require a clearance step with DI or AW to remove non-volatile residues from the surface after cleaning.<sup>16</sup>

Table 4 lists the materials, application, and clearance method for each cleaning system evaluated. The cleaning systems, unless otherwise stated, were applied with the painting mock-ups mounted vertically on a plastic (polyoxymethylene) board with metal clamps to mimic the vertical working angle of a hypothetical in-situ cleaning of the Aula paintings.

#### **Cleaning system optimisation and evaluation methodology**

The cleaning systems were applied to the mock-ups in two stages; parameter optimisation, followed by the cleaning tests (Tables 2 and 4). The cleaning system optimisation and evaluation methodology used built on previous research into cleaning modern paints [29, 34, 35].

#### **Stage one—cleaning trials on mock-up set 1 (M1): initial measurements, optimisation and selection**

Initial cleaning trials on M1 were carried out to determine the relative cleaning efficiency and effect of the three SPB powders (wheat starch, Arbocel<sup>®</sup> A and Arbocel<sup>®</sup> B), CO<sub>2</sub>-snow blasting with a liquid and gas CO<sub>2</sub> source, and the four Nanorestore Gels<sup>®</sup> (HWR, MWR, Peggy 5 and Peggy 6), and to explore and to optimise the working parameters of each of the three systems.

*Blasting media velocity:* Velocity of the SPB and CO<sub>2</sub>-snow particle streams was measured at ~2.5, ~5.0, ~10.0, and ~25.0 cm working distance with a Kestrel 3000 air velocity meter (Kestrel Meters, PA USA). The effect of SPB and CO<sub>2</sub>-nozzle distance to painted mock-up surface was then evaluated (see Additional file 2: Table S3). The SPB powders and CO<sub>2</sub>-snow were applied to mock-up surfaces until a ‘stopping sign’ amended from Chung et al. [34] was observed: the mock-up looked clean to the unaided eye, pigment loss became visible, the surface was disrupted with scratches or impact holes,

<sup>16</sup> The use of pH adjusted water for clearance was based on Stavroudis’ [80] recommendations for aqueous gel solutions. The CSGI datasheet recommends clearance with a hydrogel (DI) and water only [72, 73].



**Table 4** Materials, application and clearance of the cleaning options tested on mock-ups

Cleaning system options explored	Preparation	Application	Clearance
Soft particle blasting Wheat starch (20 µm) 500 g/L, pH 4.0–7.5 Arboce <sup>®</sup> A (40 µm) 190–250 g/L, pH 5.0–7.0 Arboce <sup>®</sup> B (120 µm) 150–182 g/L, pH 5.0–7.0	Soft particles used as dispatched. Chambers filled 2/3 full to ensure that the airflow can swirl the particles inside the chambers	Based on initial cleaning trials, a 1.2 size nozzle was directed at a 40–45° angle to the surface with the working pressure set to minimum (c. 1.8 bar/26.1 psi). Application: intermittent blasts by switching the hand switch on and off every two to three seconds to achieve an even particle stream. Stage two with Arboce <sup>®</sup> A, nozzle distance to surface: G mock-up: 6–7 cm, Pu mock-ups: 3–4 cm, Pd mock-ups 7 cm	Cleaning particles and displaced soiling removed with an air gun followed by brushing with soft brushes
CO <sub>2</sub> -snow Liquid and gas CO <sub>2</sub> source The cover gas was nitrogen	Cover gas heated for at least 20 min prior to cleaning	Compound Venturi and surrounding cover gas nozzle was introduced at 90° angle to the plane of the sample and c. 30 cm distance to gradually reduce the sample surface temperature and avoid condensation [14]. The nozzle was brought closer to the surface at a 40–45° angle to c. 3–5 cm from the sample surface. Continuous CO <sub>2</sub> -snow flow for c. 5 s with side-to-side sweeping action	Not required because CO <sub>2</sub> -snow particles sublimate. Progressing with cleaning in the direction of the CO <sub>2</sub> stream avoids ejecting soiling onto already-cleaned areas
Nanorestore Gels <sup>®</sup> MWR, HWR, Peggy 5, Peggy 6 Aqueous cleaning solutions: DI water: c. pH 6.9, 2 µm/cm Adjusted waters (acetic acid and dilute ammonium hydroxide): pH 5.0–7.5, 1000 µm/cm. Buffered waters: MES pH 5.5, MES pH 6.0, Bis-tris pH 6.5, TRIS pH 7.5 (only in free liquid trials). Chelating agents: TAC: 0.5%–1% w/v, pH 7.1, 4.2–8.9 mS/cm, 0.5%–1% w/v Citric acid/NaOH; pH 5.5–6.5, 4.4–9.4 mS/cm. Non-ionic surfactants: ECOSURF <sup>™</sup> EH 6 (HLB 10.8) and ECOSURF <sup>™</sup> EH9 (HLB 12.5)	The nano-gels come pre-made in a plastic bag with a single sheet of c. 10 x 15 cm <sup>2</sup> immersed in demineralised water. Nano-gels are immersed for 24 h in DI water prior to use or before loading with cleaning solutions. Nano-gels are immersed in selected cleaning solutions for at least 12 h prior to use	Nano-gels were blotted using Evolon <sup>®</sup> tissues to remove excess water. Light finger pressure was applied to optimise adhesion when the gel was applied to the surface. The gels were gently peeled off the surface. Stage one: free liquid trials with manufactured swabs on M1. Cleaning trials on M1 with 3.5 x 2 cm <sup>2</sup> pieces of nano-gels loaded with DI, adjusted waters, chelating agents, and surfactants and applied to each sample type for one minute. Stage two: Pieces of 5.5 x 5 cm <sup>2</sup> nano-gel applied to M2, loaded with optimal system based on observations from Stage one and applied for one minute. G mock-ups: Nanorestore <sup>®</sup> MWR gel, 0.5% w/v citric acid/NaOH pH 6.5, 4.5 mS/cm. Clearance: water adjusted to pH 6.5. Pu mock-ups: Peggy 6, 1% w/v citric acid/NaOH pH 6.5, 9.2 mS/cm. Clearance: Peggy 6 with water adjusted to pH 6.0 Pd mock-ups: MWR, water adjusted to pH 6.0	Not required for pure hydrogels. Nano-gels loaded with chelating agents or surfactants require a second clearance step using the same gel type loaded in water
Dry, white, latex-free polyurethane (PU) sponge	Used as received, without modification	Parallel strokes applied with gentle finger pressure in vertical, horizontal, and diagonal directions. G mock-ups: 12 strokes, Pu mock-ups: 18 strokes, and Pd mock-ups: 9 strokes	Not required for PU dry sponges

or the surface was exposed for one minute since the last noticeable cleaning effect.

**CO<sub>2</sub>-snow treatment temperatures:** The minimum temperature of the CO<sub>2</sub>-snow jet stream emitted from a full CO<sub>2</sub> gas tank (850 psi) was recorded with a K-type 533-42 digital thermometer (Cole-Parmer, IL, USA) with and without warm nitrogen cover gas. The temperature distribution across the mock-up surfaces after one minute of CO<sub>2</sub>-snow exposure was measured with a ThermoCAMTM B400 (FLIR Systems Inc. OR, USA) when the CO<sub>2</sub>-gas tank pressure was 800 psi and the cover-gas-heater was at its hottest setting.

**Optimal nano-gel chemistry:** Initial trials were carried out using free liquids applied with manufactured cotton swabs to decide on the most optimal aqueous solution for the nano-gels. The four Nanorestore Gels<sup>®</sup> were first tested as hydrogels loaded in DI water (pH 6.9, 2 µS) to explore the inherent cleaning properties of each nano-gel. The nano-gels were also tested when loaded with a chelating TAC solution at 1% w/v (pH 7.1, 8.9 mS/cm). The most promising gel-types from the DI and TAC trials were also tested with a selection of the most optimal aqueous solutions from free liquid trials with the aqueous cleaning solutions listed in Table 4. The contact time between the nano-gel and surface was set to one minute for all trials to limit variables.

The most promising options and optimised working parameters for SPB, CO<sub>2</sub>-snow and Nanorestore Gel<sup>®</sup> for each mock-up type were taken forward to Stage two.

#### **Stage two—cleaning tests on the main sample set (M2): comparative testing on the Aula painting mock-ups**

The second, and main stage of the evaluation on the M2 mock-ups involved comparing and evaluating the cleaning effect and efficiency of the most promising options from SPB, CO<sub>2</sub>-snow and Nanorestore Gels<sup>®</sup> identified in Stage one. The cleaning results were compared to those of traditional PU sponges. The SPB, CO<sub>2</sub>-snow, and PU sponges were applied as described in Table 4 until one of the 'stopping points' described as per Stage one occurred. The Nanorestore Gels<sup>®</sup> were applied for one minute (to limit variables) as in Stage one, with a hydrogel clearance step applied as appropriate, also for 1 min.

#### **Cleaning system evaluation and star diagrams**

For the cleaning evaluations on M1 and M2, an established method for rating empirical observations was chosen using star diagrams with a scale from 1 (inadequate/poor) to 5 (most appropriate) [29, 33–35]. Fuller stars

and higher rating numbers represent more promising cleaning systems.<sup>17</sup> The evaluation parameters, as shown in Additional file 2: Tables S4 and S5, are commonly used by conservators to assess cleaning methods in real cleaning situations.<sup>18</sup>

#### **Visual documentation**

Visual assessment of the M1 and M2 mock-ups was carried out before and after cleaning in ambient- and raking light and in ultraviolet (UV) radiation using a UV-A (315–400 nm) floodlight (Labino, Vallentuna, Sweden), and with the aid of an MZ6 stereomicroscope (Leica Microsystems, Wetzlar, Germany).

#### **Colourimetry**

Colour measurements were carried out before and after cleaning, and on unsoiled control M2 mock-ups, using a M-700d Spectrophotometer (Konica Minolta, Tokyo, Japan). Specular reflectance data was collected with the specular components excluded (SCE) based on CIELAB colour space. Ten repeat colour measurements were carried out for each cleaning technique of the three mock-ups, and average values and standard deviations were calculated. Deviating measurements were discarded based on the Grubbs test [81]. The colour difference  $\Delta E$  was determined using the CIEDE2000 formula [82, 83]. Values below 1.0  $\Delta E$  are generally considered imperceptible to the human eye [84]. Error bars were calculated as explained in Additional file 3: Appendix S1.

#### **Glossimetry**

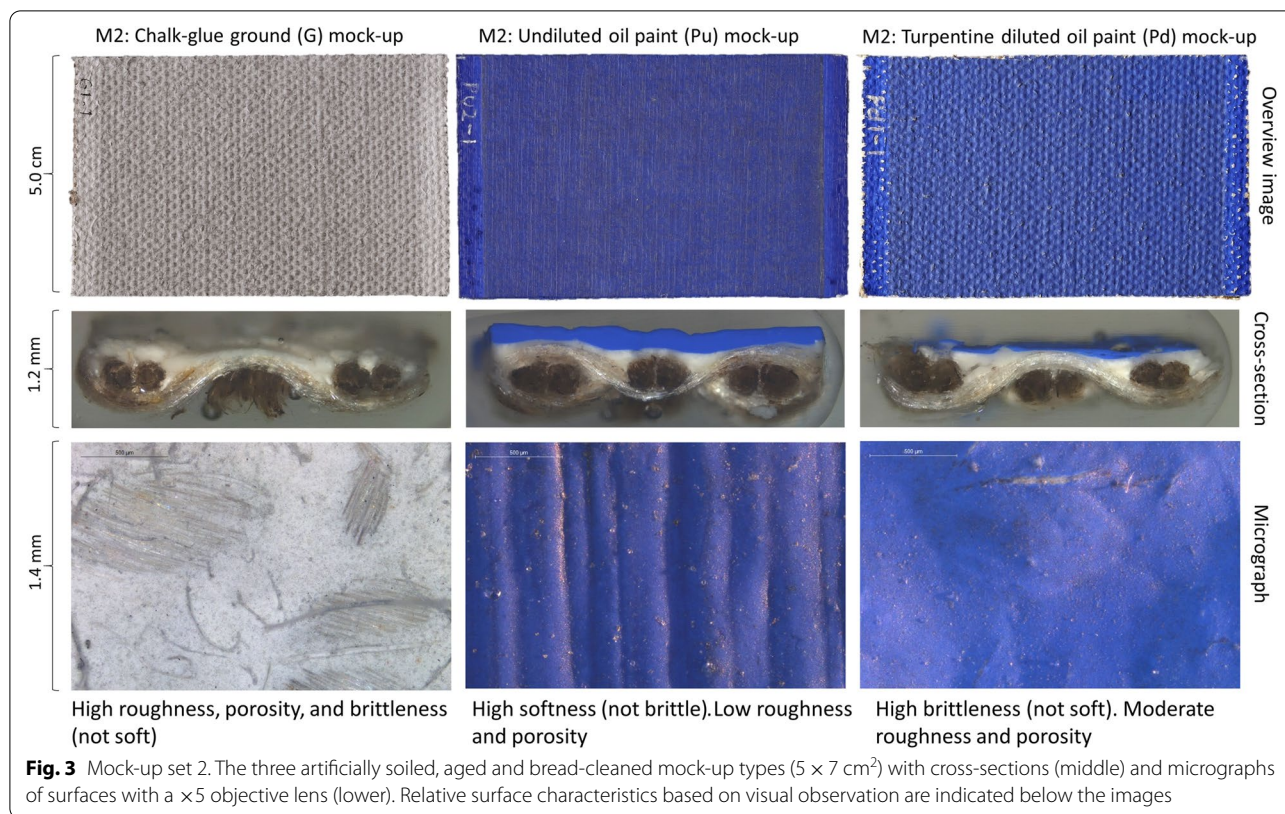
Gloss measurements were performed before and after cleaning using a 480 Triple angle glossmeter (Elcometer, Manchester, UK). Initial gloss measurements carried out at 60° showed values below 10 gloss units (GU) for all mock-ups, indicative of matte surfaces. Therefore, a measurement angle of 85° was used. In the 0–10 GU range, the Elcometer 480 has a repeatability of  $\pm 0.1$  GU and reproducibility of  $\pm 0.2$  GU. Final values were obtained by averaging ten measurements from three mock-ups of the same type. Error bars were calculated as explained in Additional file 3: Appendix S1.

#### **Microscopy**

A benchtop DM2700 M Microsystem light microscope (LM) (Leica Microsystems, Wetzlar, Germany) was used to study cross-sections from the M2 control set in order to determine variations in layer thickness between the three mock-up types. Layer thickness and variations

<sup>17</sup> The star ratings have been off-set for overlap visibility and do not represent small differences in the ratings given.

<sup>18</sup> Parameters A–C and F (and d–e) were rated from qualitative evaluation, while parameters D and E were rated from quantitative data.



across textured surfaces influence the sensitivity of the surface towards mechanical cleaning. Photomicrographs were obtained using a Leica MC190 HD camera and the Leica Application Suite v.4.13 image acquisition software. Changes to the surfaces of M1 and M2 were imaged in bright field (BF) with N PLAN EPI objectives 5×/0.12 POL and 20×/0.40 POL at the same spot before and after cleaning. Surfaces were also documented with slight right-hand illumination (Leica CLS100) and in UV, using a fluorescence excitation Leica EL6000 light source and a D filter cube; BO 355–425, 455, LP 470.

**Scanning electron microscopy (SEM)**

A selection of M2 mock-ups was examined before and after cleaning using a Quanta 450 scanning electron microscope (FEI, Hillsboro, OR, USA) with the aim of detecting surface changes after cleaning. Mock-ups (5 × 7 cm<sup>2</sup>) were mounted inside the vacuum chamber with carbon sticky tape on the sample stage, without any surface preparation. Morrison et al. [75] were consulted for appropriate magnification and imaging conditions for documenting cleaning tests on paint surfaces. Secondary-electron SEM images were acquired under high vacuum at low accelerating voltage (1.7 kV), working distance between 7.6 and 10.0 mm, and electron-beam-spot size 6.0, at 100× and 500× and 1000× magnification. The

magnification was slightly adjusted for each surface to sharpen the image.

**Fourier-transform infrared (FTIR) spectroscopy**

Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy was carried out on unsoiled M2 control mock-ups to compare infrared absorption bands at the very end of the accelerated ageing and bread cleaning steps to the naturally aged controls, and to compare the spectra to those of materials from the Aula paintings. A Spectrum One spectrometer (Thermo Fischer Scientific, MA, USA) with diamond ATR crystal was used with a medium-band mercury cadmium telluride (MCT) Detector with 0.25 mm detector area. 64 scans were collected at 4 cm<sup>-1</sup> resolution across 4000 to 650 cm<sup>-1</sup>. The data was processed with Spectrum 5.1 software. Measurements were obtained in triplicate.

**Results and discussion**

**Condition of mock-ups before cleaning**

Figure 3 shows three of the artificially aged, soiled, and bread-cleaned M2 mock-ups and lists their surface properties based on visual observation. The scores for chalking and water-sensitivity are provided in Table 2. Given the use of contemporary materials and the inherent

limitations of artificial ageing, the mock-ups were not expected to exactly replicate the surfaces and cleaning responses of the Aula paintings, finished by Munch in 1911–16. Nonetheless, the artificial soiling and ageing procedures were successful in integrating the soiling (Additional file 1: Figure S7) and rendering the mock-ups more vulnerable to mechanical and aqueous cleaning.

As a result of the different accelerated ageing, artificial soiling and bread cleaning steps, the chalking and water-sensitivity of M1 and M2 differed (Table 2). Generally, the chalk-glue ground (G) and diluted cobalt blue oil paint (Pd) mock-ups behaved similarly and demonstrated more chalking and sensitivity to water than the undiluted cobalt blue oil paint (Pu) mock-ups. The Pu mock-ups were slightly less water-sensitive than the cobalt blue paint on *The Sun* (Additional file 2: Table S2). Dry swab-rolling tests indicated that the M1-G and M2-G mock-ups transferred unbound ground particles in a manner similar to the *Alma Mater* chalk-glue ground. In the M2 mock-ups, the soiling appeared more embedded in the more medium-rich (and soft) undiluted paint (Pu) than on the lean G and Pd mock-ups, despite the rougher and more porous surface texture of the two latter samples. This indicated that paint softness is likely to have affected the soiling adhesion more than surface roughness and porosity (see Footnote 3).

The FTIR spectra of the aged and unsoiled M2 control G mock-ups, and the ground of *Alma Mater* (Additional file 1: Figure S8a) showed stretching bands for carbonate ions ( $\text{CO}_3^{2-}$ ) at 1795, 1390, 870 and 710  $\text{cm}^{-1}$  that relate to the chalk, which largely overlap with the characteristic absorption bands of protein in animal glue except for the amide I band [85]. The weak IR absorbance bands at 1645  $\text{cm}^{-1}$  might correspond to the C=O stretching of amide I.

Changes in the IR absorption bands in spectra of the unsoiled cobalt paint (M2 Pu and Pd controls) after accelerated ageing (Additional file 1: Figure S8b, c) indicated the presence of degradation products associated with water-sensitivity in modern oil paint [86, 87]. Decreased intensity of the C=O glycerol ester band at  $\sim 1720 \text{ cm}^{-1}$  suggests hydrolysis of ester groups in the oil medium.<sup>19</sup>

The broadening of the band at  $\sim 1705$  (shoulder), the development of bands at  $\sim 1640$  (probably asymmetric COO–stretching) and at  $\sim 1320 \text{ cm}^{-1}$  (assigned to C–O stretching) were attributed to the formation of free carboxylic acid (fatty acid) moieties promoted by oxidation and hydrolysis during the humid ageing [35, 38, 87, 88].

A more intense metal carboxylate absorption at  $\sim 1640$  relative to the ester band ( $\sim 1720 \text{ cm}^{-1}$ ) was seen in the spectrum for the cobalt blue oil paint from *The Sun* compared to the spectra of the M2-Pu and M2-Pd mock-ups, along with more intense bands with maxima at 1460 and 1420  $\text{cm}^{-1}$  (attributed to the symmetric stretch of  $\text{COO}^-$ ) (Additional file 1: Figure S8b, c). Bands at these wavelengths have been associated with metal soaps (metal carboxylates) [89],<sup>20</sup> suggesting that these degradation products (as expected) are more prominent in the Munch cobalt blue paint than in the mock-ups.

Bands for sulfate (from the barium sulfate extender) included the S–O stretching at 1180, and the (symmetrical) vibration of  $\text{SO}_4^{2-}$  at 1110 and 1080  $\text{cm}^{-1}$  were present in both the M2-Pu and M2-Pd mock-ups and the sample from *The Sun*.

### Stage one—initial trials exploring working parameters on mock-up set 1 (M1)

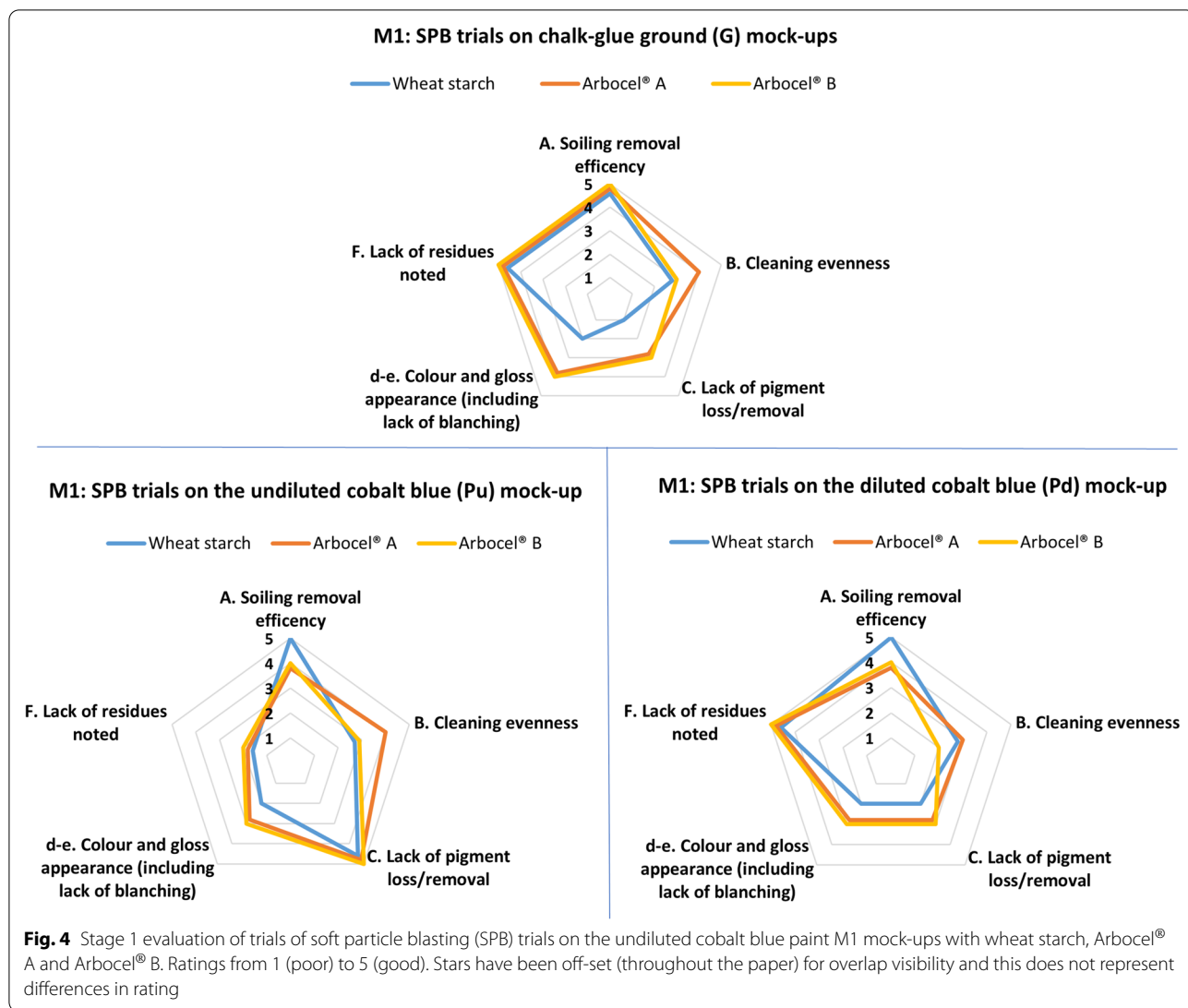
Table 2 lists the cleaning options tested on M1.

#### M1: soft particle blasting (SPB) trials

Initial tests of the velocity of the SPB cleaning particles suggested that they maintain a slightly higher speed than compressed air alone (Additional file 1: Figure S9a). The velocity of the particle stream dropped quite rapidly from one to five centimetres and reduced gradually as the distance increased, suggesting that cleaning was most active at the nozzle to surface distances in the one-to-five-centimetre range. The trials indicated a relationship between visible cleaning, surface scratching/pigment loss, and nozzle-to-surface distance (see Additional file 2: Table S3). Figure 4 summarises the results of the SPB cleaning trials. Wheat starch removed soiling most efficiently across all mock-up types (Rating 5), but created more undesirable surface changes than the less abrasive Arbocel® A and B. The Arbocel® particles performed quite similarly to one another in terms of cleaning efficacy, pigment loss, and colour and gloss appearance. Arbocel® A cleaned slightly more evenly across all mock-up types (Rating 3–4), which might be due to its smaller particle size (40  $\mu\text{m}$ ) than Arbocel® B (120  $\mu\text{m}$ ) (Rating 2–3). The M1-G and M1-Pd mock-ups were affected by all SPB-abrasive particles and received pigment removal ratings of 1 and 2 for wheat starch and 3 for the Arbocel® abrasives respectively. Abrasion of the highest points of the rougher and more highly textured M1-G and M1-Pd surfaces was observed under magnification. These results must be considered within the context of the thin (29  $\mu\text{m}$

<sup>19</sup> The reduction of the ester band was more prominent for M2-Pd than M2-Pu, which suggests that the thinned and porous paint of the M2-Pd was more affected by hydrolysis than the undiluted M2-Pu paint.

<sup>20</sup> Metal soaps are formed from free fatty acids (from breakdown of the oil medium) and metal ions (from pigments/extendors) [89].



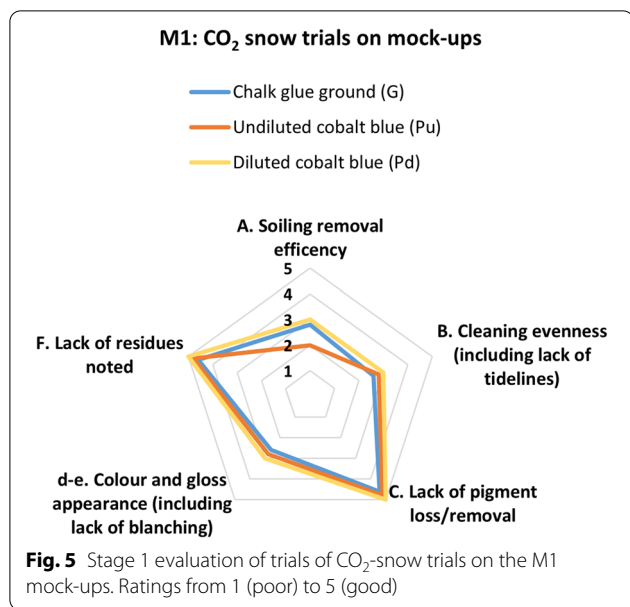
average thickness) paint layer of the M1-Pd mock-ups, and the brittle and porous ground layer (136 µm average thickness) typical of the M1-G mock-ups, which contribute to the fragility of these surfaces.

Unlike M1-G and M1-Pd, no visible pigment loss or abrasion was seen with any of the three SPB powders on the M1-Pu mock-ups, which had a thicker (239 µm average) and more medium-rich (and soft) paint layer with visible brush marks (see Fig. 3). All of the SPB abrasives scored satisfactory-to-good for soiling removal efficacy on the M1-Pu mock-ups (Rating 4–5), and moderate-to-good in terms of cleaning evenness (Rating 3–4). Observation in raking light showed that the M1-Pu mock-ups cleaned with wheat starch SPB (Rating 2 on colour and gloss appearance) became glossier than the uncleaned, unsoiled M1-Pu control. Unlike the M1-G and M1-Pd mock-ups, all the SPB media accumulated on the M1-Pu

mock-ups during cleaning and required a clearance step with compressed air between exposures, which delayed assessment post-cleaning. The three SPB media were thus assigned good ratings (Rating 5) for lack of residues on the M1-G and M1-Pd mock-ups, and poor ratings (Rating 2) on the M1-Pu mock-ups. The extent of blasting media build-up on the Pu mock-ups was similar for all the SPB powders and may be explained by the medium rich and relatively soft surfaces of this mock-up type. No cleaning particle residues were observed on any mock-ups after the surfaces were cleared with compressed air.

**M1: CO<sub>2</sub>-snow trials**

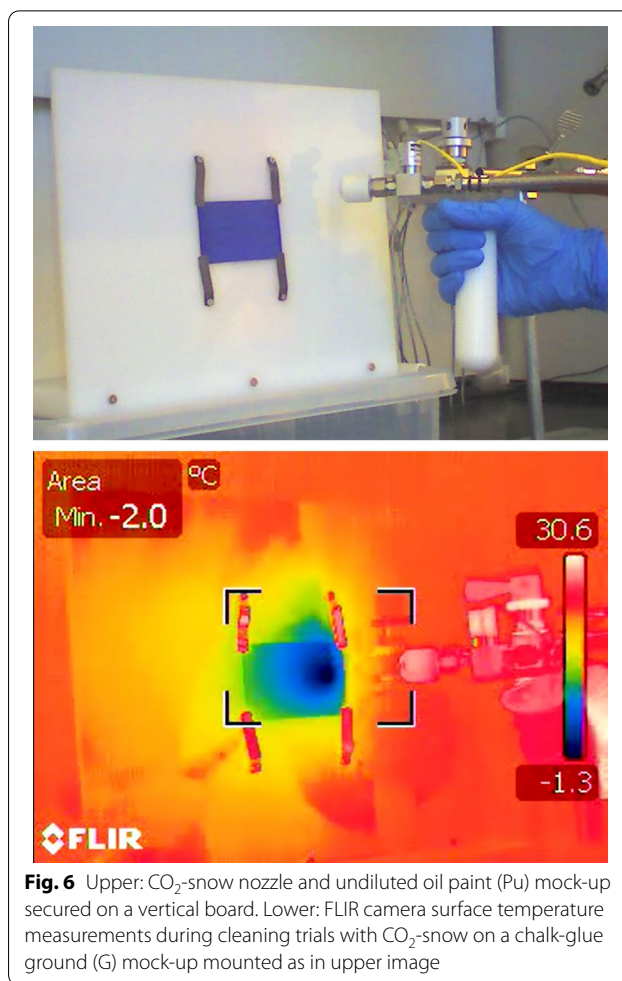
Initial trials showed that CO<sub>2</sub>-snow from a gas source was easier to control and created less surface condensation than snow from liquid CO<sub>2</sub>. Therefore, gas-derived snow was chosen for all further tests and the liquid-derived



snow will not be discussed further. Trials with CO<sub>2</sub>-snow on M1 indicated low-to-moderate soiling removal efficacy (Rating 2–3) and a low risk of pigment loss (Rating 5) (Fig. 5). The velocities required to generate and apply CO<sub>2</sub>-snow to the surface are significantly higher than with SPB (Additional file 1: Figure S9b). Nonetheless, the abrasive effect of the semi-dense CO<sub>2</sub>-snow particles was lower than that of the SPB particles, and unlike SPB, CO<sub>2</sub>-snow scored good on lack of pigment loss (Rating 5). Low surface temperatures were an additional concern with this technique. The lowest temperature recorded on the digital thermometer in the path of the snow stream – 30 °C, is unacceptable for some materials. The thermal camera recorded sub-zero surface temperatures on the brittle M1-G and M1-Pd mock-ups but not on the more medium rich M1-Pu (Fig. 6). The thicker paint layer of the M1-Pu mock-ups may partly explain the difference in surface temperature of the mock-ups. It was not clear whether the paint, ground, and canvas were affected or if cooling was limited to the surface. All surfaces rapidly warmed to around 15 °C immediately after exposure and achieved equilibrium with the ambient temperature (22 °C) after 3 to 4 min. Condensation and snow build-up occurred on the mock-ups when the nozzle-to-surface distance was reduced to around one centimetre or with prolonged snow exposure on the same spot.

**M1: trials with Nanorestore Gel® Dry and Peggy gel series**

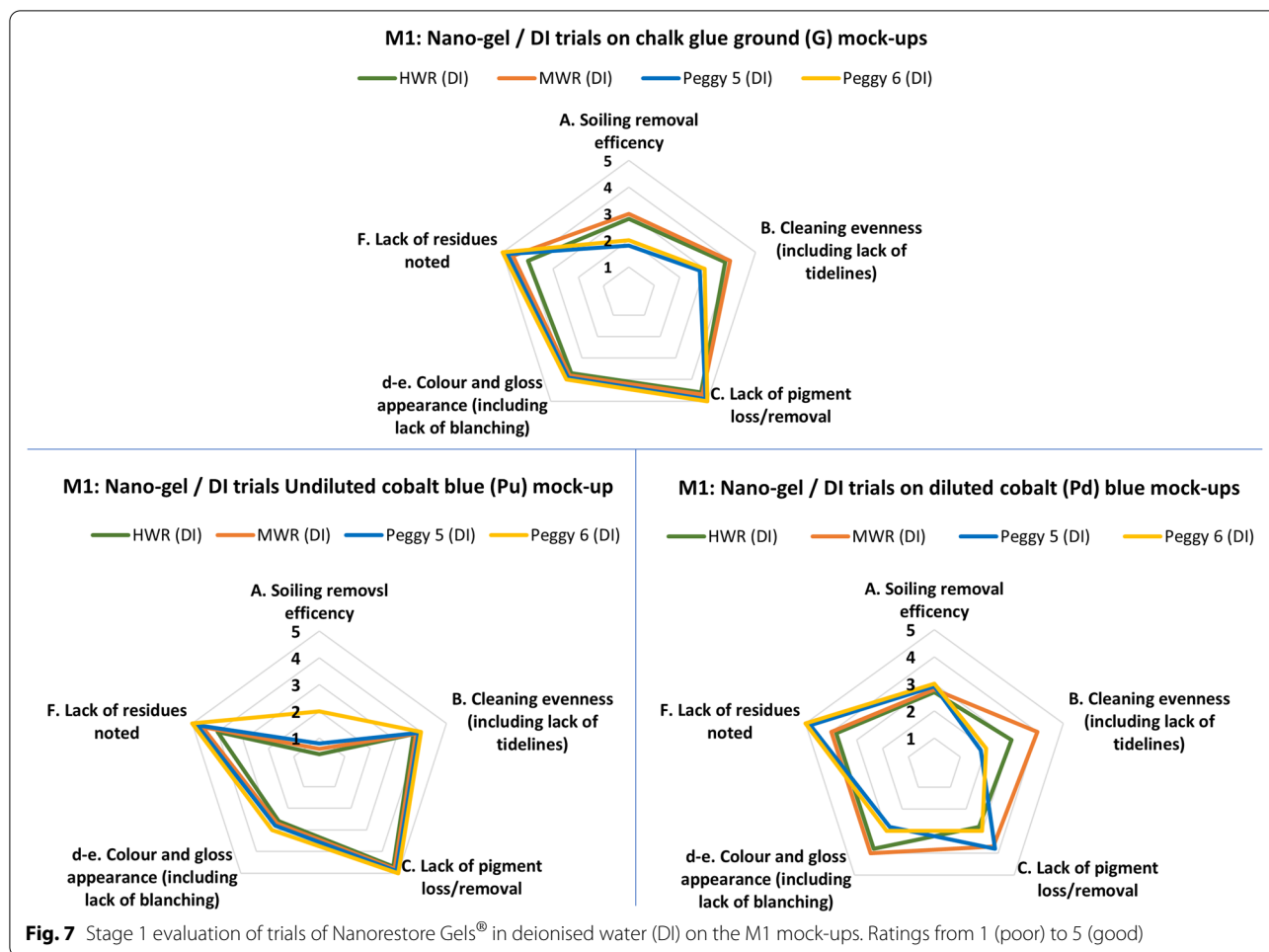
The observations from the free-liquid trials (see Table 4), that were carried out in preparation for the trials with the Nanorestore Gel® Dry and Peggy gel series, supported previous work showing that higher pH solutions



generally resulted in enhanced soiling removal [35]. The numerical rating of these trials is provided in Additional file 2: Table S6a–c.

Lowering the pH below 6.5 reduced the risk of pigment removal on the cobalt blue oil paint mock-ups (M1-Pu and M1-Pd) compared to that of DI water alone. However, the M1-G mock-ups seemed to be more sensitive to adjusted water (AW) at pH 6 and below than to AW pH 6.5 and to DI water (pH 7.1). The buffered waters (BW) (pH 5.5–6.5) did not enhance soiling removal significantly compared to AW at the same pH, hence these were ruled out due to the additional clearance step.

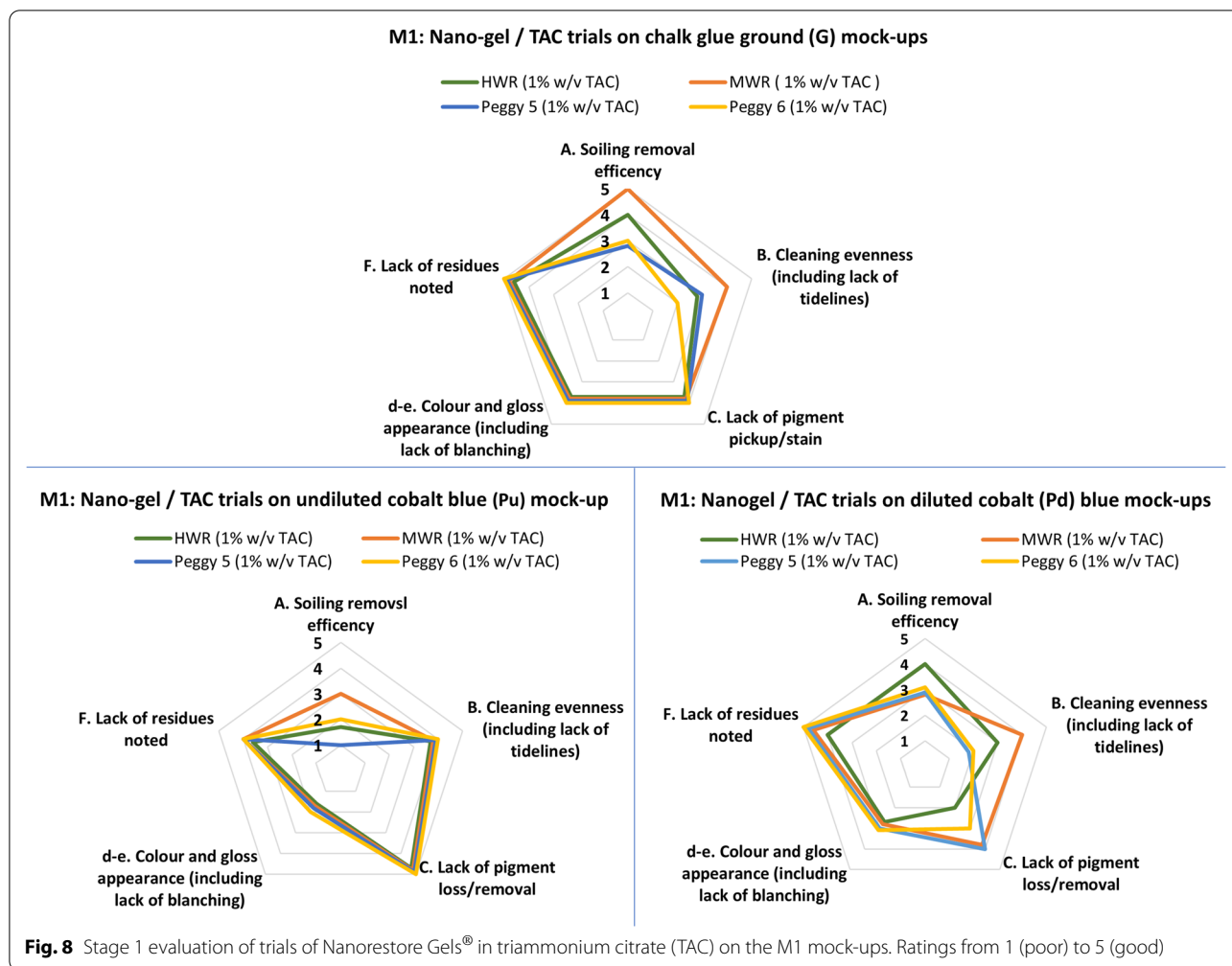
Free liquid trials showed that citric acid/NaOH solutions with pH > 6.0 and surfactant solutions increased cleaning performance over DI and AW to a similar extent as TAC. Because the trials suggested that the risk of pigment loss/removal was slightly lower with AW than with DI, the AW with the same pH as the cleaning solution were used for the clearance steps when appropriate (see Footnote 16).



*Nano-gel/DI water:* HWR and MWR Dry series nano-gels loaded in DI water revealed minimal-to-moderate cleaning efficacy (Rating 1–3) on the M1-mock-ups (Fig. 7). These two Dry series nano-gels were more efficient at removing soiling (Rating 3) than the Peggy 5 and Peggy 6 nano-gels (Rating 2) on these lean M1-G mock-ups. Soiling removal was barely visible with any of the nano-gels in DI on the medium-rich M1-Pu surfaces, probably due to the lower wettability and more heavily embedded soiling of M1-Pu. It was expected that the flexibility and moderately water-retentive properties of the Peggy nano-gels would translate to better soiling removal efficiency due to enhanced conformation with the paint surface. For the M1-G mock-ups, however, the slightly sticky surface of the Dry nano-gel series appeared beneficial for lifting and removing the surface soiling. The lean paint and small test area ( $2.5 \times 2.5 \text{ cm}^2$ ) of the M1-Pd mock-ups treated with Peggy 5 and 6 nano-gels were susceptible to tideline formation. Two minutes blotting time slightly reduced the appearance of tidelines. Larger gel cleaning areas may offer more opportunity to

control tidelines as achieved by Bartoletti et al. [29]. With the exception of some minor pigment loss on the M1-Pd mock-ups (Rating 3–4), there was no visible pigment loss or removal of loose fragments from M1-G and M1-Pu with any of the nano-gels in DI after cleaning (Rating 5).

*Nano-gel/TAC:* The addition of chelating 1.0% w/v TAC solutions, followed by a clearance step with the same nano-gel type and DI water (Table 4), increased soiling removal by at least one rating-point of each nano-gel on the M1-G-mock-ups (Fig. 8). Investigation under magnification showed some small chalk-ground fragment losses from the upper textures (Rating 4). These losses might be explained by citric acid and citrate salts being powerful calcium chelators [90], or by its effect on the hide glue in the chalk-glue matrix. The cleaning efficiency of the nano-gels on M1-Pd and M1-Pu mock-ups also seemed to increase with TAC, however this was difficult to discriminate visually due to the more embedded soiling on these mock-up surfaces (Fig. 8). The combination of HWR nano-gel and TAC resulted in the removal of paint fragments from the upper texture of the M1-Pd mock-up



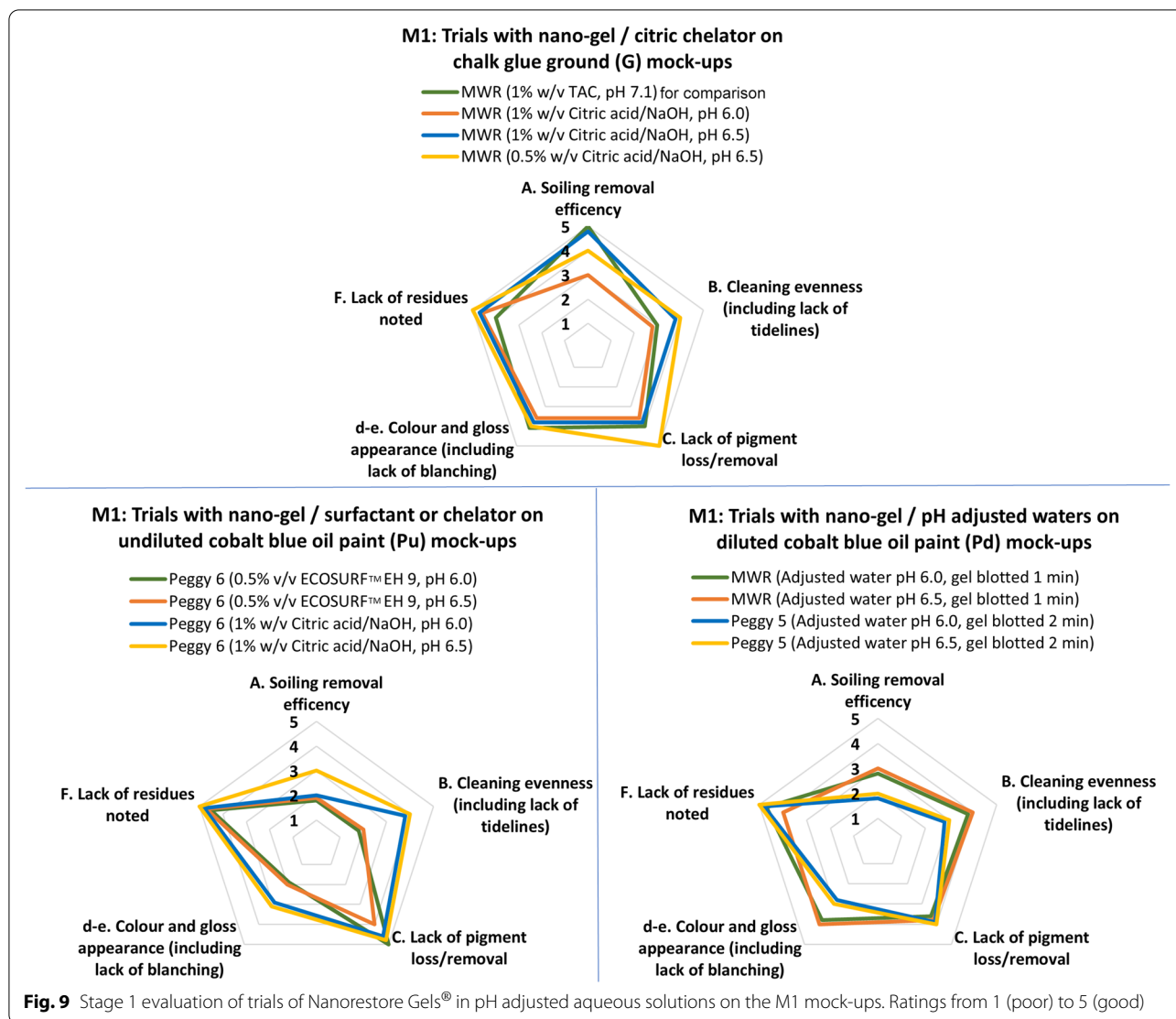
**Fig. 8** Stage 1 evaluation of trials of Nanorestore Gels® in triammonium citrate (TAC) on the M1 mock-ups. Ratings from 1 (poor) to 5 (good)

(Rating 2), and slight colour transfer was observed on the Peggy 6 nano-gel with TAC (Rating 3 on lack of pigment loss).

*Nano-gels/tailored solutions:* Fig. 9 summarises the results of the trials with the most promising nano-gels (selected from the nano-gel/DI and nano-gel/TAC trials) loaded with the most promising liquid solutions (selected from the free liquid trials). Some of these options performed more optimally than the same nano-gels in DI and loaded with TAC. MWR nano-gel with a 1.0% w/v citric acid/NaOH pH 6.5 (9.1 mS/cm) solution followed by a clearance step with AW pH 6.5 (1 mS/cm) scored higher overall on the M1-G mock-ups than the nano-gels with 1% w/v TAC (pH 7.1, 8.9 mS/cm), cleared with DI water (pH 6.8, 2 μS/cm). Reducing the concentration of citric acid to 0.5% w/v at pH 6.5 maintained good soiling removal (Rating 4) and minimised the visible loss of chalk-glue ground fragments (Rating 5) on M1-G. The liquid trials showed that the soiling removal ability of the AW, and the citrate solutions with pH < 6.0 was negligible

for M-Pu surfaces, and were thus not considered. Peggy 6 nano-gels loaded with 1.0% w/v citric acid/NaOH solutions with pH 6.5 (9.2 mS/cm) scored higher (Rating 3) than the same nano-gels with 1.0% w/v TAC (Rating 2) (Figs. 8 and 9) on M1-Pu on colour and gloss. All nano-gels and cleaning-solution combinations scored low-to-moderate on soiling removal efficiency on M1-Pu (Rating 2–3). Peggy 6 loaded with 0.5% v/v ECOSURF™ EH 9 non-ionic surfactant in AW at pH 6.0 and 6.5 (1 mS/cm) enhanced soiling removal (Rating 2) over DI alone (Rating 1), but also caused unwanted surface changes, including blanching and reduced gloss (Rating 2) when compared to DI (Rating 3) (Fig. 8). Nano-gels with chelating agents and surfactants were not considered for M1-Pd because of the increased risk of undesirable surface changes observed during the liquid trials. MWR nano-gel in AW pH 6.0 (1 mS/cm) performed satisfactorily (Rating 4) on parameters B–E, and moderate on soiling removal (Rating 3) on the M1-Pd mock-ups. Because of the relatively strong soil retention of M1-Pu and low



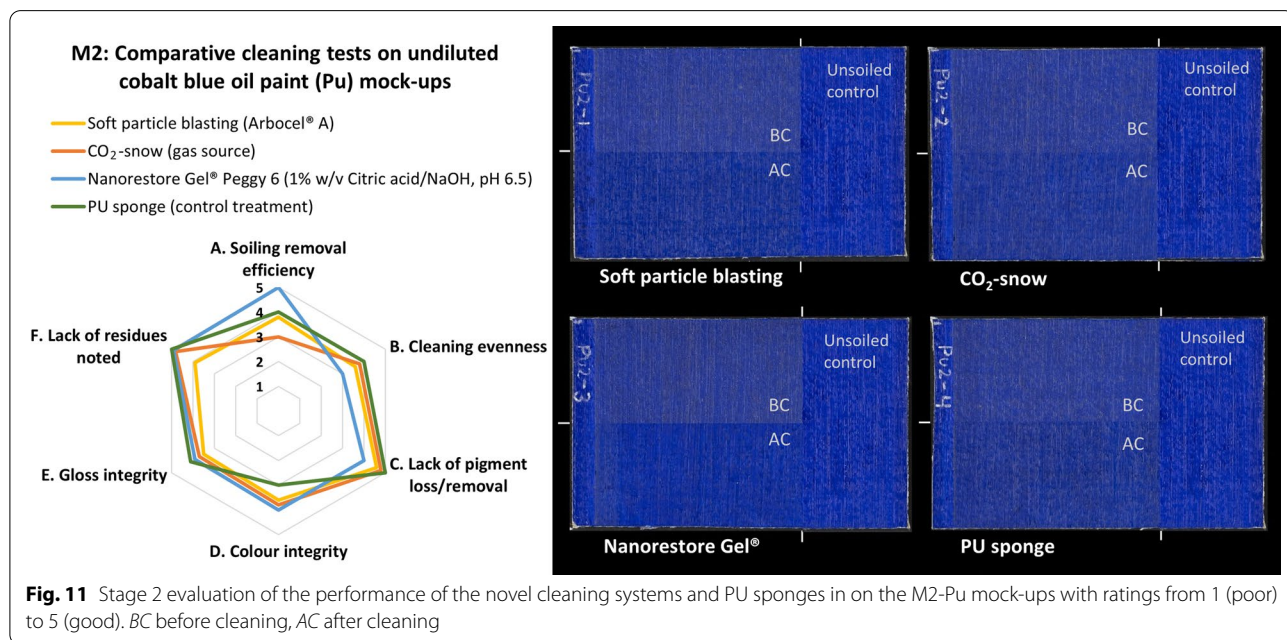
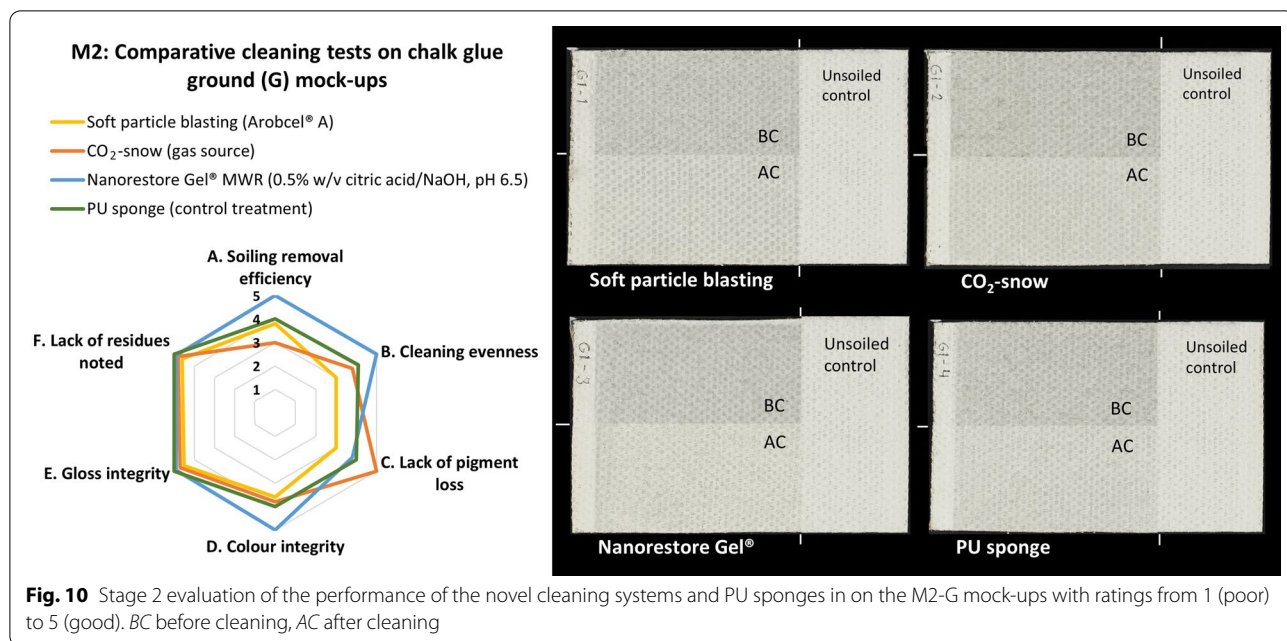


soiling removal efficiency of the nano-gels at pH 6.0–6.5 (Rating 2–3), there appeared to be no clear advantage in lowering the pH for the M1-Pd mock-ups below 6.0.

**Conclusions from stage one trials on M1**

As a result of these initial trials, the conclusion was drawn that the SPB with Arbocel® A performed consistently better than wheat starch and slightly better than Arbocel® B on the three M1 mock-up types (Fig. 4). Therefore, Arbocel® A was thus taken forward to Stage two. Despite the low surface temperatures measured on mock-ups treated with the CO<sub>2</sub>-snow from gas source, there were no visible signs that the method affected the oil paint mock-ups other than removing soiling. Because of the low risk of abrasion and pigment loss with CO<sub>2</sub>-snow (Fig. 5) compared to the other cleaning systems, this was taken forward to cleaning tests in

Stage two on M2. Nanorestore Gel® MWR loaded with 0.5% w/v citric acid/NaOH at pH 6.5, followed by a clearance step with the same nano-gel loaded with adjusted water at the same pH (see Table 4), performed well on the M1-G mock-ups on soiling removal and lack of pigment loss (Fig. 9). Soiling removal was poor-to-moderate with all the Nanorestore Gels® and cleaning-solution combinations on the M1-Pu mock-ups, with a slightly higher score obtained with Peggy 6 in 1% w/v citric acid/NaOH, pH 6.5 and a clearance step, which was therefore taken forward to Stage two (Table 4). Although none of the nano-gels and cleaning solutions proved optimal for the M1-Pd mock-ups, the MWR nano-gel with AW pH 6.0 performed slightly better overall and was also taken forward to Stage two.



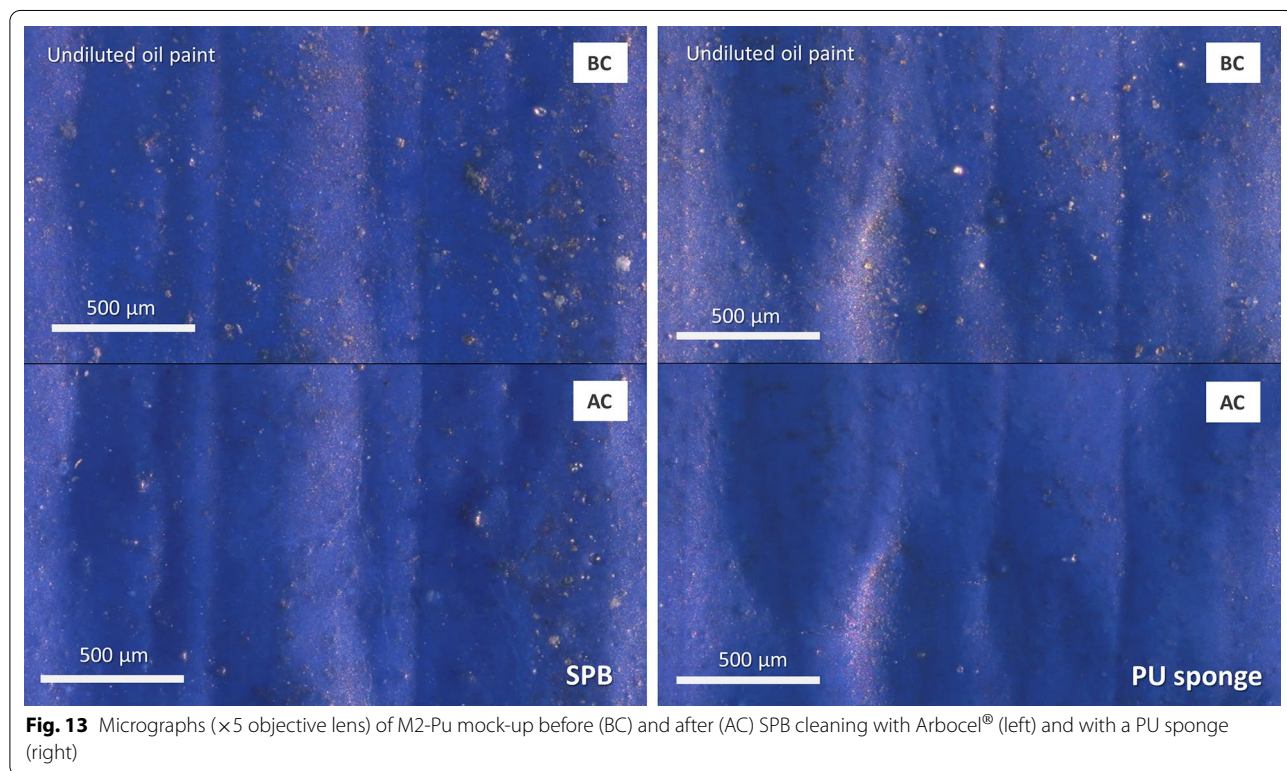
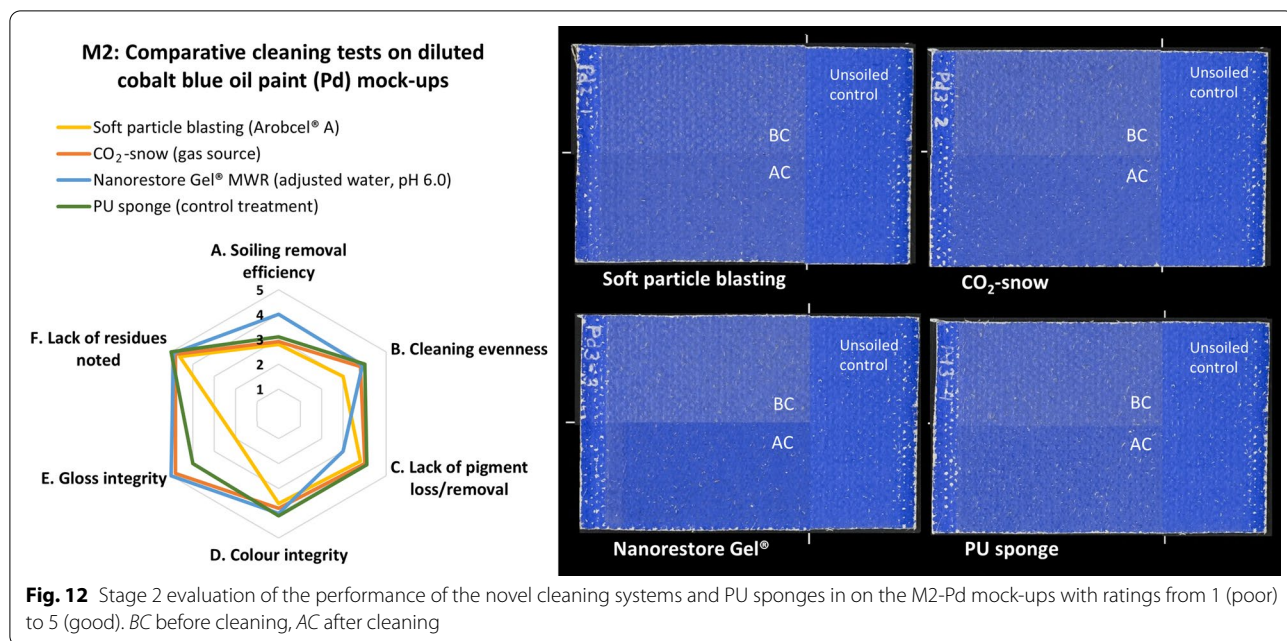
**Stage two—comparative cleaning system tests on the main mock-up set (M2) representing challenging areas of the Aula paintings**

This section discusses the comparative results of soft particle blasting with Arbocel® A, CO<sub>2</sub>-snow, Nanorestore Gel® MWR and Peggy 6, and white latex free PU sponges (Table 2). Results are based on visual assessment and investigations using magnification with LM and SEM, colour- and gloss measurements before and after

cleaning. Cleaning tests were carried out on three mock-ups of each type per cleaning technique. Additional file 2: Table S4 and S5 lists the rating criteria for the evaluation parameters used. The results are summarised in Figs. 10, 11, 12.

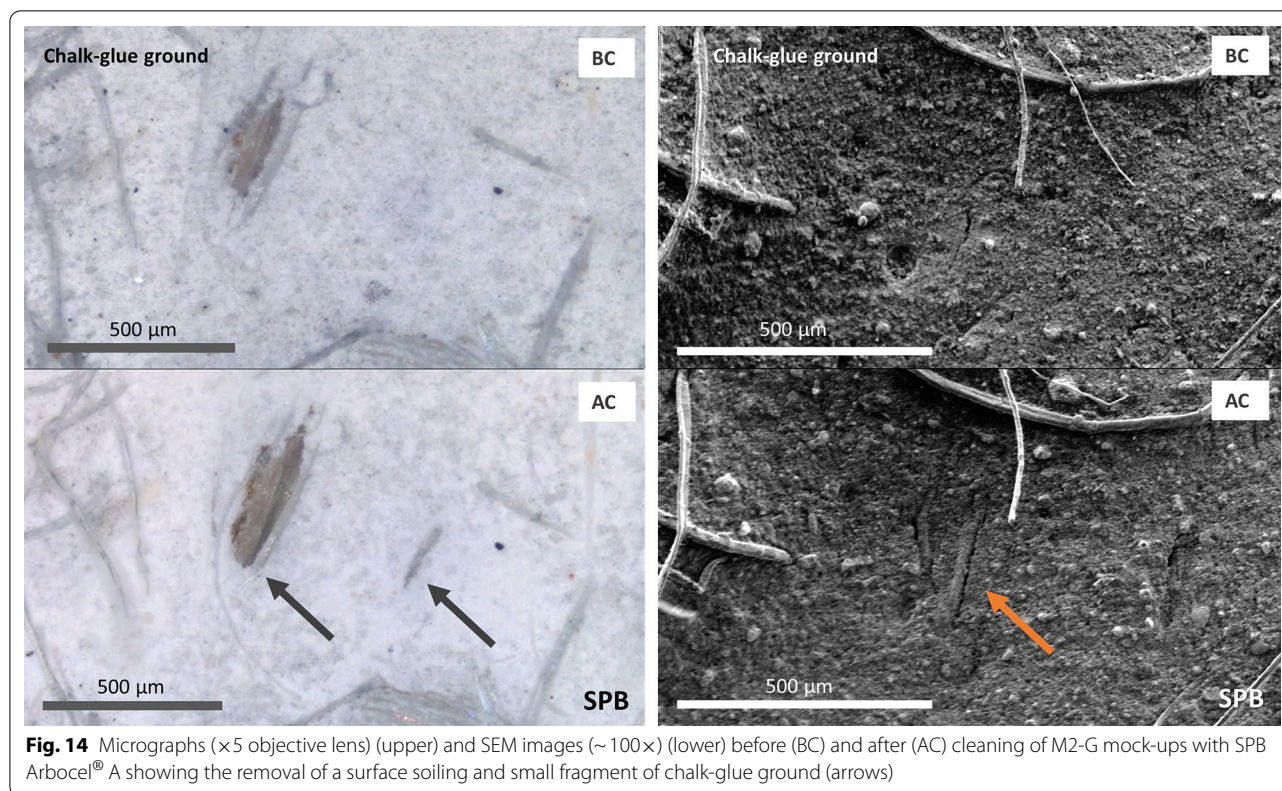
**M2: soft particle blasting (SPB) cleaning tests**

Arbocel® A scored satisfactory (Rating 4) in terms of cleaning efficiency and moderate (Rating 3) on evenness



on the M2-G mock-ups (Fig. 10). The soiling removal efficiency was rated 4 on the M2-Pu and rated 3 on the M2-Pd mock-ups, like that of PU sponges (Figs. 11 and 12). Images obtained under optical microscope suggest slightly more uneven cleaning of SPB cleaned M2-Pu

mock-ups, at least in local areas, than PU sponge cleaned M2-Pu mock-ups (Fig. 13), but both scored 4 overall on cleaning evenness. It was more difficult to achieve effective and even cleaning (Rating 3) results with SPB on the thin and brittle paint layer of the M2-Pd mock-ups with



a relatively large surface roughness, than with the other cleaning systems (Rating 4).

The varied surface appearance and roughness of the M2-G mock-ups, with exposed, darker canvas knots in the upper textures of the M2-G mock-ups (after pre-cleaning with bread loaf) (Fig. 3), meant that it was difficult to detect losses during cleaning using SPB. Investigation under magnification after cleaning showed that some small fragments of the ground had been removed on the M2-G mock-ups (Rating 3 on lack of pigment loss/removal) together with the soiling, as seen in Fig. 14. SPB resulted in barely visible pigment loss on a few of the brittle upper textures of the M2-Pd mock-ups (Rating 4), but not in any of the areas documented with micrographs or SEM before and after cleaning. This suggests that the cleaning action was relatively gentle even on the brittle and disrupted paint layer of these mock-ups (Fig. 15). No abrasion or pigment loss was noted on the M2-Pu mock-ups (Rating 5).

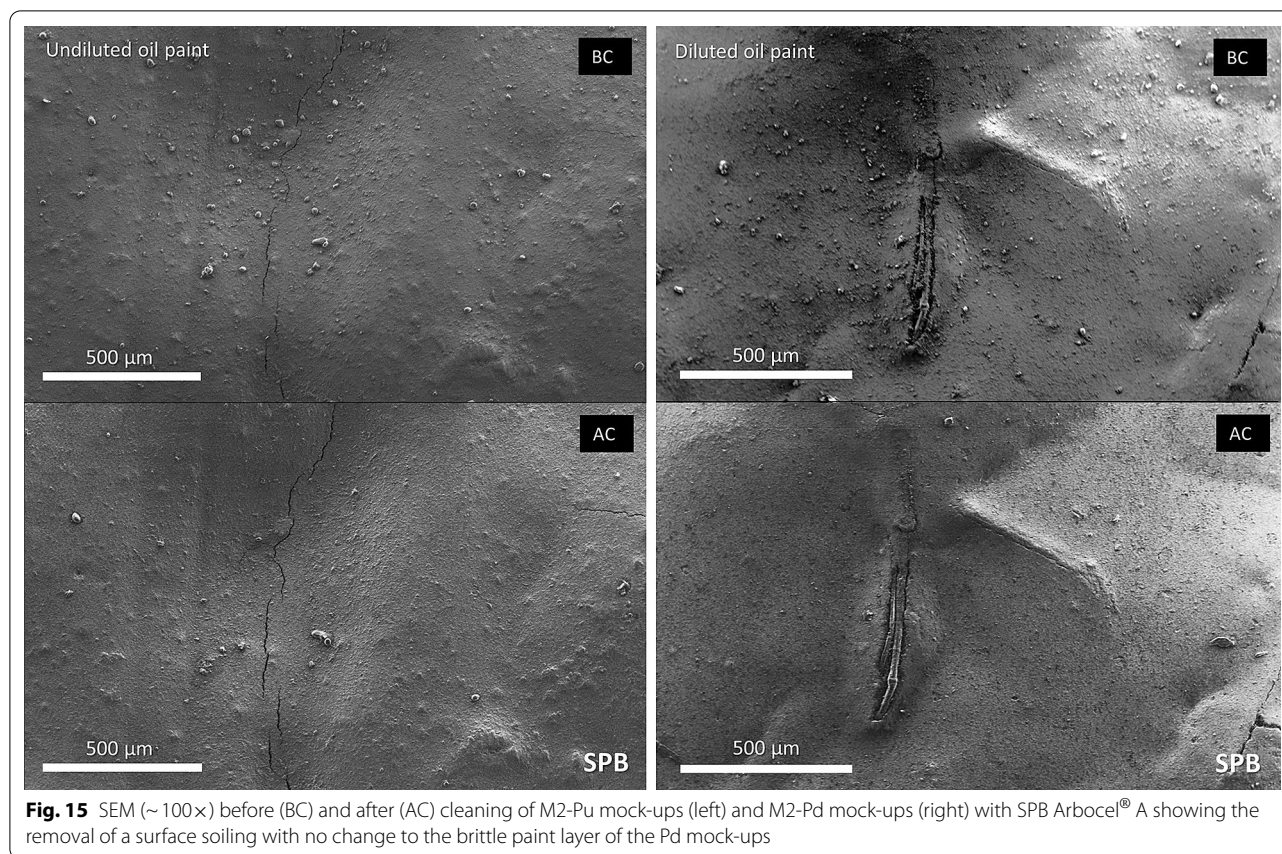
SPB scored satisfactory on the M2-G mock-ups in terms of colour (Rating 4) and gloss integrity (Rating 5), with a visible increase in lightness, and with a higher resemblance to the accelerated aged, unsoiled control after cleaning (see Additional file 2: Table S4). This indicates that a substantial amount of the darker soiling was removed. Colour measurements of the M2-Pu and

M2-Pd mock-ups after cleaning confirmed lower  $\Delta E$  values (Rating 4 on both) to that of the unsoiled controls than before cleaning (Additional file 1: Figure S10b, c). The surface gloss of the M2-Pu mock-ups increased by 1 GU to 3.1 GU on average after cleaning (Rating 4), which was still low compared to the surface gloss of the unsoiled control (7.5 GU) (Additional file 1: Figure S11b). The surface gloss of the M2-Pd mock-ups did not change significantly (Rating 2), as they maintained a matt appearance compared to the unsoiled control.

As for the SPB trials on the M2-Pu mock-ups, some build-up of Arbocel® A cleaning residues occurred on the surface of these mock-ups during cleaning, which delayed the assessment of the cleaned areas (Rating 4 on lack of residues) (Fig. 11). No Arbocel® A cleaning particle residues were noted on the M2-G and M2-Pd mock-ups after clearance with compressed air (Rating 5).

#### M2: CO<sub>2</sub>-snow cleaning tests

CO<sub>2</sub>-snow cleaning removed soiling evenly from the M2 G, Pu, and Pd mock-ups (Rating 4) (Figs. 10, 11, 12). It was the least soiling removal efficient cleaning system for M2-G (Rating 3) (Fig. 16) and M2-Pu (Rating 3). It performed similarly to SPB and PU sponges on M2-Pd (Rating 3).



**Fig. 15** SEM ( $\sim 100\times$ ) before (BC) and after (AC) cleaning of M2-Pu mock-ups (left) and M2-Pd mock-ups (right) with SPB Arbocel<sup>®</sup> A showing the removal of a surface soiling with no change to the brittle paint layer of the Pd mock-ups

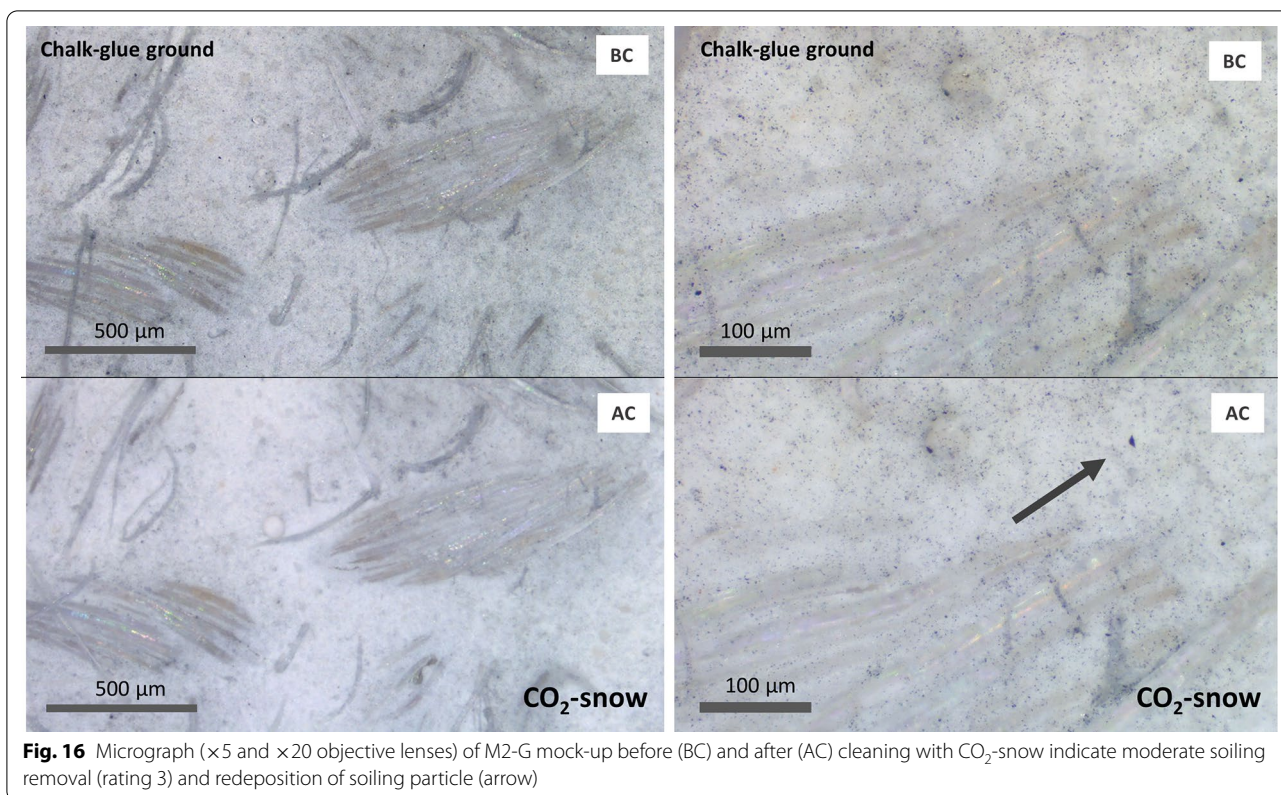
CO<sub>2</sub>-snow removed less pigment than the other cleaning systems (Figs. 10, 11, 12). No surface abrasion or paint loss was visible under magnification on M2-G (Rating 5) and M2-Pu mock-ups (Rating 5). A few fragments were removed from one of the three M2-Pd mock-ups (Rating 4) (Fig. 17). SEM imaging showed widening ( $\leq 1\ \mu\text{m}$ ) of a crevice in the paint layer of a cleaned M2-Pu (Fig. 18). The increased gap size may suggest soiling removal, slight erosion, or compression and expansion of the paint due to the low temperatures involved in the CO<sub>2</sub>-snow cleaning.

Cleaning with CO<sub>2</sub>-snow decreased the  $\Delta E$  relative to the M2 unsoiled controls (Rating 4), confirming that a significant amount of dark soiling particulate had been removed (Additional file 1: Figure S10a–c). Cleaning with CO<sub>2</sub>-snow resulted in a higher increase in gloss on the M2-G mock-ups than the other cleaning systems, with values closest to the unsoiled control (Rating 5) (Additional file 1: Figure S11a). However, this increased surface gloss fell below 0.5 GU for all systems and was close to the experimental error. Like SPB, CO<sub>2</sub>-snow cleaning of the M2-Pu mock-ups resulted in a slight gloss increase of 1 GU (Rating 4) (Additional file 1: Figure S11b). The surface gloss (3.3 GU) of the Pd mock-ups after CO<sub>2</sub>-snow

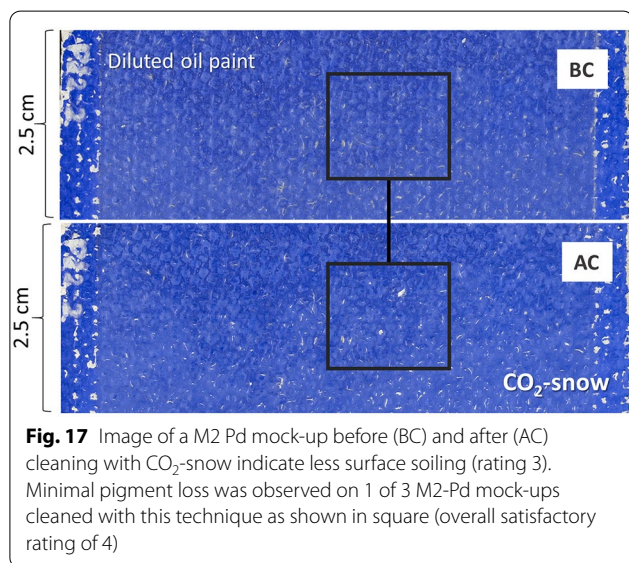
cleaning was closer to the unsoiled control (3.9 GU) (Rating 5) although this was also close to the experimental error (Additional file 1: Figure S11c). CO<sub>2</sub>-snow does not leave residues (Rating 5).

#### **M2: nanorestore Gel<sup>®</sup> cleaning tests**

Cleaning tests with the MWR nano-gels with a 0.5% w/v citrate at pH 6.5 resulted in an even (Rating 5) and good soiling removal (Rating 5) from the M2-G mock-ups, as noted in Fig. 10. Unlike the other cleaning systems, the MWR nano-gel type and cleaning solution resulted in a close to complete removal of the dark (black carbon) particles within the artificial soiling from the lean (low softness) M2-G mock-ups, as seen with magnification (Fig. 19). The M2-Pu mock-ups, with their relatively high surface softness and embedded soiling were efficiently cleaned (Rating 5) with Peggy 6 nano-gels loaded with 1% w/v citric acid/NaOH (pH 6.5, 9.2 mS/cm) (Figs. 11 and 20). However, some variations in cleaning evenness were observed on the nano-gel cleaned M2-Pu mock-ups (Rating 3). For example, SEM images showed particulates (possibly remaining surface soiling) in a crevice in one of the M2-Pu mock-ups after cleaning with Peggy 6 nano-gel, as seen in Fig. 21. MWR nano-gel with AW (pH



**Fig. 16** Micrograph (×5 and ×20 objective lenses) of M2-G mock-up before (BC) and after (AC) cleaning with CO<sub>2</sub>-snow indicate moderate soiling removal (rating 3) and redeposition of soiling particle (arrow)



**Fig. 17** Image of a M2 Pd mock-up before (BC) and after (AC) cleaning with CO<sub>2</sub>-snow indicate less surface soiling (rating 3). Minimal pigment loss was observed on 1 of 3 M2-Pd mock-ups cleaned with this technique as shown in square (overall satisfactory rating of 4)

6.0, 1 mS/cm) scored satisfactory on soiling removal and evenness from the M2-Pd mock-ups (Rating 4 on both parameters) (Figs. 12 and 22).

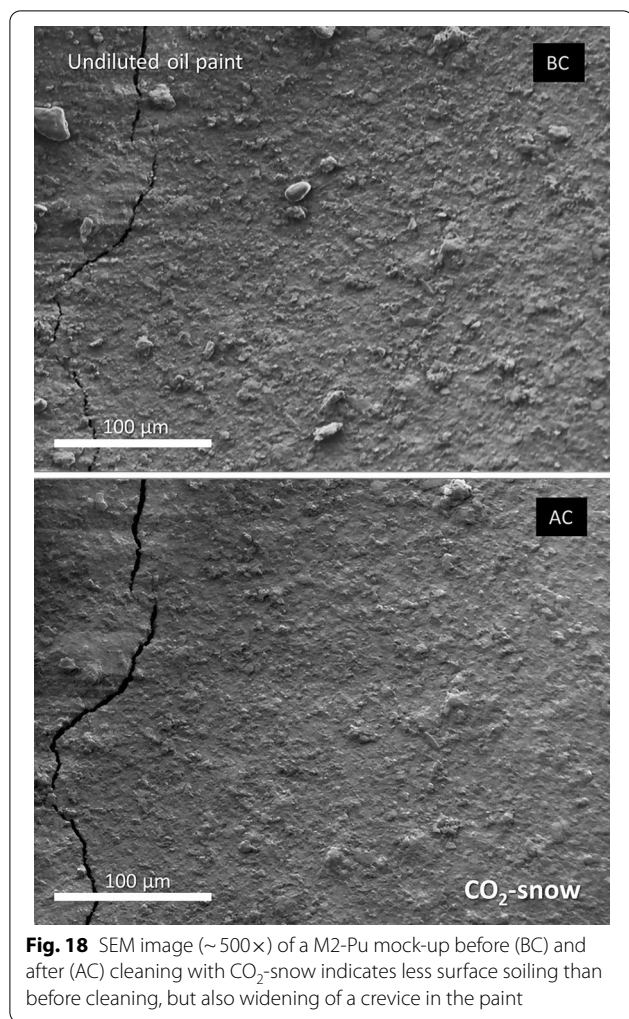
No paint loss was visible from using these MWR nano-gels with the naked eye on the M2-G mock-ups. However, investigation under magnification showed

that the gel had removed some small fragments from the ground (Rating 4) as seen in Fig. 19. A few pigment losses were also observed with the naked eye on one (of three) of the M2-Pd mock-ups after the MWR nano-gel had been peeled off the surface (Rating 3) (Fig. 22). Factors contributing to the variations in pigment loss could be inconsistencies in condition between mock-ups or a slight variation in moisture content of the nano-gels from blotting. The MWR nano-gel was rated 2 on lack of pigment removal on the M2-Pd mock-up, but 4 on the two other M2-Pd mock-ups, thus resulting in an overall score of 3 for this parameter.

Loss of trace pigments (Rating 4) was visible on the Peggy 6 nano-gel after cleaning, but not in the clearance step on the M2-Pu mock-ups.<sup>21</sup> The observations of the effect of the cleaning solution support previous studies that recommend cleaning and clearance solutions with pH 4.5–6.0 for water-sensitive, oxidised oil paints [34, 35].

Colour measurement data showed a clear increase in lightness on the MWR nano-gel cleaned M2-G mock-ups and overall values closest to those of the unsoiled control

<sup>21</sup> The same nano-gel type, loaded with buffered waters, or a chelating solution at concentrations below 1.0% w/v and at pH 4.5–6.0, may have been more appropriate for these Pu mock-ups to reduce the risk of pigment loss.



**Fig. 18** SEM image (~500×) of a M2-Pu mock-up before (BC) and after (AC) cleaning with CO<sub>2</sub>-snow indicates less surface soiling than before cleaning, but also widening of a crevice in the paint

(Rating 5) (Additional file 1: Figure S10a). The average colour values obtained after Peggy 6 nano-gel cleaning of the M2-Pu mock-ups were also closer to that of the unsoiled control (Rating 4) (Additional file 1: Figure S10b). Like CO<sub>2</sub>-snow, MWR nano-gel scored 5 on the M2-Pd mock-ups and resulted in a surface gloss closest to that of the unsoiled control (Additional file 1: Figure S11c).

The Nanorestore Gels<sup>®</sup> loaded with AW or chelating citrate solutions left no visible gel residues after the clearance step (Rating 5). In a residue study on Nanorestore Gels<sup>®</sup> and TAC using micro FTIR-2D spectroscopic imaging, Bartoletti et al. [29] found no indication of residues on unvarnished paint surfaces, which suggests that if any residues are present, the amounts lie below the 5 mg/m<sup>2</sup> detection limit of the instrument used.

### M2: PU sponge cleaning tests (control treatment)

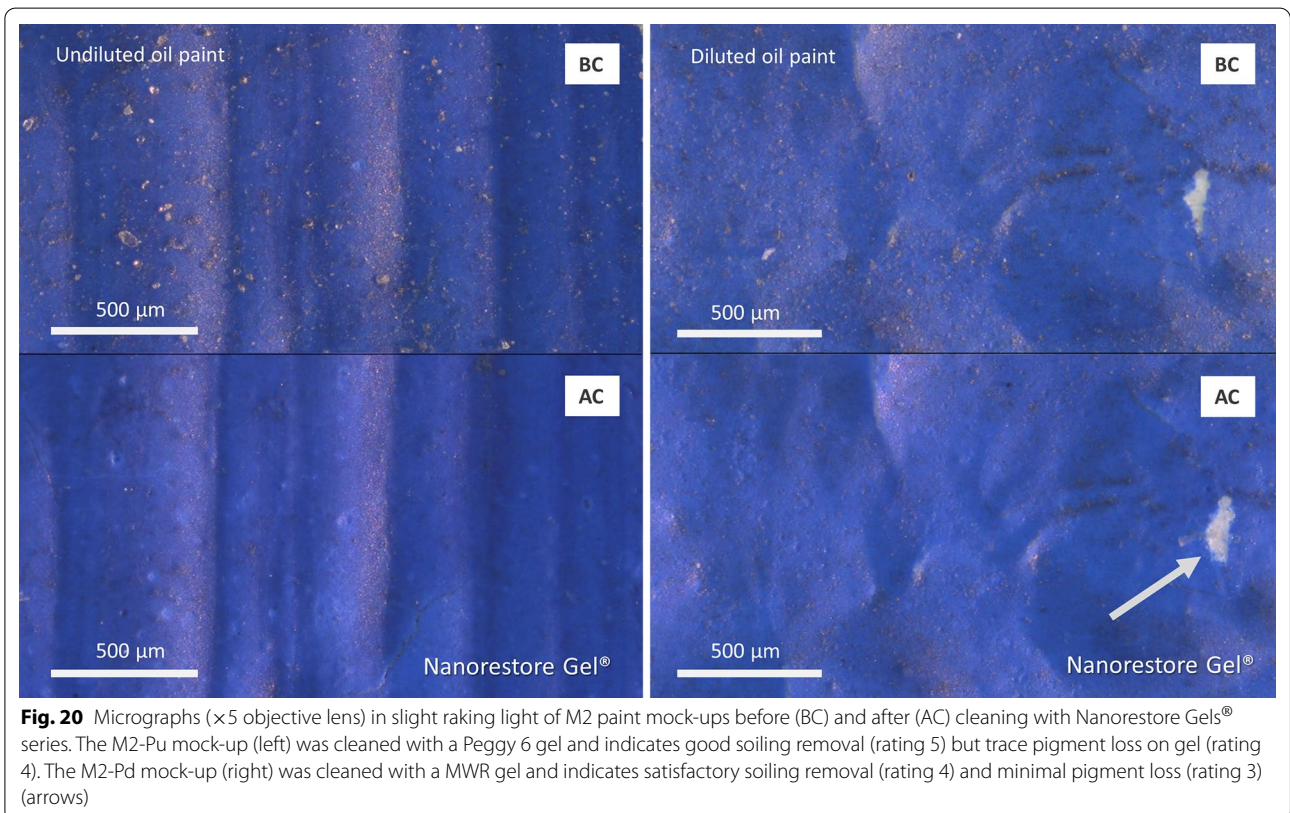
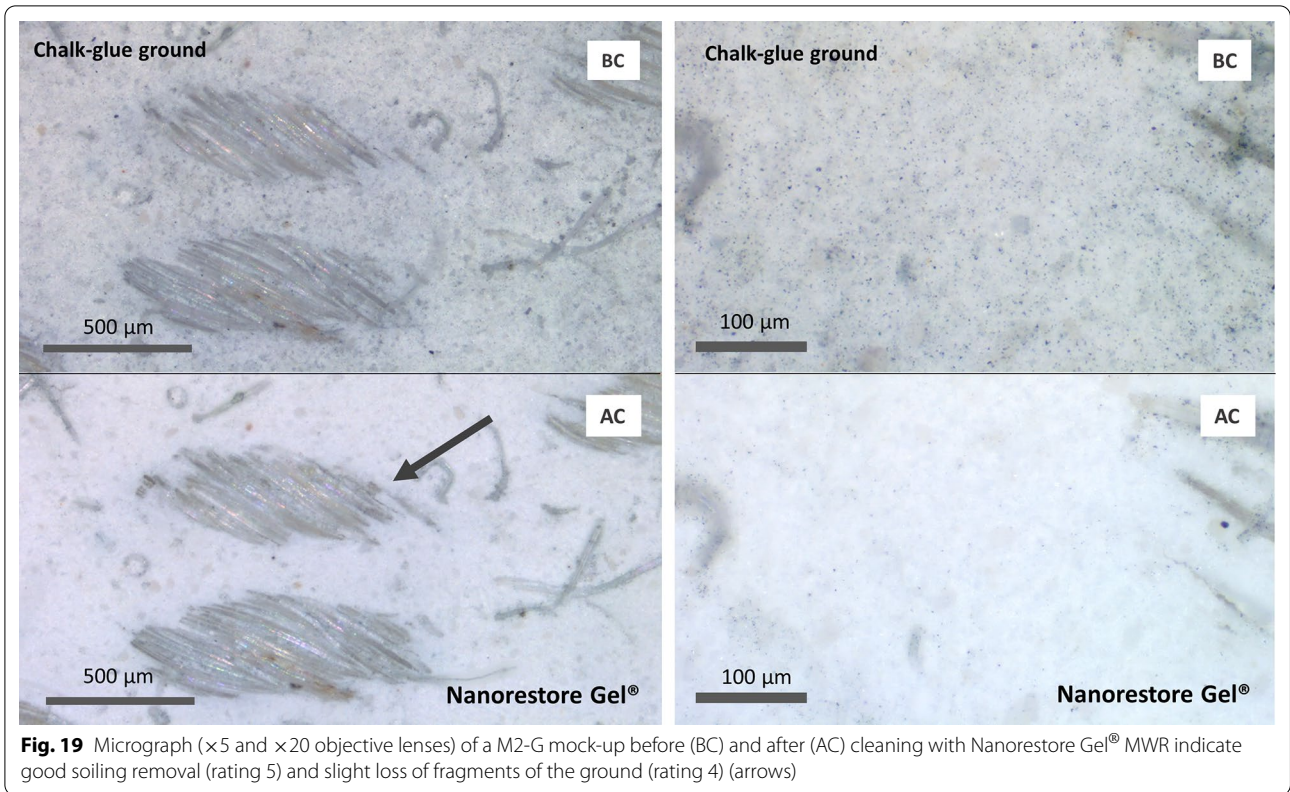
The scores for the control treatment with PU sponges are provided in Figs. 10, 11, 12. The sponges scored satisfactory (4) on cleaning efficiency and evenness on the M2-G mock-ups overall, but the cleaning was not always consistent, as seen in Fig. 23. Microscopic directional lines, interpreted as micro-scratches, appeared on the surface of one M2-Pd mock-ups after cleaning as seen in Fig. 24, and may have been caused by the dragging along of solid soiling particles by the sponge during cleaning. These lines were only visible in SEM at 500×, and not on the two other M2-Pd mock-ups cleaned with PU sponges. Similar lines were not observed with the other cleaning systems, which underlines the caution required when using mechanical action on these types of surfaces.

### Conclusions from stage two cleaning tests on M2

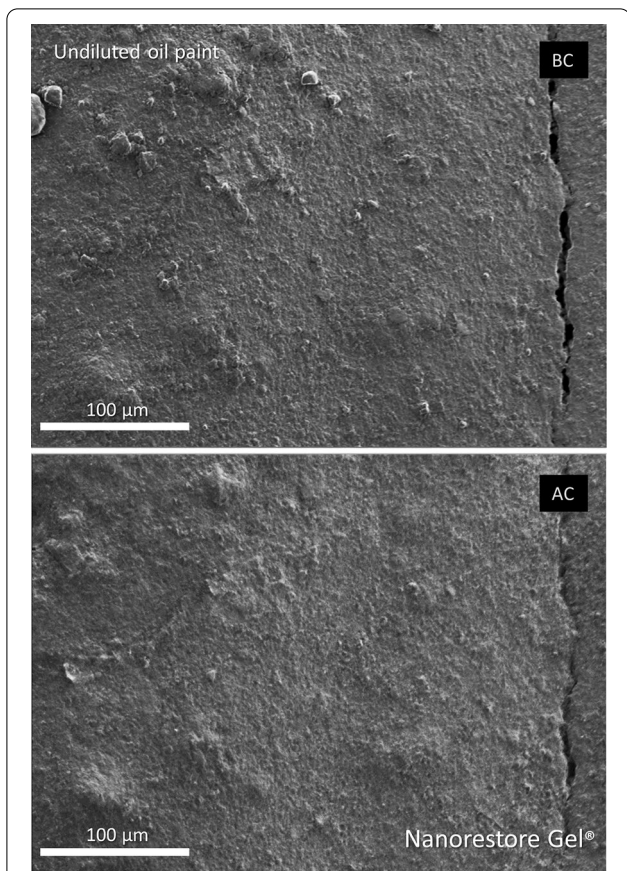
As shown in Table 5, a summary of the observed effects and soiling-removal efficiency of the novel cleaning systems on the M2 mock-ups, each system offered advantages and disadvantages compared to PU sponges, and the relative benefits and disadvantages depended on the nature of the layer to be cleaned. CO<sub>2</sub>-snow scored lowest in removing soiling, however this was the only technique that did not cause visible loss of ground fragments from the friable M2-G mock-ups (Rating 5). SPB scored 3–4 on soiling removal efficiency, nonetheless, pigment loss varied (Rating 3 on M2-G and M2-Pd mock-ups, and Rating 5 on M2-Pu mock-ups). The Nanorestore Gels<sup>®</sup> loaded with citrate solutions received the highest score (Rating 5) for cleaning efficiency on both the G and Pu mock-ups. However, the nano-gels scored lower on pigment loss on the M2-Pu (Rating 4) and M2-Pd (Rating 3) mock-ups than the other systems.<sup>22</sup>

Additional file 1: Figure S12 presents the general score of the cleaning systems on the parameters G–I: ‘ease of application/clearance’, ‘appropriate application time’, and ‘health and safety for humans’ relating to their user-friendliness during cleaning (see criteria for the parameters in Additional file 2: Table S5). This figure shows that the Nanorestore Gels<sup>®</sup> scored highest of the novel systems for these parameters.

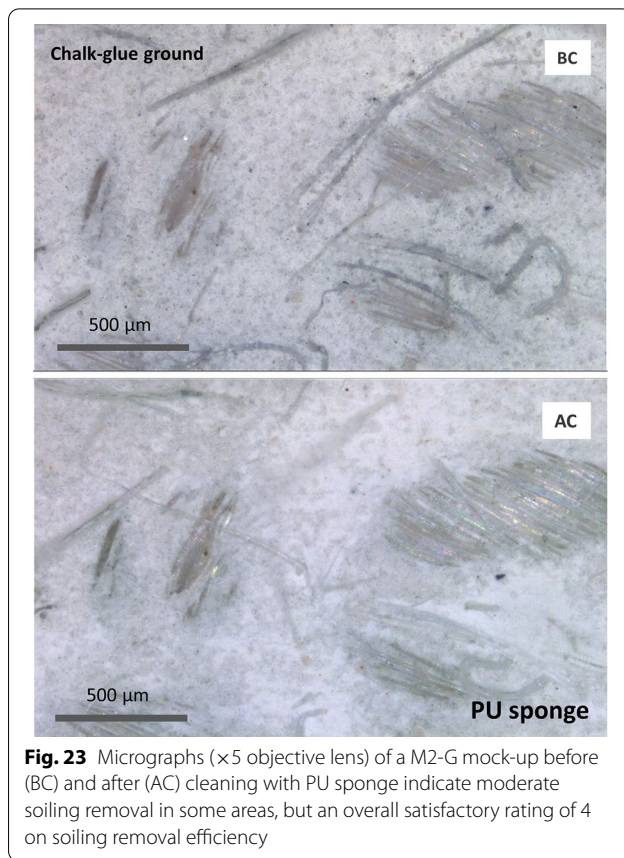
<sup>22</sup> It is likely that small adjustments of the cleaning solution, such as reducing the pH and/or the varying the concentration of citric acid, may reduce this risk to an acceptable level for the Pu and Pd mock-ups while also achieving more efficient soiling removal than the PU sponges.



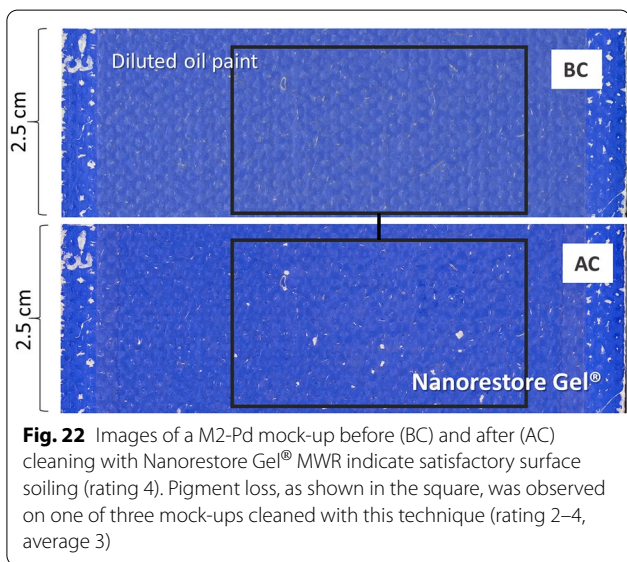




**Fig. 21** SEM images (~500×) of a M2-Pu mock-up before (BC) and after (AC) cleaning with Nanorestore Gel® Peggy 6 indicate less surface soiling than before cleaning (rating 5), but filling of a paint crevice



**Fig. 23** Micrographs (×5 objective lens) of a M2-G mock-up before (BC) and after (AC) cleaning with PU sponge indicate moderate soiling removal in some areas, but an overall satisfactory rating of 4 on soiling removal efficiency



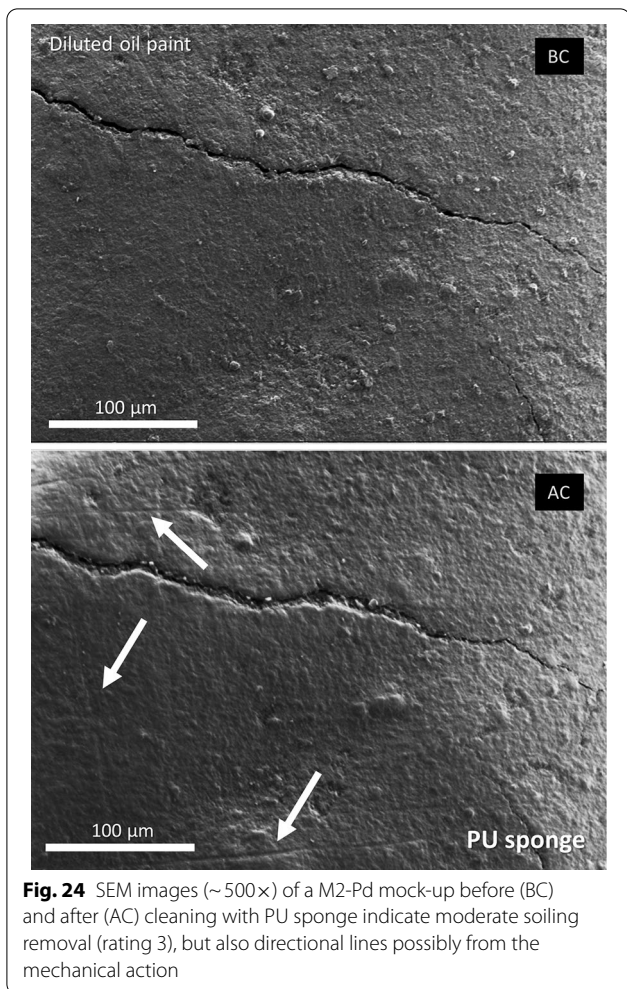
**Fig. 22** Images of a M2-Pd mock-up before (BC) and after (AC) cleaning with Nanorestore Gel® MWR indicate satisfactory surface soiling (rating 4). Pigment loss, as shown in the square, was observed on one of three mock-ups cleaned with this technique (rating 2–4, average 3)

### Implications of the cleaning system evaluations for the development of future cleaning protocols for the Aula paintings

The cleaning tests on mock-ups simulations of Edvard Munch’s Aula paintings provide useful insights into the general effects and efficacy of soft particle blasting, CO<sub>2</sub>-snow, and Nanorestore® gel cleaning systems on unvarnished paint and grounds surfaces, and into safe working parameters for SPB and CO<sub>2</sub>-snow.

Figures 11, 12, 13 represent a numerical rating of each system for each parameter, without separating between the relative importance of those parameters.<sup>23</sup> Future in-situ cleaning tests on the Aula paintings will further guide decisions on cleaning, including how each parameter should be weighted. Lack of pigment loss and high cleaning efficiency generally carry much weight in the selection of cleaning systems for heritage objects, as reflected in the requirements of cleaning noted by Bartolletti et al. [29].

<sup>23</sup> In a real cleaning situation, these considerations may be weighted differently and may vary from one cleaning situation to another, and it could be useful to give weights to each of the parameters and calculate an average score for each method.



**Representability of the cleaning tests on the M2 mock-ups in the context of the original paintings**

There are clear limitations to working with small, newly made mock-ups that cannot accurately represent 100-year-old monumental artworks like the Aula paintings. Since water-sensitivity tests suggest that the cobalt blue paint in the Aula may be marginally more sensitive to water than the mock-ups (based on the number of swab rolls, Additional file 2: Table S2), an increased vulnerability toward pigment loss in response to Nanorestore Gels® may be anticipated than was observed in the tests with mock-ups.

Even and consistent cleaning of the abrasion-sensitive M2-G and M2-Pd mock-ups proved to be quite challenging with SPB and CO<sub>2</sub>-snow. Small variations in air and CO<sub>2</sub>-tank pressure and in the number of particles hitting the surface during cleaning were unavoidable with the current equipment. Satisfactory and even cleaning would be even more challenging on large, continuous areas of the Aula paintings, with larger local variations in condition (including areas with invisible paint delamination and metal soaps) and surface soiling. The use of cut-outs of Melinex® shaped to the area to be cleaned or to be protected, might be helpful for selective cleaning of areas with a variety of paint compositions, surface textures, and conditions such as those present in the Aula. Likewise, the effects of side-by-side cleaning and overlaps that are cleaned twice was also not considered in the rating of the Nanorestore Gels® on the mock-ups. However, the result of a study where the Peggy 6 was used for cleaning water-sensitive and relatively monochrome painted surfaces

**Table.5** Summary of the observed effects and efficiency of the novel cleaning systems on the M2 mock-ups

System	Mechanism	Cleaning efficiency	Associated risks to paint/ground layer	No, or low risk of
Dry PU sponges	Mechanical	Minimal to moderate	Pigment loss/removal, scratching/polishing, undesirable gloss change, re-depositing and embedding of remaining soiling particles	Cleaning system residues
SPB	Air abrasion	Moderate to satisfactory	Pigment loss/removal, abrasion, undesirable gloss change, cleaning particle residues	Integrating remaining soiling particles
CO <sub>2</sub> -snow	Air abrasion/chemical	Minimal	Pigment loss/removal, undesirable gloss change, condensation, re-deposition and/or integration of soiling	Cleaning system residues and scratching or abrasion
Nano-gels	Mechanical/chemical	Good	Pigment loss/removal, staining, swelling, leaching, possible metal soap formation undesirable gloss change, integration of remaining soiling particles, cleaning-solution residues	Scratching or abrasion

[29] suggested that control of tidelines may be achievable with the careful reapplication of nano-gels as required.

Disadvantages linked to practical aspects, like parameters G–I, often become more influential in real cleaning situations than they are in laboratory trials.<sup>24</sup> Although it was relatively easy to clear the surfaces and to control dusting of soft particle residues during the SPB cleaning of the M2-mock-ups in a benchtop cleaning set-up, it might be experienced as a larger drawback in an in-situ cleaning situation. For this, particulate respirators and a mobile extraction and filter unit recommended by the producer would help to reduce health hazards and control dusting.<sup>25</sup> Past work has also demonstrated the possibility to control dusting by directing the particle stream towards a filtered nozzle of a vacuum cleaner during cleaning [51].

Unlike SPB, CO<sub>2</sub>-snow cleaning leaves no enduring blasting-media-residue behind. However, redeposition of soiling or recontamination [54] could be a risk on larger surfaces and may influence cleaning evenness. In addition, CO<sub>2</sub>-snow requires strict air quality monitoring, ventilation, and sometimes supplied air to mitigate health hazards associated with elevated CO<sub>2</sub> exposure. Such health and safety measures are relatively easy to arrange in a benchtop cleaning situation but would require more thought if CO<sub>2</sub>-snow were to be used in-situ.

#### **Potential of the novel cleaning systems for in-situ cleaning tests of the Aula**

The paintings such as the Aula group, which present different surfaces with individual variations in soiling state and condition, may benefit from a combined, varied approach. Nanorestore Gels<sup>®</sup> may be suitable for scratch- and abrasion-sensitive painted surfaces, the SPB for water-sensitive surfaces with imbibed soiling that are not as sensitive to mechanical action as the M2-G and M2-Pd mock-ups,<sup>26</sup> and the CO<sub>2</sub>-snow for abrasion-sensitive surfaces provided that the low surface temperatures could be further controlled.

Based on the overall performance of the cleaning systems on the M2 mock-ups and weighed against the anticipated challenges with each system as a cleaning scenario

in the Aula, the Nanorestore Gels<sup>®</sup> appear slightly more promising than the other novel cleaning systems, mainly because of the soiling removal efficiency and reduced mechanical action of the nano-gels compared to the other cleaning systems. The results therefore suggest that the nano-gels in particular show enough potential to be taken forward to in-situ cleaning tests in the future.

#### **Further considerations and work**

Important aspects to consider in the selection and optimisation of cleaning systems for in-situ cleaning tests in the Aula include the effect of the chosen cleaning system on future soiling and re-treatability of such unvarnished surfaces [35].<sup>27</sup> A potential negative side-effect of water-based cleaning, especially on porous paint layers where the moisture uptake may be significant even with water-retentive nano-gels, is the potentially accelerating effect on chemical changes such as metal-soap and metal-oxalate formation [92, 93], for instance in areas of zinc- and lead-containing grounds and paints such as present in the Aula paintings [10, 94]. However, metal soaps are also known to stabilise paint.

Both mechanical action (such as the bread cleaning and PU sponge cleaning of the Aula paintings) and elevated moisture involved in surface cleaning may increase the retention of soiling particles and further integrate them into water-sensitive cultural heritage materials [19, 40, 95–97]. Thus, any soiling that remains in the interstices of the Aula paintings after a partial soiling removal could compromise removal of the remaining soiling in the future, even if the cleaning technology were to advance significantly. The novel cleaning systems' effects on *re-cleanability* should therefore be part of an evaluation of benefits like brighter and more saturated colours, and the risks associated with partial soiling removal. Similarly, the risks of not cleaning and not removing surface soiling are important to consider as part of any balanced discussion, as high relative humidity and changes in the environmental conditions contribute to the long-term tenacity and reactivity of soiling [40, 97]. These are but some of the many aspects that add to the risk and challenges of cleaning unvarnished oil paintings such as the Munch Aula paintings.

Preventing deposition of new soiling is a priority for the Aula paintings [2, 3, 9, 98, 99]. The removal of soiling that is already present requires further optimising and in-situ testing with novel cleaning systems such as those presented in this paper, including the development of innovative techniques for in-situ documentation and

<sup>24</sup> In many situations, the costs related to the cleaning material/instrument are also influential in the choice of system. This parameter was not included in the initial evaluation of the novel cleaning systems on mock-ups.

<sup>25</sup> Mobile adjustable extraction and filter unit, available from Deffner and Johann.

<sup>26</sup> The newest version of the Resko Airblaster (II WPS) by Deffner & Johann, is optimised for even lower pressure ( $\leq 1$  bar) than the one used in this study, which suggest that SPB may also be suitable for sensitive surfaces such as these.

<sup>27</sup> The term 're-treatability' was introduced by Appelbaum [91] as a requirement for treatment of cultural heritage that considers the consequences of short- and long-term effects of a treatment on the ability of a surface to be

Footnote 27 (continued)

successfully treated again. In the context of cleaning, a take on this term would be 're-cleanability'.

for the exploration of short- and long-term effects of the surface cleaning [11, 100–102].

## Conclusions

This article presents the methodology and results of research into the effect and efficiency of soft particle blasting (SPB), CO<sub>2</sub>-snow cleaning, and Nanorestore® Dry and Peggy gel series hydrogels relative to dry polyurethane (PU) sponges on mock-ups composed of cobalt blue oil paints on chalk-glue ground that were created within the context of the Munch Aula Paintings Project. The results of soil removal from the three mock-up structures (G, Pu and Pd) demonstrated that soiling retention and the effect and efficiency of the cleaning systems were strongly influenced by the condition and surface properties of the painted surfaces, as well as by the working parameters of the cleaning systems.

The air abrasive SPB technique had advantages over PU sponges on medium rich cobalt blue oil paint (Pu) mock-ups but presented a greater risk of pigment loss and abrasion to upper textures of the thin, lean chalk-glue ground (G) and turpentine-diluted oil paint (Pd) mock-ups. CO<sub>2</sub>-snow cleaning showed promise with moderate cleaning efficiency and low abrasive risk even on the thin surface layers of ground (G) and diluted oil paint (Pd) mock-ups. However, the effects of surface cooling require further investigation. The Nanorestore Gels® with chelating solutions and pH 6.0–6.5 showed enhanced soiling removal ability on the G and Pd mock-ups as compared to the PU sponges. The nano-gels also showed potential for improved removal of embedded soiling from the Pu mock-ups, but also a risk of pigment loss with the cleaning solution used.

Of the three novel cleaning systems, the properties of the Nanorestore Gel® series in particular, with further tailoring and/or modifications of cleaning solution and application time, make them potentially suitable for cleaning moderately water- and abrasion-sensitive painted surfaces, such as the Aula paintings. This study also informs future research development and treatment protocols using methods which offer a low-risk solution for the removal of the soiling layers which currently dull and disguise the originally vivid colours of these monumental oil paintings by Edvard Munch.

## Abbreviations

a\*: Green–red component: negative value = green. Positive value = red. Grey: a\* = 0; AC: After cleaning; ATR: Attenuated total reflectance; AW: pH and conductivity adjusted water; b\*: Blue–yellow component: negative value = blue. Positive value = yellow. Grey: b\* = 0; BC: Before cleaning; F: Bright field; Bis–tris: Bis(2-hydroxyethyl)amino-tris(hydroxymethyl)methane; BST: Black standard temperature; CHT: Chamber temperature; CO<sub>2</sub>: Carbon

dioxide; DI: Deionised water; FTIR: Fourier transform infrared spectroscopy; G: Ground (chalk-glue ground mock-up); GU: Gloss units; HLB: Hydrophilic-lipophilic balance; L\*: Lightness: darkest black: L\* = 0. Brightest white: L\* = 100; LM: Light microscope; M1: Mock-up set 1; M2: Mock-up set 2 (main sample set); MAP: Munch Aula Paintings Project; MCT: Mercury cadmium telluride; MES: 2-(N-Morpholino) ethanesulfonic acid; Pd: Paint diluted (diluted cobalt blue oil paint mock-up); Pu: Paint undiluted (undiluted cobalt blue oil paint mock-up); PU: Polyurethane; PVP: Polyvinyl pyrrolidone; RH: Relative humidity; SCE: Specular component excluded; SD: Standard deviation; SEM: Scanning electron microscope; SPB: Soft particle blasting; TAC: Triammonium citrate; Tris: (Hydroxymethyl) trisaminomethane; UV: Ultraviolet radiation; WD: Working distance; Δ\*: Difference in absolute colour coordinates: sample minus standard; ΔE: Total colour difference (Delta Empfindung). ≤ 1.0 not perceptible by human eyes.

## Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s40494-021-00599-w>.

**Additional file 1: Figure S1. a** Low-vacuum SEM–EDX of an oil paint from *The Sun* suggested a cobalt blue pigment (PB28 cobalt aluminate CoO·Al<sub>2</sub>O<sub>3</sub>, 2–27 μm) and barium sulfate (probably synthetic, 0.8–3.5 μm) extender in a drying oil-based medium. Greyscale threshold images suggested area fractions of 14–19% of filler to bulk paint (cobalt blue pigment and oil fraction). **b** Low-vacuum SEM–EDX of a ground from *Alma Mater* suggested calcium to be the major element, attributed to chalk (CaCO<sub>3</sub>) (probably manufactured). BSE images suggested spherical chalk particles c. 0.2–4 μm, with most of the particles between 1 and 2 μm. **Figure S2.** SEM secondary electron image of a polyurethane cleaning sponge (~100×) used for the control treatment. **Figure S3.** SEM secondary electron images of wheat starch, Arbocel® A and Arbocel® B. ~300× magnification. **Figure S4.** Soft particle blasting set-up: oil free air compressor, nozzle with hand switch, air gun with Y-connector, air blaster, blasting cabinet (not shown) and soft abrasives (not shown). Main unit supplier: Deffner & Johann. Stipulated line = connection or continuation. **Figure S5.** CO<sub>2</sub>-snow cleaning set-up: dual gas Venturi nozzle, CO<sub>2</sub>-gas tank with pressure gauge, compressed air heater, foot switch, nitrogen gas (not shown), CO<sub>2</sub> detector (not shown), fume hood (not shown). Main unit supplier: Applied Surface Technologies. Stipulated line = connection or continuation. **Figure S6.** Hydro-gel sheet with detail of high-water-retention nano-gel. Supplier: Center for Colloid and Surface Science. Aqueous cleaning solutions selected from the Modular Cleaning Program. **Figure S7.** Accelerated aged control mock-ups (M2): unsoiled (upper) and artificially soiled (lower). 60× objective, Hirox RH-2000-3D digital microscope (Hirox Europe, Limonest, France). The soiled mock-ups demonstrate the darkening and mottling effect of soiling. **Figure S8. a** FTIR spectra of the chalk-glue ground mock-ups before (upper) and at the end (middle spectra) of ageing and bread cleaning procedures, and of the chalk-based ground of Munch's *Alma Mater* (lower). The Si–O–Si stretching bands in the Munch sample at 1200–1000 (1190, 1150 and 1090 cm<sup>-1</sup>) were attributed to trace ultramarine pigments (Na, Al, Si, S confirmed with SEM–EDX). These and traces of Pb and Zn, possibly deriving from small additions of lead and zinc white, were excluded from the mock-up ground to simplify the composition. The band with a maximum at 1030 cm<sup>-1</sup> (assigned to SO<sub>4</sub><sup>2-</sup> or Si–O–Si stretching) in the spectra of the aged and bread cleaned unsoiled M2-G mock-ups is probably contamination. No corrections to spectra. **b** Surface ATR-FTIR of M2-Pu mock-ups before (red line) and at the very end (blue line) of ageing and bread cleaning procedures. The black line shows the FTIR spectrum acquired with transmission spectroscopy of a sample of cobalt blue bulk paint and of the blue oil paint from Munch's *The Sun*. No corrections to spectra. **c** Surface ATR-FTIR spectra of the Pd mock-ups before (red line) and at the very end (blue line) of ageing and bread cleaning procedures, and of the blue oil paint of Munch's *The Sun* (black line). The spectrum for the Pd mock-up has a weak absorption band at 870 cm<sup>-1</sup> attributed to chalk from the ground layer. No corrections to spectra. **Figure S9. a** Velocity of SPB abrasive powders compared to compressed air alone. Average of ten measurements. Standard deviation as error bars. **b** Velocity of the CO<sub>2</sub>-snow stream compared to that of

SPB with Arbocel® A. Standard deviation as error bars. **Figure S10. a–c** Colour measurements<sup>1</sup>. **Figure S11. a–c** Gloss measurements<sup>2</sup>. **Figure S12.** Performance of cleaning systems on parameters (G–I) related to user-friendliness.

**Additional file 2: Table S1.** Artificial soiling composition. Adopted from an artificial soil mixture used by Ormsby et al. [43]. **Table S2.** Condition assessment tests. **Table S3.** Air abrasive trials. Visible cleaning and undesirable surface change at nozzle distance to surface. **Table S4.** Parameters A–F for evaluating the effect and efficiency of the cleaning systems. **Table S5.** Parameter G–I for evaluating the practical user-friendliness of the cleaning systems. **Table S6. a** Numerical rating of the free-liquid trials on M1-G. **b** Free-liquid trials on M1-Pu. **c** Free-liquid trials on M1-Pd.

**Additional file 3: Appendix S1.** Propagation of uncertainty for colour and gloss measurements.

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### Authors' contributions

LPS was the Ph.D. student Conservation Studies UiO researcher (2017–21) and carried out investigations of the Aula paintings; constructed the mock-ups; performed the cleaning tests, colour and gloss measurements and documentation (with the exception of SEM); interpreted most of the results; wrote the manuscript, and; prepared all images and data for publication. TF (UiO) conceptualised the research in collaboration with LPS (UiO), BAO (Tate) and MSW (UvA), and leads the wider Munch Aula Paintings Project. TF, BAO, MSW and TG supervised LPS. BAO contributed significantly to the methodology for the cleaning tests and evaluation; to the interpretation of the results, and to the structure of the manuscript. MSW made important contributions to the mock-up design and structure of the manuscript. OM (GCI) supported and contributed to the CO<sub>2</sub>-cleaning test methodology, FLIR imaging, velocity testing. TG (NILU) contributed to the interpretation of the colour and gloss measurements and prepared Additional file 3: Appendix S1. CCS (KHM) analysed (transmission FTIR and SEM–EDX) and interpreted samples of the Aula paintings and the mock-ups in collaboration with LPS. All authors edited and made critical revisions to the manuscript prior to submission and after review. All authors read and approved the final manuscript.

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### Availability of data and materials

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

### Declarations

#### Competing interests

Tate (aka Ormsby) was a partner in the NANORESTART (2015–2018) project where the Nanorestore® Peggy series gels were developed and trialled [103].

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