Dry Cleaning Approaches for Unvarnished Paint Surfaces

Maude Daudin-Schotte, Madeleine Bisschoff, Ineke Joosten, Henk van Keulen, and Klaas Jan van den Berg

ABSTRACT. A range of materials used in conservation practice were selected to perform dry cleaning tests of water- and mechanically sensitive, soiled, and artificially aged paint surfaces. Results were assessed visually, by light and electron microscopy, as well as through gloss measurements based on topography integrity, gloss integrity, clearance of residues, cleaning power, aging stability of residues and paint surfaces after testing, and UV fluorescence changes. Of the tested materials, yellow microfiber cloth, white akapad, and polyurethane-based makeup sponges were shown to be the most efficient and safe materials on different paint surfaces. Groom/stick and Absorene were problematic, especially for underbound, matte paints, leaving resilient hardening residues. Polyvinyl chloride erasers left plasticizer residues, with the potential for softening the paint layer with aging. It was noted that the stability and usefulness of materials such as polyurethane makeup sponges may be compromised if the manufacturer changes their chemical composition.

INTRODUCTION

The removal of dirt from an unvarnished paint surface may be very challenging, especially when the deposit is patchy and resilient or in cases where fragile unvarnished underbound paint surfaces are sensitive to aqueous solvents. In these cases or when the dissolved dirt can impregnate the paint surface irreversibly, alternative nonsolvent cleaning methods are mandatory.

Noncontact methods such as laser cleaning have been proposed but are generally considered both unsafe and too costly for unvarnished paintings. Dry surface cleaning is an alternative that is occasionally practiced by painting conservators, employing a large range of specific materials like sponges, erasers, malleable materials, and microfiber cloths. However, since there is a strong concern about their potential damaging effects on surfaces, these materials have not yet been fully integrated into current practice. Only a few studies have focused on the use of dry cleaning materials in conservation (Wehlte, 1971; Schorbach, 2009), and most of them are related to textile (Estabrook, 1989) and paper conservation (Brokerhof et al., 2002; Noehles, 2002).

A project carried out at the Cultural Heritage Agency of the Netherlands (RCE, formerly known as ICN) in collaboration with painting conservators in the Netherlands and the United Kingdom has aimed at a better understanding of the properties of dry cleaning materials in relation to the physical and optical integrity of the paints (Burnstock et al., 2006; Ormsby et al. 2006; Morrison et al., 2007), the potential for removing any residues off the surface, and the long-term effects of residual materials on the painting. Analytical

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and practical investigations of the dry cleaning materials have shed light on the nature and potentially detrimental effects of the materials (van Keulen et al., 2010).

This paper presents the testing methodology and results of dry cleaning materials on underbound and solvent-sensitive surfaces (E. Froment, University of Amsterdam, unpublished internal report, "Cleaning Workshop: A Collaboration between Amsterdam University and the Cultural Agency of the Netherlands," 2009 and M. Daudin-Schotte, Cultural Heritage Agency of the Netherlands, unpublished internal report from the 2006–2009 Research Project "Application of Dry Cleaning Methods on Unvarnished Modern Paintings," 2010). The results are discussed in the light of cleaning effectiveness related to topography changes and potentially harmful residues.

EXPERIMENTAL METHODS AND MATERIALS

Cleaning Materials

After preliminary cleaning tests on soiled and artificially aged oil paint surfaces with more 20 cleaning materials used in conservation (Daudin-Schotte, 2010; Van Keulen et al., 2010), a selection of the best performing and most commonly used materials was chosen for further research (see Table 1). The materials' composition was obtained through chemical analysis (H. van Keulen, M. Groot Wassink, S. de Groot, I. Joosten, M. Daudin-Schotte, M. van Bommel, and K. J. van den Berg, Cultural Heritage Agency of the Netherlands, unpublished data) and from manufacturers' data sheets.

Aging procedures were performed for 4–6 weeks at temperatures of 50°C–60°C and relative humidity (RH) variations from 27% to 70%–80% every six hours. Light aging was carried out with fluorescent tubes (10,000 lux) for approximately 600 hours at a temperature of 23°C and RH of 44%, equivalent to 11.5 years of aging under museum conditions, assuming reciprocity. The aim was to assess each cleaning material's stability as well as potential changes to paint surfaces from residues after each cleaning test.

Paint Surfaces

Test samples were organized in three series, using canvas prepared on cardboard.

I. The first series of tests were performed on a naturally aged 30-year-old monochrome oil painting on canvas (van den Berg et al., 2008). The top paint layer consisted of a monochrome light green oil painting containing zinc, lead, and titanium white with a barium sulfate filler in addition to two as yet unidentified organic yellow pigments. A very thin strongly fluorescent surface layer is visible under UV light, possibly a skin of the medium.

II. Water-sensitive cadmium red, cadmium yellow, and ultramarine blue tube oil paints from Talens Rembrandt Artists' Quality (Mills et al., 2008) were painted out on artists' boards, cured in ambient conditions for four months, and artificially aged for 2,700 hours at 10,000 lux at room temperature. After aging, the samples were stored at ambient conditions for 4 months, soiled with dust collected from the cellar of the ICN building, and stored in a greasy environment (the kitchen of the ICN Ateliergebouw) for 4 months.

III. Gouache samples were painted out on artists' boards, mixing one measure of tube paint of Talens ECOLA Plakkaatverf with the same measure of pure pigment from Verfmolen "De Kat" (Zaandam, Netherlands) to produce slightly underbound matte surfaces (cadmium red, cadmium yellow, and ultramarine

TABLE 1. Dry cleaning materials tested in this study. Each test was followed by brushing and vacuuming of the surface.

Type	Product Name	Picture	Composition[a]	Application	Manufacturer/ Suppliers	Description (observed when tested)
Malleable materials	Absorene		Filler: starch; solvent: white spirit	Rolled with hand over the surface, in tube shape	Absorene Company Inc (England)	Quite sticky, malleable
	Groom/stick		Isoprene rubber, chalk	Applied rolled around a wooden stick like a cotton swab	Picreator Enterprises Ltd. (England)	Very sticky, malleable.
Erasers	Edding R10		Polyvinyl chloride (PVC), di-isooctyl phthalate (DIOP)	Applied with a minimum pressure, in circle movements	Local stationers (international)	Relatively hard material; harder than Pentel ZF11 and Bic Galet

(*continued*)

TABLE 1. (*Continued*)

Type	Product Name	Picture	Composition[a]	Application	Manufacturer/ Suppliers	Description (observed when tested)
Erasers	Pentel ZF 11		Polyvinyl chloride PVC), phthalates (DIOP, DMP, MEHP); butoxytriglycol, dioctylazelate; chalk	Applied with a minimum pressure, in circle movements	Stouls (France)	Relatively hard material; harder than Bic Galet
	Bic Galet		Factis (vulcanized vegetable oil) chalk	Applied with a minimum pressure, in circle movements	Local stationers (international)	Softest eraser with highest amount of crumbs
Cloths	Yellow micro-fiber cloth		Polyethylene terephthalate (PET); polyester: Nylon 6 (polyamide)	Folded and applied in figure eight shape movements	Blokker, local drugstore (Netherlands)	Nonwoven cloth.
Sponges	Smoke sponge		Isoprene rubber, sulfur chalk, not completely vulcanized natural rubber	Applied with a minimum pressure, in circular movements	Conservation by design Ltd. (England)	Rubbery texture, flexible material.
	Akapad White		Styrene butadiene rubber (SBR), vulcanized castor oil, antioxidant NG-2246	Applied with a minimum pressure, in circular movements	Akachemie, Deffner & Johann (Germany)	Self-consuming material, more compact than Akapad yellow
Makeup sponges	Etos (white, triangle shape)		Isoprene rubber, butylated hydroxytoluene (BHT)	Piece of sponge applied in figure eight shape movements and slight pressure; used as obtained and rinsed in demineralized water prior to use	Etos stores (Netherlands)	Very soft and flexible texture
	Hema (white, triangle shape)		Styrene butadiene rubber (SBR), butylated hydroxytoluene (BHT), diethyldithiocarbamate mercaptobenzothiazole	Piece of sponge applied in figure eight shape movements and slight pressure; used as obtained and rinsed in demineralized water prior to use	HEMA stores (Netherlands)	Very soft, flexible texture, comparable to isoprene rubber make-up sponges
	QVS (white, triangle shape)		Polyurethane ether (TDI)	Piece of sponge applied in figure eight shape movements and slight pressure; used as obtained and rinsed in demineralized water prior to use	Probably discontinued product, QVS, drugstores (England)	Very soft and flexible
Gum powder	Draft clean powder		Yellow particulates: styrene butadiene rubber (SBR); brown particulates: factis	Sprinkled over the surface; cotton pad was used with even and soft application	Conservation by Design Ltd. Archival aids (England)	Differences in particulate sizes depending on the brand

[a]Composition information is from ICN Web site table; see text.

blue were used to allow optical comparisons with series II). Samples were soiled as in series II.

Dry Cleaning Tests

Cleaning tests were performed under ambient temperature and humidity (±22°C at 50% RH) at the ICN laboratories. After each test the paint samples were brushed and vacuumed. Test results were first observed visually (normal light, UV fluorescence, raking light) and then with light microscopy (polarized light, UV fluorescence, raking light), followed by electron microscopy (low vacuum, acceleration voltage from 1.7 to 20 kV, backscattered electron and low-vacuum secondary electron at magnifications of 100× to 2500×). Gloss measurements were performed to complete microscopic visual assessment. The following pieces of equipment were used: a ZEISS Axioplan 2 light microscope with ZEISS neofluar lenses and Axiovision 4.4 software, a Jeol JSM 5900 lV scanning electron microscope (SEM), a Tri-glossmaster 20-60-85 glossmeter from SHEEN, and a Sony Cybershot DSC-F505V digital camera.

Observations were recorded in evaluation tables (Table 2) with attention to six criteria: topography integrity, gloss integrity, removal of residues, cleaning power, stability of the paint surface after testing and after artificial aging, and (if applicable) UV fluorescence changes. The syntheses of the results were then represented in star diagrams (Figure 1).

RESULTS

The results of the experiments on the water-sensitive oil and gouache paints are presented in Table 3.

TABLE 2. Example of the evaluation table used in this study: Results of the Absorene tested on the cadmium red gouache. Grades are from 0/10 (null) to 10/10 (excellent). — = no data

Tested materials	Topography integrity	Gloss integrity	Change under UV light	Clearance of residues (per cm^2)	Cleaning power	Stability with aging
Number 3: Absorene[b]	Abrasion (10/10)	5/10 (significant decrease in gloss)	None	Quantity on the picture spot (film deposit)	Evenness (5/10)	Change in color: more cloudy and gray
	Polishing (9/10)	5/10 (significant decrease in gloss)	None	Color (—)	Paint layer (6/10)	Change in color: more cloudy and gray
	Flattening (8/10)	5/10 (significant decrease in gloss)	None	Size (—)	Crumbs (—)	Change in gloss: more matte
	Cracks and holes (10/10)	5/10 (significant decrease in gloss)	None	Tenacity (—)	Material (3/10)	Other: thin, hard skin impregnated into the paint layer
	Global evaluation: 9.4/10	Global evaluation: 5/10	Global evaluation: None	Global evaluation: 1/10	Global evaluation: 5/10	Global evaluation: 1/10

[a] Increase or decrease, observed with the naked eye.

[b] Cleaning achieved for a 2 minute application and 5 s vacuuming and brushing (if no dust remains, it becomes stickier).

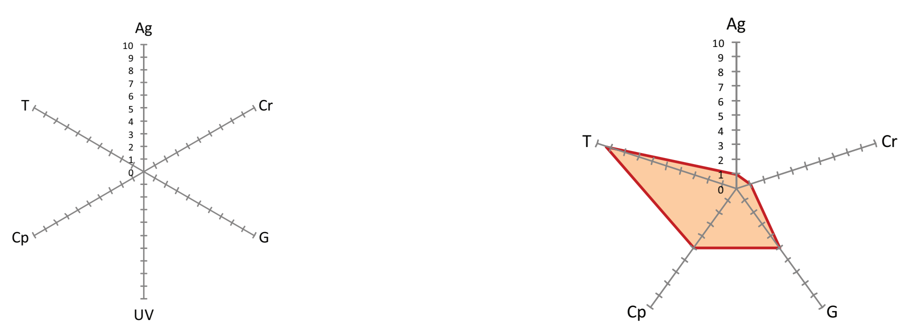
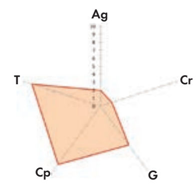
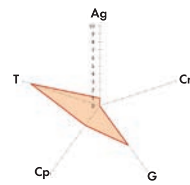
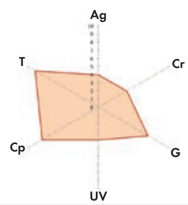
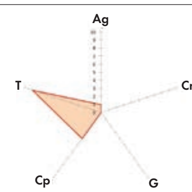
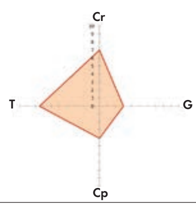
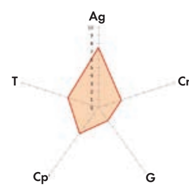
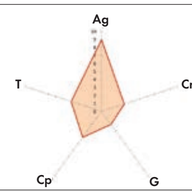
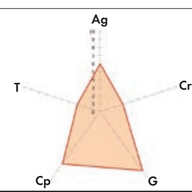
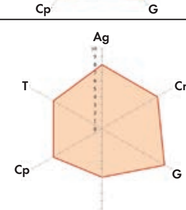
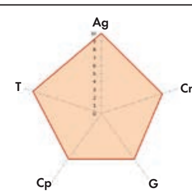
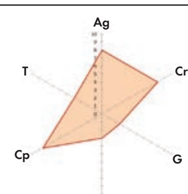
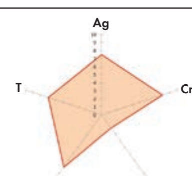


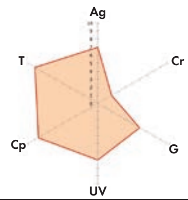
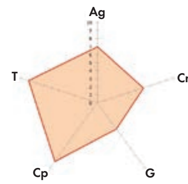
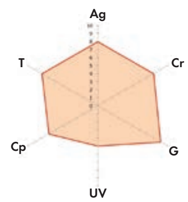
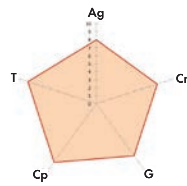
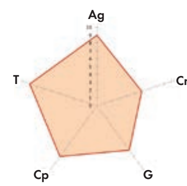
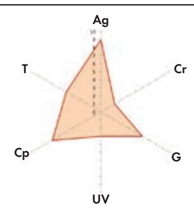
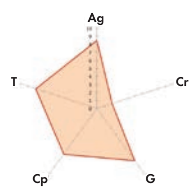
FIGURE 1. Star diagram examples. (left) Not filled in. Note that 0/10 corresponds to an extremely poor result, and 10/10 corresponds to an excellent test result. T = topography integrity; Ag = stability of paint surface after testing and artificial aging; Cp = cleaning power; Cr = clearance of residues; G = gloss integrity. (right) Example of a star diagram with Absorene scores from tests on gouache (see Table 2).

TABLE 3. Average dry cleaning test results on oil paint (sample II) and gouache (sample III). T = topography integrity; Ag = stability of paint surface after test and after artificial aging; Cr = clearance of residues; G = gloss preservation; UV = preservation of the paint layer aspect under UV fluorescence; Cp = cleaning power. See Table 1 for materials images.

Material class	Material name	Average result on series II (oil paint layer sensitive to water)[a]	Average result on series III (underbound gouache paint layer)[a]	Handling remarks	Observations after aging (indication of aging tendencies of residues)
Malleable	Absorene				The “pink plasticine” became rock hard; an oily substance was leached out during the aging process, mixed with a very hard translucent substance (gray crystals)
	Groom/stick			Rolled around wooden stick for ease of use	Much stickier after aging and still glossy; it has softened into a liquid shape; on very thin areas, it became translucent and matte, like a little gray skin (this corroborates its aging on paint surfaces)
Erasers	Edding R10				A little bit yellower and less flexible
	Pentel ZF11	Not tested			It generated a little bit of oily substance during aging; the eraser is also slightly less flexible
	Bic Galet		Not tested		No change
Cloths	Yellow microfiber cloth			Cloth with velvety characteristics, quite thick; produces threads when cut off	No change
Sponges	Smoke sponge			Greasy surface becomes harder and unusable within months; store protected from air	More compact, less flexible, harder, and yellower than before aging.

(*continued*)

TABLE 3. (*Continued*)

Material class	Material name	Average result on series II (oil paint layer sensitive to water)[a]	Average result on series III (underbound gouache paint layer)[a]	Handling remarks	Observations after aging (indication of aging tendencies of residues)
Sponges	White Akapad			Soft contact with paint layer	Slightly more compact, yellower on one side; otherwise, it remains comparable with brand new Akapad
Make-up sponges	Etos rinsed (isoprene rubber)			Strong yellowing when rinsed with demineralized water	Much more yellow and harder
	QVS rinsed (polyurethane ether)	Not tested		Swells in water during rinsing; becomes less compact and even more flexible after rinsing and drying	Overall comparable with a nonaged rinsed QVS, although it has become slightly less flexible than before aging
Gum powder	Draft clean powder DCP3			Sprinkled over the surface; cotton pad was used to evenly and softly scrub	The smallest particulates became slightly stickier; the other particulates remain comparable to the brand new gum powder

[a] Number of axes depends on the relevance of each criterion during tests.

Abrasion and Polishing versus Cleaning Efficacy

For all materials, except the malleable class, the mechanical action is the basic cleaning principle, which implies close contact between the cleaning material and paint surface. As a result, potential damage, such as abrasion, flattening, and polishing of the surface topography, is particularly pertinent.

The test results show that the Akapad white and makeup sponges were the least abrasive polishing materials. Both materials were very efficient as well, especially Akapad for the removal of embedded and resilient dirt. Figures 2 and 3 show light microscopy and SEM results for the polyurethane QVS sponge tested on a cadmium yellow gouache paint sample.

In contrast, and as perhaps suspected, the erasers (PVC or factis based) proved to be the most harmful materials (Figure 4). Tests on paint sample I, oil paint, resulted in a strong loss of UV fluorescence because of abrasion of the skin of medium (Figure 5) as well as rubbing on the topography (clearly visible in SEM images; Figure 6). Furthermore, after testing on series II and III, surface scratches were observed with light microscopy (see Figure 4).

Residual Materials from the Cleaning Agents: Crumbs and Stability with Aging

In addition to issues of mechanical abrasion, what is of great concern, even if less visible, is the potential long-term detrimental action of the residue from the cleaning materials left as a sticky particulate residue or as a film of material. Assessments were made on the basis of the chemical analysis of tested paint surfaces as well as visual observations, taking into account the

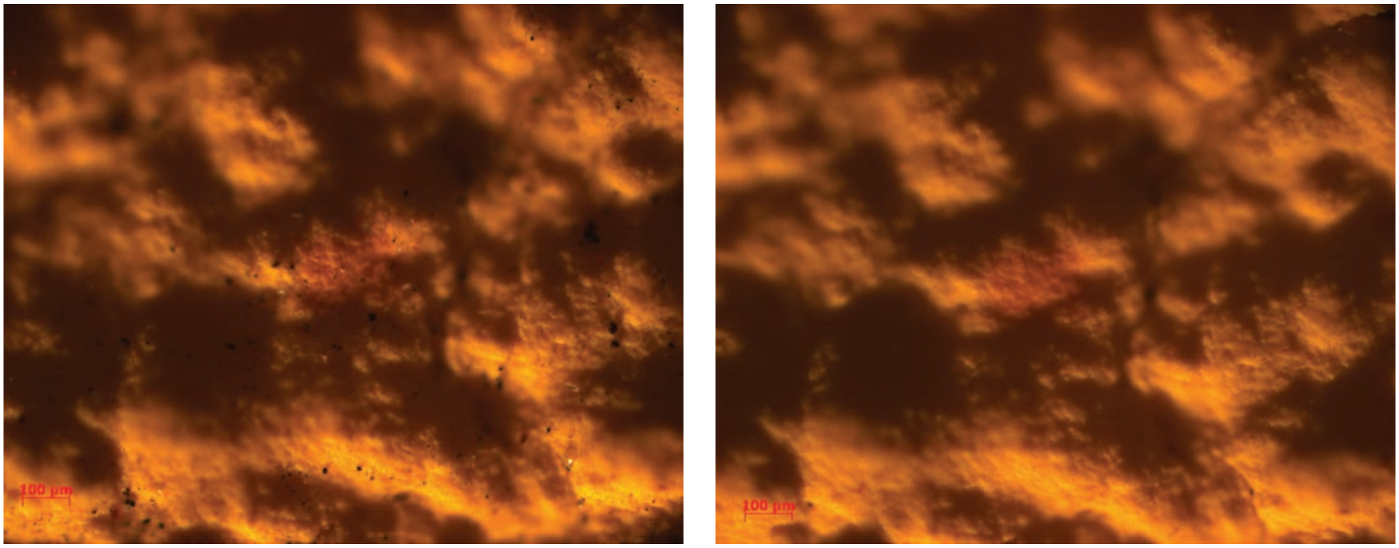


FIGURE 2. Cadmium yellow gouache sample, (raking) light microscopy at 100× magnification, (left) before and (right) after testing with rinsed polyurethane ether makeup sponge (QVS). The topography is preserved, which is confirmed with SEM observations (Figure 3) .

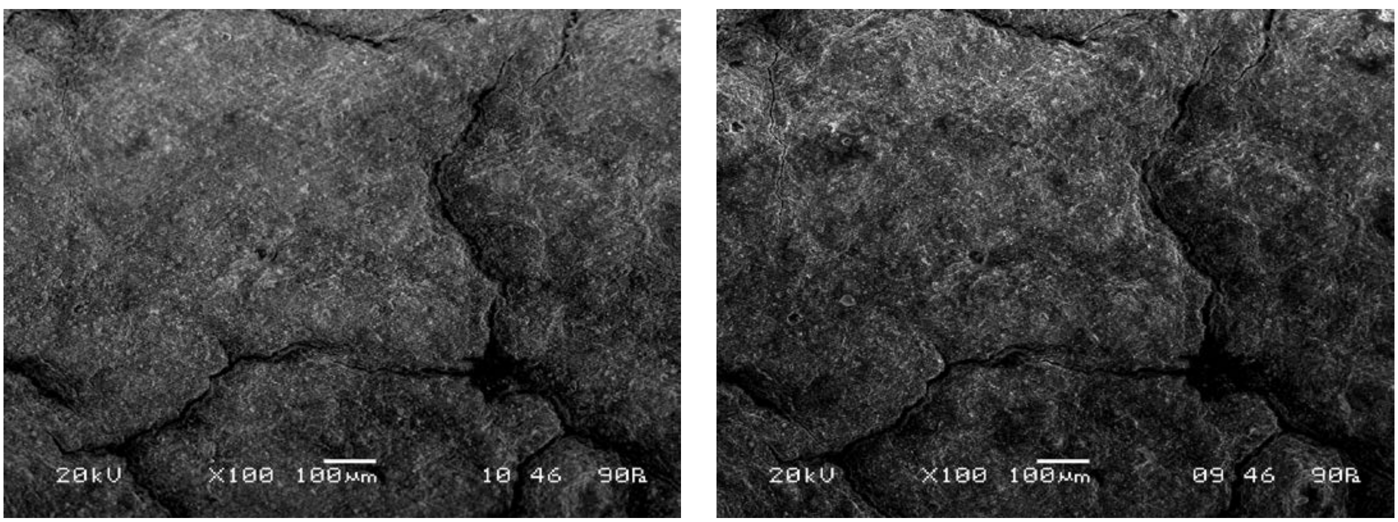


FIGURE 3. Cadmium yellow gouache sample, (left) before and (right) after testing with rinsed polyurethane ether makeup sponge (QVS); SEM images (LSEI mode) at 100× magnification.

extractable components that are potentially harmful to the paint surface.

Chemical residues were only detected in test samples treated with PVC erasers, for which plasticizers were detected (van Keulen et al., in preparation). This is of concern since plasticizers can soften the paint surface, leaving it more sensitive to dust and vulnerable to abrasion or polishing.

Groom/stick and Absorene were found to leave a film deposit or particulate residue on both well-bound and porous paint layers (see Figures 7, 8, and 9), which proved to harden and embed into the paint layer with aging. This was also observed with kneaded gums and gum powders, albeit to lesser degrees.

With an average maximum of 2 particles/cm^2, makeup sponges, smoke sponges, and cloths left the least particulate residue while achieving a generally good cleaning level. These materials also age relatively benignly. No chemical residues are expected to be left by cloths, and none were detected analytically on the paint samples treated with smoke sponges.

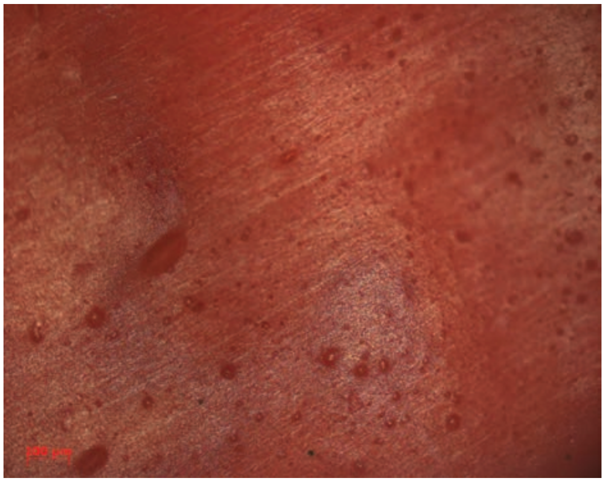


FIGURE 4. Local abrasion with scratches observed on red cadmium oil paint surface tested with a Bic Galet (series II) eraser.

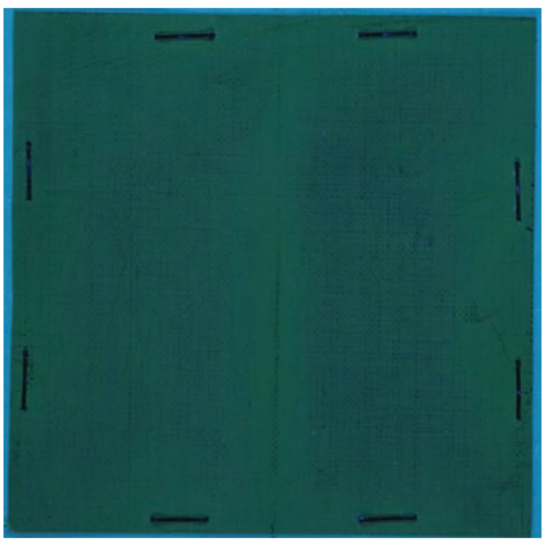


FIGURE 5. Oil paint sample after (left) one- and (right) three-minute tests with a Magic Rub PVC eraser, showing a strong decrease in UV fluorescence in treated areas (series I).

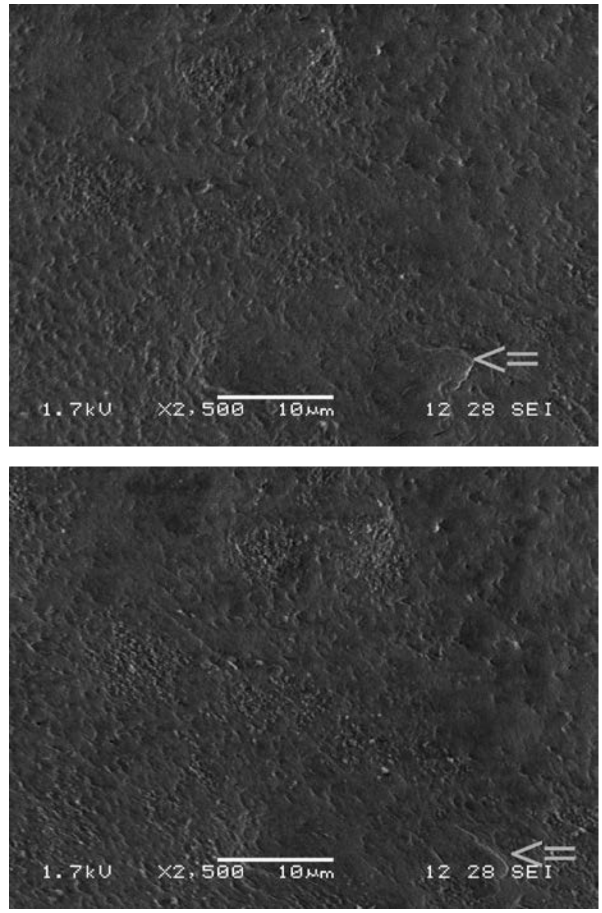


FIGURE 6. Series I Magic Rub eraser test performed on an oil paint sample, SEM SE 2500× magnification. (top) One-minute test and (bottom) three-minute test. The polishing of the surface has clearly increased with increased rubbing time; note the change in the micro-relief (bottom right corner).

DISCUSSION AND CONCLUSIONS

Treatment Purpose versus Optimum Preservation of Surfaces Characteristics

Dry cleaning by rubbing the surface will cause friction and may cause abrasion, flattening, or polishing of the surface depending on the specific mechanical properties of the material. This is avoided by malleable materials, which exhibit a different mechanical behavior but carry the risk of leaving relatively resilient material residue on the surface.

Of all the cleaning materials tested, makeup sponges proved to be efficient and among the safest materials to use. The fine structure and softness of these sponges, primarily produced for skin cosmetic application, enhance their use for gentle dirt removal from delicate surfaces. Most makeup sponges are produced from isoprene, styrene butadiene rubber (SBR), and mixtures of both on an industrial scale. The analyzed SBR-isoprene sponges all contain antioxidants and accelerators used in the rubber-making process. A minor part of the sponges consists of polyurethane, which contains hardly any additives.

A disadvantage is that the availability and/or composition of makeup sponges cannot be guaranteed because of potential changes in composition during manufacturing. For example, the additive-free QVS sponge successfully tested in this study

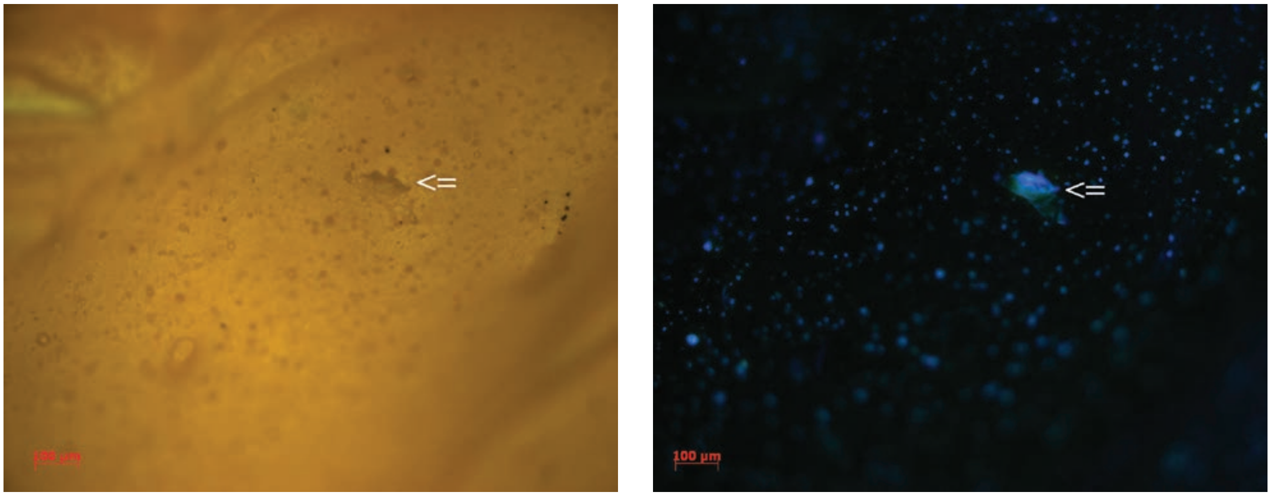


FIGURE 7. Test performed on a cadmium yellow oil paint sample with Groom/stick, with residual material observed with light microscopy: (left) polarized light and (right) UV fluorescence.

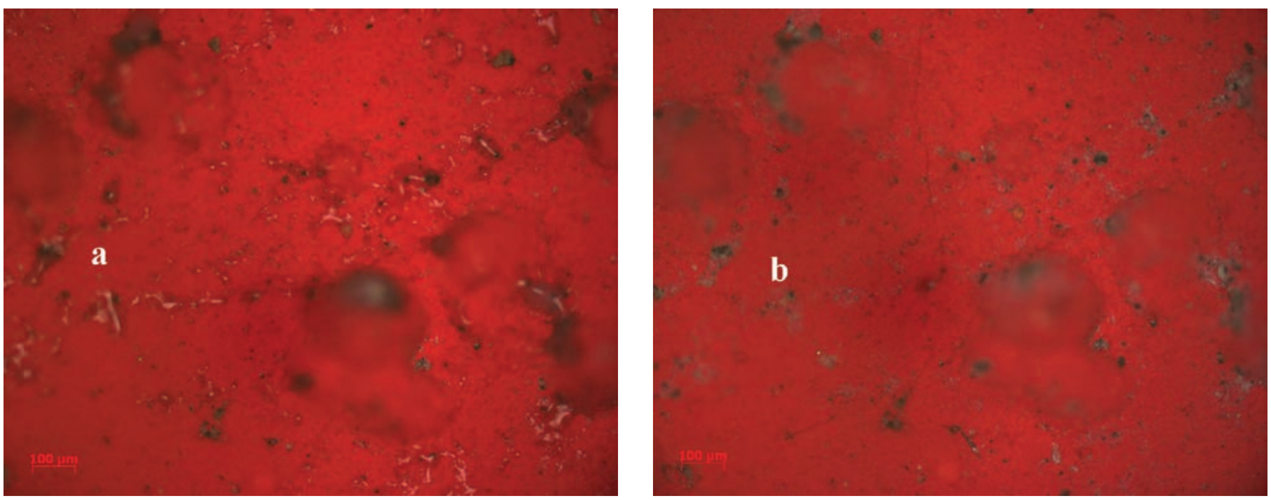


FIGURE 8. Test performed on a cadmium red gouache sample with Groom/stick, light microscopy with polarized light. (a) Appearance before aging, with blackish particulate residues left after testing, and (b) appearance after dark aging, with particulate residues dried and partly embedded in the superficial layer, combined with dirt.

appears to be no longer available on the market. Instead, the polyurethane ether-based HD sponge from Make-up For Ever (composition: polyurethane ether, Tinuvin; see http://www.makeupforever.com/#/int/en/products/tools/sponge-puff/hd-sponge/) has replaced it (this was not tested on all sample sets, but when tested, it showed comparable or even better performance than QVS and HEMA). The HD sponge only contains Tinuvin, a UV light stabilizer, as an additive. As a precaution for removal of possible additives, all makeup sponges were rinsed for 15 minutes in demineralized water and dried well before use (e.g., by pressing them between tissue paper sheets). Although the main part of their organic additives will not dissolve in water, any soluble ones could possibly be transported to the surface of the sponge and be absorbed by the tissue paper.

Of course, in reality dirt and paint surfaces may vary considerably from any test surfaces, and the combinations used in this study may represent only a small portion of those possible. The choice of dry cleaning material depends on the paint layers' characteristics, whether physical (porous, flaking paint, well bound, underbound) or aesthetical (monochrome, colored zones,

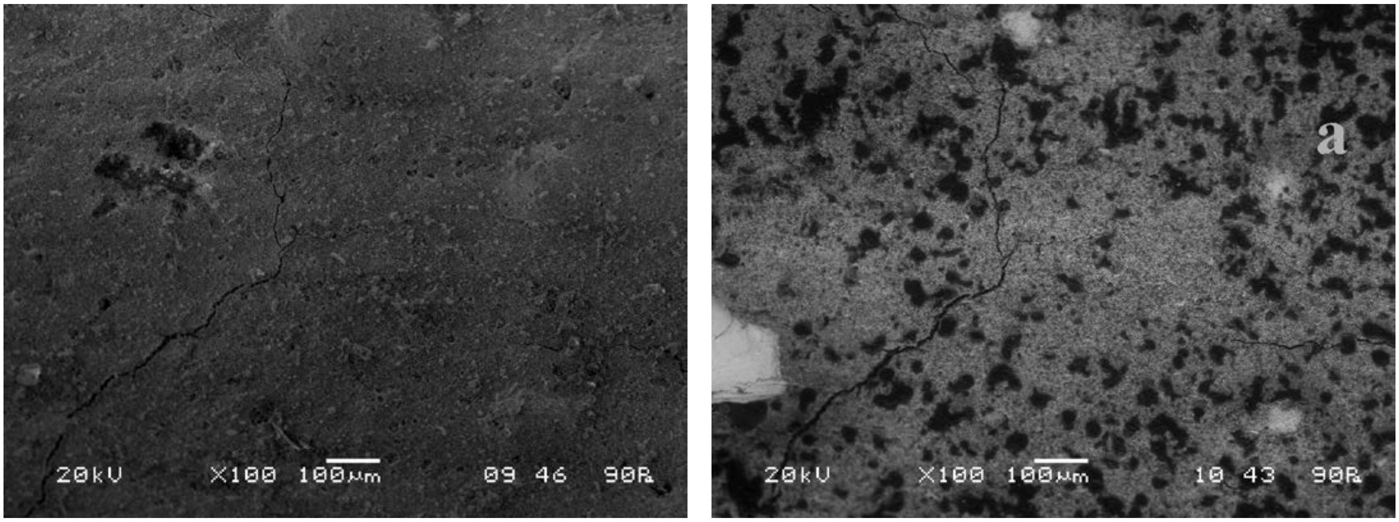


FIGURE 9. Test performed on a cadmium red gouache sample with Absorene; SEM images (low-vacuum secondary electron mode). (left) Before testing and (right) after testing. Numerous Absorene particulate residues are present as dark (organic material) stains (a).

flat, impasted, matte, glossy), and the type of dirt (impregnated, dry, fat, smooth, or grainy).

In addition, different parameters, such as handling and structure, of the dry cleaning material, e.g., even or uneven, absorbent, or malleable, interfere with the cleaning process and influence the results. Considering this, the cleaning tests gave good insight into the working properties and potentially harmful side effects of cleaning materials, with some proving applicable in conservation. On the basis of these observations and considerations, every conservator has to achieve an optimal balance of acceptable results for each specific treatment, as there is no general, straightforward approach for cleaning surfaces with dry materials. To assist in this process, a gradual test approach is presented in the Practical Guidelines section.

Practical Guidelines

For all kinds of paint layers the following materials can be used: (1) polyurethane ether-based makeup sponges (rinsed with demineralized water), (2) yellow microfiber cloths, (3) Akapad white, and (4) smoke sponges (for semiglossy to glossy paint layers only). Additional precautions are as follows:

- In case of granular dust, brush and vacuum clean before dry cleaning.
- Use brand-new materials only to avoid abrasions caused by a degraded surface and unstable residues from old materials.
- Brush surface thoroughly after using Akapad white (at least three times) to remove particulate residues.
- For all sponges, use them only in precut small piece to reduce the amount of residue.
- Rinse these small pieces of makeup sponges for 15 minutes in demineralized water and dry well before use (e.g., by pressing them between sheets of tissue paper).

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