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SOOT REMOVAL FROM ACRYLIC EMULSION PAINT TEST PANELS: A STUDY OF DRY AND NON-CONTACT CLEANING

Keywords: dry cleaning, non-contact cleaning, atomic oxygen, carbon dioxide snow, bread, soot, acrylic emulsion paint

ABSTRACT

Acrylic emulsion paints are sensitive to traditional cleaning with solvents and water. Dry cleaning methods offer an alternative, but there are few in-depth studies on their use. Selected dry cleaning methods (commercial erasers and sponges, and homemade bread) and non-contact methods (atomic oxygen and carbon dioxide snow) were tested on 25-year-old acrylic emulsion paints and an acrylic emulsion gesso test panel from real and simulated fires. Water and solvents were used for comparison and as a link to scientific research on wet cleaning. Paint surfaces were examined visually and microscopically and analyzed by gloss meter and colorimeter. Water, Absorene sponge and homemade bread removed soot on the acrylic gesso panel without causing any visible surface alterations. Organic pigments in acrylic paints were more susceptible to removal by cleaning.

RÉSUMÉ

Les peintures à base d'émulsion acrylique sont sensibles au nettoyage traditionnel avec des solvants et de l'eau. Les méthodes de nettoyage à sec constituent une alternative, seulement il existe peu d'études approfondies sur leur usage. Une sélection de méthodes de nettoyage à sec (gommes à effacer et éponges du commerce, pain fait maison) et de méthodes sans contact (oxygène atomique et neige carbonique) ont été testées sur des peintures à base d'émulsion acrylique âgées de 25 ans et sur un panneau test en gesso à base d'émulsion acrylique en situation d'incendies réels et simulés. De l'eau et des solvants ont été employés à titre de comparaison et pour faire le lien avec la recherche scientifique sur le nettoyage par

INTRODUCTION

Soot is carbon dust formed by gas-phase decomposition of hydrocarbons during fire. It is composed of ultrafine particles (~2.5 microns) smaller than most pigments (2.5 to 10 microns). Depending on the fuel source and composition, gas-phase soot may contain polycyclic aromatic hydrocarbons and aliphatic carbons. Fine soot particles can penetrate interstices and become embedded in painted surfaces (Figure 1).

The challenges involved in removing soot from acrylic emulsion paint include the inherent softness of the paint and its sensitivity to water and solvent, the risk of removal of pigments, and extraction of soluble components. Research on the cleaning of acrylic emulsion paint has focused mainly on the effects of wet-cleaning (Ormsby 2009). With few exceptions (Estabrook 1989, Saulnier 2005, Daudin-Schotte 2010), dry-cleaning methods have not been subjected to systematic research, perhaps because of the difficulties inherent in the use of erasers and sponges that require physical contact to remove dirt from painted surfaces.

Recently, however, the potential benefits of emerging non-contact techniques have been investigated, including the use of carbon dioxide (CO_2) snow and atomic oxygen. CO_2 snow is used to clean the surface of optical and medical research samples. In the field of conservation, CO_2 snow has been used to clean smoke-damaged books (Silverman 2006, 2009) and contemporary art objects (Shockey 2009). CO_2 snow works by momentum transfer: the micron-sized snow particles collide with surface particulates and displace them. Solvency and freeze fracture can occur simultaneously with momentum transfer, improving the cleaning effect of CO_2 snow. When CO2 particles hit a solid surface, the pressure produced can exceed triple-point pressure, causing some of the solid CO_2 to revert to liquid phase, which can absorb hydrocarbons via solvency. Temperature depression can also cause "freeze fractures" in the bonds between particulates and the surface, making particulates easier to remove (Applied Surface Technologies 1996, Shockey 2009).

Atomic oxygen cleaning exploits the high-reactivity of free atomic oxygen atoms, which can break carbon and hydrogen bonds, thereby removing carbon-rich substances by converting them into volatile species. Highly oxidized materials, such as metal oxides in pigments, are not affected.

voie humide. Les surfaces peintes ont été examinées visuellement et au microscope, et analysées à l'aide d'un brillancemètre et d'un colorimètre. L'eau, l'éponge Absorene et le pain fait maison ont décrassé le panneau de gesso acrylique sans causer d'altérations visibles en surface. Les pigments organiques contenus dans les peintures acryliques se sont montrés plus sensibles à l'élimination lors du nettoyage.

RESUMEN

Las pinturas de emulsiones acrílicas son sensibles a la limpieza tradicional con disolventes y agua. Los métodos de limpieza en seco ofrecen una alternativa, pero hay pocos estudios detallados sobre su uso. Se hicieron pruebas con algunos métodos de limpieza en seco (borradores y esponjas comerciales, y pan casero) y métodos sin contacto (oxígeno atómico y nieve carbónica) en cuadros de emulsión acrílica de 25 años y en un panel de prueba de gesso y emulsión acrílica de incendios reales y simulados. El agua y los disolventes se utilizaron para hacer comparaciones y para relacionar el estudio con las investigaciones científicas sobre limpieza en húmedo. Las superficies de pintura se examinaron visualmente y a nivel microscópico y se analizaron con un medidor del brillo y un colorímetro. El agua, la esponja Absorene y el pan casero eliminaron el hollín del panel de gesso acrílico sin provocar ninguna alteración visible en la superficie. Los pigmentos orgánicos de las pinturas acrílicas eran más propensos a removerse con la limpieza.

Since 1994, Sharon Miller and Bruce Bank have used atomic oxygen to recover fire-damaged art works (Rutledge 2000, Miller 2005) and this technique is being further researched for new applications in museum conservation. The present study evaluates the effectiveness of dry cleaning on acrylic emulsion paint samples, using various techniques to examine and characterize the surfaces.

EXPERIMENTAL MATERIALS

Acrylic gesso panel

An acrylic emulsion gesso panel was acquired from the remains of a 1995 apartment fire. The panel contained both clean and sooty areas. Soot-covered strips removed from the bottom right portion of the panel were divided into 1 × 2 -inch (2 × 5 -cm^2) pieces for systematic testing and evaluation (Figure 2).

Acrylic paint samples

In 1995, sets of glass slides and gesso panels were painted with seven different heavy-body acrylic emulsion paints of known composition. The paints used were provided by Golden Artist Colors. Half the samples were painted with no visible brush marks, and the other half was painted in impasto. In 1996, one set of samples was exposed to a simulated fire, while the second set remained unexposed (Figure 3). The three paints used in this study were pigmented with pyrrole orange (NA), naphthol red light (PR-112), and cadmium yellow medium (PY-35). These organic and inorganic pigments are bright enough for dislodged matter to be easily detected. Only the thinly painted panels were tested because their surfaces were large enough to provide a separate section for testing each cleaning material, and for gloss meter and colorimeter evaluation.

Commercial cleaning materials

The authors tested seven commercial dry-cleaning products recommended by conservators with experience in treating smoke-damaged artworks: Rubgum eraser, Staedtler Mars plastic eraser, Groom/Stick cleaner, Absorene sponge, yellow Wishab sponge, white Wishab sponge, and Qosmedix make-up sponge (Table 1) (Roberts 1988, Spafford-Ricci 2000, Heydenreich 2005, Levenson 2010).

Homemade bread

Bread has traditionally been used by conservators to clean paintings with very sensitive surfaces (Tsang 2008). For each test, a fresh batch of bread was made, using only water, flour, yeast, and a little salt (no sugar or butter).

CO_2 snow

CO_2 snow is made by combining gaseous CO_2 with dry nitrogen gas for moisture displacement. Tests were conducted by objects conservators Hugh

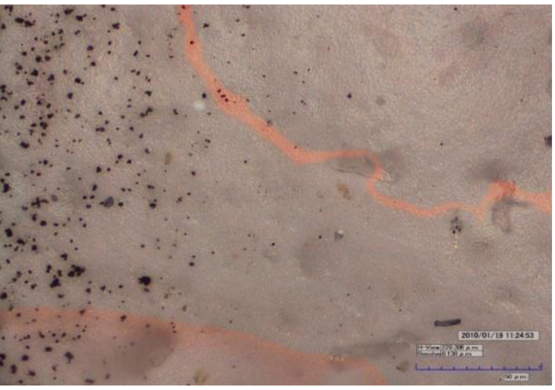


Figure 1
Soot on the surface of an acrylic gesso panel, as seen with the Hirox microscope

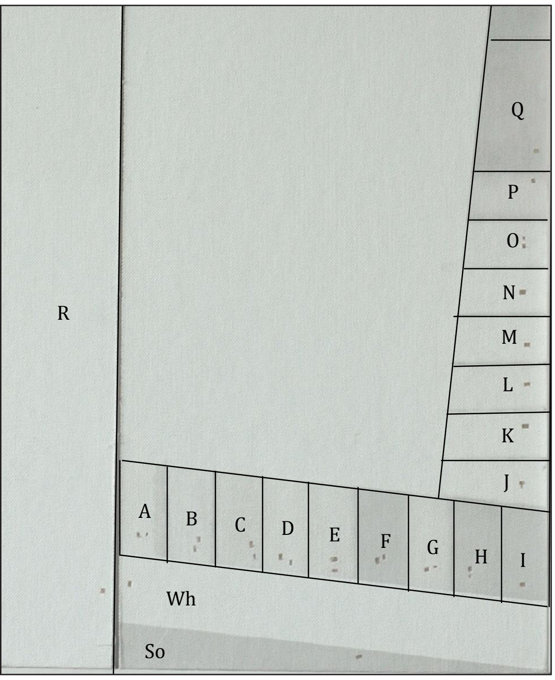
Shockey and Laura Kubick, using a dual gas unit located at the Lunder Conservation Center, Smithsonian American Art Museum (SAAM).

Table 1

Commercial dry-cleaning materials* tested

Name	Type	Composition
Rubgum eraser	Block rubber	Vulcanized vegetable oil
Staedtler Mars plastic eraser	Block rubber	Polyvinyl chloride, dialkyl phthalate, calcium carbonate, possibly titanium
Groom/Stick cleaner	Moldable material	Vulcanized polyisoprene, calcium carbonate
Absorene sponge	Sponge	Vulcanized rubber, calcium carbonate
Yellow Wishab cleaning sponge	Block/Sponge	Styrene butadiene rubber, vulcanized castor oil, antioxidant
White Wishab cleaning sponge	Block/Sponge	Styrene butadiene rubber, vulcanized castor oil, antioxidant
Qosmedix make-up sponge	Sponge	Latex-free polyurethane foam

*All items were acquired in 2010. Composition descriptions are based on information provided by manufacturers and other studies.[3,4]



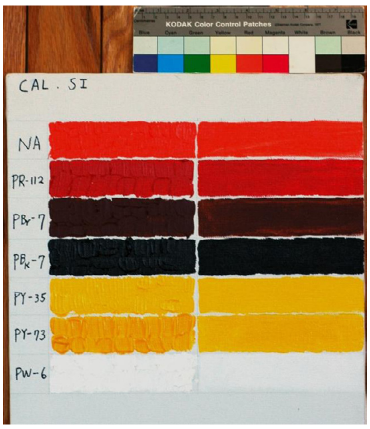


Figure 2
Soot-covered acrylic gesso panel with diagram of cleaning materials tested. A: water; B: ethanol; C: Stoddart solvent; D: bread; E: Rubgum eraser; F: Groom/Stick; G: Absorene sponge; H: white Wishab sponge; I: yellow Wishab sponge; J–N: water with several detergents; O: Staedtler Mars plastic eraser; P: Qosmedix make-up sponge; Q: CO_2 snow; R: atomic oxygen; So: soot-covered area; Wh: white area (no soot)

Figure 3
Acrylic emulsion paint test samples on commercial gesso ground. Right column: smoothly brushed. Left column: impasto

Atomic oxygen

Atomic oxygen cleaning tests were conducted in 1996 by Sharon Miller and Bruce Bank at the National Aeronautics and Space Administration (NASA), using a small isotropic atomic oxygen chamber.

Water and solvents

Convention cleaning materials such as water and solvents cleaning were tested to establish a baseline comparison for the dry-cleaning materials. Deionizer water, anhydrous ethyl alcohol (ethanol), and Stoddard solvent were used.

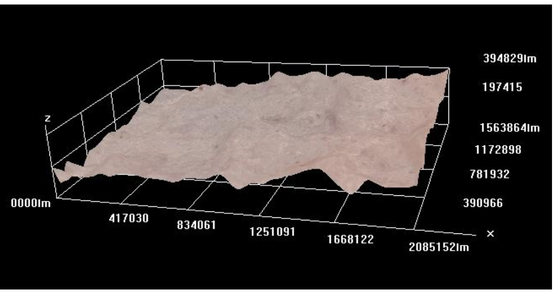
TESTING PROCEDURES

Commercial dry-cleaning products were tested in two phases on soot-covered areas of the gesso panel described above. In the first phase, each sample was stroked ten times in one direction with an eraser or sponge, exerting mild pressure by finger. In the second phase, each sample was stroked until no further improvement could be observed. Bread was kneaded and tested in a similar manner. This approach allowed the authors to observe the efficacy of each method, employed at different pressures for varying amounts of time on the surfaces. CO_2 snow tests were also performed in two phases for comparison with the dry cleaning tests with erasers and bread. Phase one consisted in a shorter period of cleaning, about 30 seconds, which was considered a regular treatment for that type of surface by the conservators. Phase two of CO_2 cleaning was aimed until no further improvement of soot removal was observed.

The first phase test was repeated using flat acrylic paint samples not exposed to fire, to evaluate the effects of the cleaning treatments. Materials that crumbled during testing were collected and saved for observation. Some cleaning methods were tested on soot-covered impasto samples to study their practicality and effectiveness in cleaning uneven surfaces. Crumbs were cleaned with a soft brush, which was cleaned between tests.

Atomic oxygen cleaning was tested on these same samples in 1996, as previously described (Miller 1997). The cleaned samples from that test were further investigated in this study. The samples cleaned in 1996 were stored in clean and stable environmental controlled museum facility. The RH was kept at 45–55% and temperature was kept at 68–70°F. A control strip (Wh area, Figure 1), where no cleaning test was done, was kept on the test panel and used as blank control for gloss and color measurements. The cleaning tests were established as relative comparison, not absolutely comparison.

Water and solvent tests were done by dampening the cotton swabs in water and solvents, a conventional cleaning method used by paintings conservators.



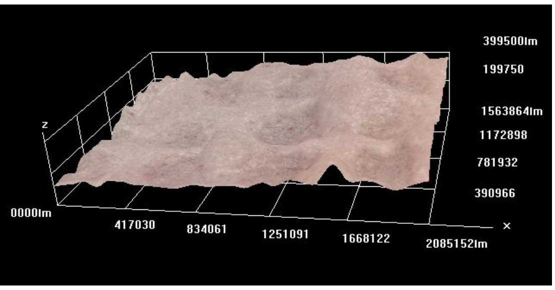


Figure 4
3D image of gesso cleaned with homemade bread showing clean peaks and valleys

Figure 5
3D image of dry-cleaning with gum eraser showing clean peaks and sooty valleys

INSTRUMENTATION

All samples were examined under a Wild Heerbrugg microscope and photographed at x25 magnification with a Leica camera attached to the microscope, using Leica LAS EZ V1.5.0 software. Gloss was measured with a Gardner micro-TRI-gloss meter at 85°, the recommended angle for studying matte samples (GlossMeters 2006). However, since 85° is not a natural viewing angle, gloss was measured at 20° and 60° as well. Color was measured with a Minolta CR-300 chroma meter, using CIELAB color space coordinates. Both gloss and color measurements were taken three times in each sample/method/phase, and the average was calculated. Selected samples were also observed with a KH-7700 Hirox 3Ddigital microscope at SAAM.

RESULTS

Visual observation and microscopy

Surfaces of the acrylic gesso and acrylic emulsion paint samples were examined with the naked eye and under microscope, before and after cleaning, to evaluate the effectiveness of each cleaning method and any resulting alterations in surface integrity. Special attention was paid to surface defects potentially caused directly by abrasion from erasers or indirectly by pressure from CO_2 or atomic oxygen treatment.

The effectiveness of the cleaning methods used on the gesso panel was evaluated for evenness of soot removal, amount of soot removed, and shifting and redistribution of soot. The cleaning methods that most effectively removed soot from both peaks and valleys in the paint surfaces, in descending order, were: atomic oxygen, water, Absorene sponge, bread (Figure 4), and Qosmedix make-up sponge. The Staedtler Mars plastic eraser, Rubgum eraser, ethanol, and Stoddard solvent removed soot from peaks, but not from valleys. A Hirox image of sample E cleaned with a Rubgum eraser clearly illustrates these uneven results (Figure 5). CO_2 snow removed soot only in the second phase of treatment. Ethanol, atomic oxygen, and CO_2 damaged the surface of the gesso panel while removing the soot. Ethanol removed part of the gesso layer, atomic oxygen removed the superficial acrylic binder, and CO_2 snow created impact holes in the second phase of cleaning (Figure 6).

There were no visible changes in the surface of acrylic paint after cleaning with commercial products and bread. Crumbs from each cleaning were saved and examined microscopically. It was noted that PR-112 made with organic pigment was extremely sensitive to cleaning, and that red pigment was picked up and deposited in the crumb. Staedtler Mars plastic eraser removed more original material than other cleaners. CO_2 cleaning caused no damage observable with the naked eye to acrylic paint surfaces; however, small impact holes were seen microscopically, indicating loss of original matter. Atomic oxygen cleaning caused visible dulling of paint surfaces, possibly indicating loss of binder.

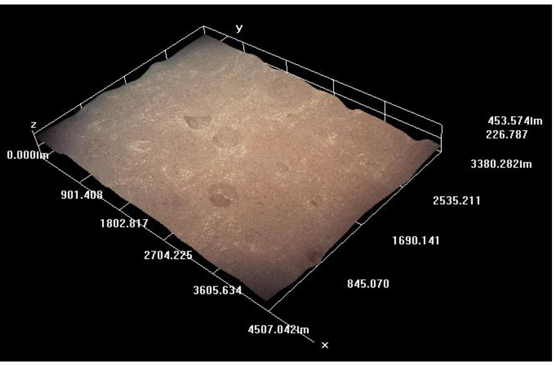


Figure 6
3D image of gesso panel cleaned with CO_2 showing surface holes caused by impact

Color and gloss

Soot removal caused color changes in the gesso panel samples relative to increases in the L* coordinate, which corresponds to lightness (Table 2). Since the original color of the panel was white, greater L* values (and consequently greater ΔL* and ΔE) indicate whiter or, in this case, cleaner samples. This parameter was used to rank the cleaning efficacy of the tested methods, which, in descending order, were: atomic oxygen, Staedtler Mars plastic eraser, water, Absorene sponge, bread, and Rubgum eraser. Wishab sponges and Groom/Stick cleaner were less effective in soot removal. Samples treated with atomic oxygen surpassed the original L* value, becoming lighter than the original. This may be an indication of surface alterations, as suggested by other tests performed in the study.

Table 2
Changes in color during two cleaning phases. The greater changes are noted in ΔL values

Sample	Phase I				Phase II			
	ΔL	Δa	Δb	ΔE	ΔL	Δa	Δb	ΔE
A	3.82	0.13	0.93	3.93	10.47	-0.14	0.43	10.48
B	-0.86	0.07	0.13	0.88	8.38	-0.10	-0.12	8.38
C	0.03	0.06	0.27	0.28	6.59	0.07	1.05	6.67
D	5.58	-0.08	0.54	5.61	10.18	-0.13	0.16	10.18
E	4.67	-0.04	0.44	4.69	9.75	-0.14	0.06	9.75
F	1.67	0.01	0.08	1.67	2.30	-0.01	0.13	2.30
G	5.00	0.07	1.24	5.15	10.26	-0.14	0.57	10.28
H	0.75	0.04	0.55	0.93	2.00	0.08	0.74	2.13
I	2.01	-0.07	0.33	2.04	3.26	-0.04	0.47	3.29
O	7.16	-0.08	0.36	7.17	11.44	-0.20	0.18	11.45
P	5.27	0.10	1.12	5.38	9.66	-0.02	1.04	9.72
Q	2.10	0.27	1.33	2.50	10.41	-0.12	0.86	10.45
R	-	-	-	-	13.51	-0.14	-1.33	13.58

In general, increased gloss value is an indicator of cleaning efficiency. In these tests, gloss changes were very low and not significant and the values obtained were sometimes inconsistent (Table 3). However, all but one of the gesso panel samples showed an increase in gloss after cleaning. The exception was the sample cleaned with atomic oxygen, where values measured at a 60° angle were inferior to those of the white control, possibly due to loss of binder during treatment.

Table 3

Gloss measurements at 20°, 60°, and 80°, after cleaning with materials described in Figure 2

Sample	20°			60°			85°		
	Bef	Aft	Aft2	Bef	Aft	Aft2	Bef	Aft	Aft2
A	0,80	1,00	1,17	2,17	2,70	3,23	0,50	0,87	0,90
B	0,80	0,80	1,00	2,27	2,20	2,83	0,50	0,70	0,70
C	0,80	0,80	1,00	2,30	2,50	3,40	0,70	1,10	1,90
D	0,80	1,00	1,20	2,50	3,30	3,83	0,73	1,20	1,20
E	0,80	1,00	1,20	2,53	3,30	3,90	0,83	1,40	1,60
F	0,80	0,90	0,90	2,43	2,87	2,97	0,67	1,00	1,00
G	0,80	1,00	1,20	2,57	3,57	4,17	0,63	0,97	1,17
H	0,80	0,80	0,83	2,50	2,70	2,83	0,70	0,93	0,97
I	0,80	0,93	1,00	2,37	3,00	3,03	0,77	1,13	1,03
O	0,80	1,00	1,20	2,57	3,27	3,77	1,13	1,93	2,03
P	0,80	1,00	1,10	2,50	3,40	3,90	1,20	1,83	2,17
Q	0,80	0,80	-	2,3	2.9	-	0,7	1,00	-
R	-	-	1,16	-	-	1,97	-	-	0,67

Regarding the acrylic paint samples, atomic oxygen cleaning caused changes in color and gloss on samples painted with organic pigments (Figures 7 and 8). Color changes in samples of paints NA and PR-112 resulted from paint loss during cleaning and exposure of the canvas support surface. As noted previously, the decrease in gloss was probably caused by loss of binder. Paints with organic pigments are more sensitive to atomic oxygen cleaning because both binder and pigment can react with the oxygen and transform into volatile compounds. No significant changes in color and gloss were observed on any other acrylic paint samples as a result of cleaning.

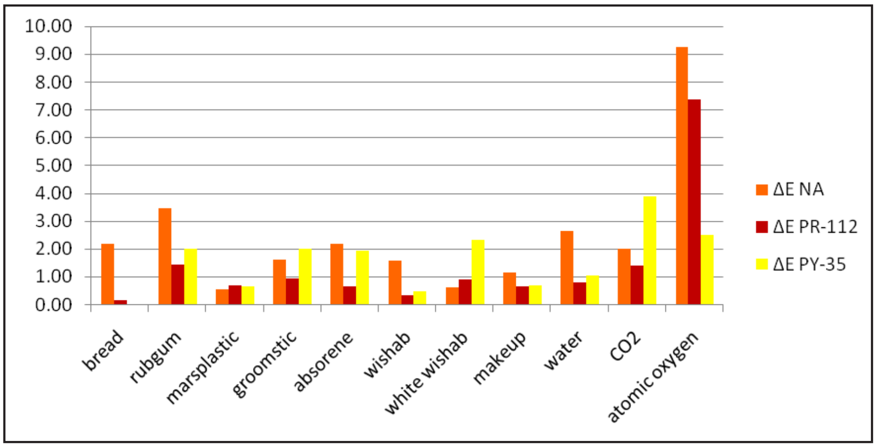


Figure 7

Color changes (ΔE) in three acrylic color samples. Significant changes were observed in the organic samples (NA and PR-112) cleaned with atomic oxygen

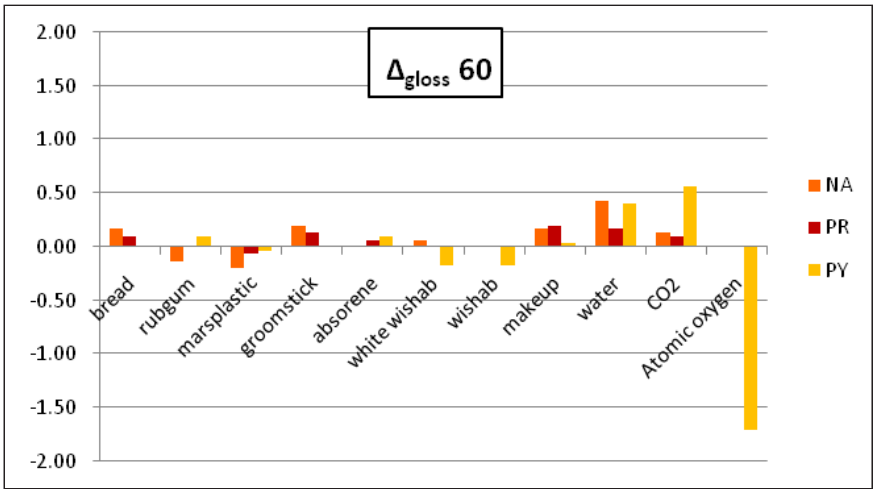


Figure 8

Changes in gloss after cleaning. Note significant change in inorganic sample treated with atomic oxygen (values unavailable for organic samples, which were covered with varnish)

CONCLUSIONS

Dry and non-contact methods of removing soot from painted surfaces were evaluated by visual observation and microscopy, and by measuring gloss and color. Our goal was to increase conservators' options for cleaning acrylic emulsion paint. Our criteria for evaluating the effectiveness of a particular cleaning method were preservation of surface morphology and homogeneity, evenness of cleaning, and ease of soot removal. Major considerations in selecting cleaning methods include the type of soil to be removed, the chemical and physical properties of the surface to be cleaned, the impact of mechanical forces, and maintenance of surface integrity. Cleaning with water, Absorene sponge and homemade bread delivered superior results in the removal of soot from an acrylic gesso panel. However, they also removed the organic pigment from PR-112 acrylic emulsion paint, with bread doing so more slowly than water. It is known that water can remove surfactants on acrylic paint, but it appears that bread may also remove surface components. This calls for further investigation. These results show that ethanol caused noticeable and significant damage to the paint's surface integrity, clearly indicating that solvents should not be used to clean acrylic emulsion paint. It was also found that in the process of dry-cleaning, paint with inorganic pigments fared better than paint with organic pigments, which can be removed from paint by both dry and wet-cleaning.

Disadvantages were discovered to both dry and non-contact cleaning methods. Dry cleaning is time-consuming and mostly offers uneven results. CO_2 does not effectively remove soot from acrylic emulsion paint, probably due to surface chemical interactions between the paint and the polycyclic aromatic hydrocarbons, aliphatic carbon, and other oxygen-rich groups in soot. To remove soot, the CO_2 had to be applied at pressures that damaged paint surfaces and created impact holes. Atomic oxygen cleaning removed soot evenly without disturbing brush strokes, but all paint samples cleaned with atomic oxygen showed a decrease in gloss due to removal of a portion of the acrylic binder, which is ethically unacceptable. Nevertheless, atomic oxygen cleaning can potentially salvage heavily soot-damaged artworks previously considered unrestorable.

Choosing the right tool can minimize the risk of inappropriate cleaning, and more tests will be conducted on the 25-year-old acrylic test samples.

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