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## **GROOMSTICK: A STUDY TO DETERMINE ITS POTENTIAL TO DEPOSIT RESIDUES**

Sara A. Moy

### **Abstract**

The use of kneadable eraser products for dry surface cleaning on works of art is a common practice adopted from paper and book conservation, but questions as to their suitability consistently arise with the availability of each new product. Since the 1960s testing has attempted to address whether erasers and other related dry cleaning materials leave residues when applied to works of art. While many products have been found to be inappropriate for use on artifacts, the viability of Groomstick, a vulcanized rubber of cis-1,4 polyisoprene has not previously been conclusively established.

This paper reviews past studies conducted on a variety of kneadable rubber products with a focus on the author's investigation of Groomstick and its potential to contaminate surfaces.

### **1. Introduction**

The potential for eraser products to damage surfaces during dry cleaning has been a concern since the 1960s, as they may disrupt the surface and/or leave traces of the eraser behind. The question of whether erasers used to remove loose contaminants and other superficial matter would leave any harmful residues in paper was addressed in 1966 when the Library of Technology Program of the American Library Association commissioned the McCrone Associates to study 17 book cleaning materials. Of the 17 cleaning materials, only one was the kneadable type, Absorene wallpaper cleaner, a starch-based pink putty. Based on microscopic evaluation and accelerated aging tests of paper cleaned with them, all cleaning materials evaluated were deemed safe for use, including Absorene (Horton 1969). It was presumed that residues left behind from some of these dry cleaning products would even be beneficial if remained on the paper (Walter C. McCrone and Associates 1966).

### **2. Kneadable rubber products**

#### **2.1 Wallpaper cleaner**

Subsequent study on Absorene and Sheffield's, the European equivalent wallpaper cleaner, advised that all eraser materials be removed from the surface of the paper to avoid the possible long-term destructive effect of the residues or crumbs, as they were found to be tenacious once they had dried (Banks 1969). It was postulated that some of these materials could be regenerated with a little water (Horton 1969), and that further solvent or wet-cleaning methods applied to the paper would cause the residues to dissolve or to swell, and to penetrate further into the paper matrix (Moffatt and Laver 1981).

## 2.2 Silly Putty

Silly Putty is a pink dough sold primarily as a children's toy. It has been classified as a kneadable material whose main component is silicon with the presence of titanium, colorants and traces of iron and chloride (Moffatt and Laver 1981). It is oily in nature and if left on a sheet of white paper for a day was found to flow down into the matrixes of the paper, making it impossible to remove and causing an oily pink discoloration (Moffatt and Laver 1981). It has been suggested by Cowen (1986) that colored materials are inappropriate and should be avoided, as they may become trapped and visible on the surface of an object.

## 2.3 Kneadable erasers

Several other kneadable eraser products have also been studied. They include the Artist Rubber manufactured by Faber Castell Corporation, Kneaded Rubber 1224 by Eberhard Faber and Rowney Kneadable Putty Rubber by Daler-Rowney. In the late 1960s these kneadable rubber erasers were described as the gentlest of all erasers, however further investigation has shown them to abrade surfaces to a greater extent than block and powder erasers (McInnis 1980). The chemical composition of these putties has been identified as polyisobutene rubber with calcium carbonate (AIC Books and Paper Group 1992; Moffatt and Laver 1981). Trace elements include chloride, sulfur, titanium, magnesium, aluminum, silicon, potassium and carbon black (AIC Books and Paper Group 1992; Moffatt and Laver 1981). It has been found that Kneaded Rubber 1224 left behind a gummy residue on Mylar film (Hueber 1985). Small residual crumbs of Artist Rubber and Kneaded Rubber 1224 have been detected in paper fibers (Pearlstein et al. 1982). The presence of sulfur in Kneaded Rubber 1224 was found to tarnish silver coupons when the rubber was left in contact (Moffatt and Laver 1981). Only the Rowney Kneadable Putty Rubber had no corrosive affect (Thomsen and Shashoua 1991).

It has been suggested that kneadable erasers could transfer oils from the fingers and dirt to the eraser and then to the object during cleaning (Cowan 1986). This was not evaluated until 1988, when the British Museum launched a study to evaluate soiled Kneadable Putty Rubber and its potential ability to transfer dirt onto clean substrates. They found that heavily soiled Kneadable Putty Rubber imparted detectable organic residues. These residues were attributed to the contaminated eraser (Thomsen and Shashoua).

## 3. Groomstick

Groomstick, another kneadable rubber product, is described by the manufacturer (Picreator Enterprises) as a "Processed kneadable rubber, extraordinarily absorptive and retentive. Permanently Tacky, non-hardening, clean to handle. Gentle, non-abrasive, non-staining cleaner of paper and archival materials. Dry-cleaner and de-greaser of hands and many other smooth or carved solids. 'Ever-lasting' service life" (Picreator Enterprises Ltd 1999) (Fig. 1).



Figure 1. Groomstick.

Like other kneadable products, Groomstick has also been studied for its ability to impart itself on to substrates. The first study of Groomstick appeared in 1981 by CCI (Moffat and Laver 1981). The Analytical Research Services division at the Canadian Conservation Institute, using x-ray primary emission spectroscopy in a scanning electron microscope, identified the material as vulcanized cis-1, 4-polyisoprene containing titanium dioxide and traces of calcium, Al, Si, K, Fe, Cl, and sulfur

This study found that Groomstick left no detectable residues and did not cause any tarnishing to silver. A subsequent study conducted in 1991 by the British Museum (Thomsen and Shashoua), also found that Groomstick, when fresh, did not impart itself onto substrates. Unlike the study conducted at CCI, tarnishing was found on silver coupons when the rubber was left in contact. They also concluded that that soiled Groomstick, like Kneadable Putty Rubber contaminated clean surfaces. In a study carried out in 1995 (Caldararo), substrates that were cleaned with Groomstick were thermally aged in order to detect observable color changes on cleaned surfaces. It was observed that aged substrates treated with Groomstick produced a yellow/brown residue on paper. A milky whitish-gray film was observed on sandpaper and a reflective surface was detected on black mat board.

#### 4. Experiment

In 1999, a study was designed to evaluate (1) the application of Groomstick under a variety of temperatures; (2) the application of aged and artificially aged Groomstick; (3) the application of soiled Groomstick to evaluate its potential ability to transfer soil onto clean substrates; and (4) examination of surface change in artificially aged substrates cleaned with fresh Groomstick.

#### 4.1 Substrates

Drawing from previous experiments performed on dry cleaning materials, five substrates were selected for this experiment. These were:

- Whatman's # 1 chromatography paper number 1 basis weight 87g/m<sup>2</sup>, thickness 0.16 mm applied on felt side
- Potassium bromide discs, 1.750g (=/- 0.015g), pressed at 25 tons
- Bueller plain waterproof silicon carbide discs metallographic grinding paper, grit-P200
- Whatman's 100% borosilicate binder free glass micro fiber filters, 25mm circles
- Whatman's flexible chromatography paper, PE SiLG/UV, 250µm layer on a flexible polyester back.

The latter two substrates were added to provide a broader range of surfaces in addition to its potential to be analyzed with little spectral interference.

#### 4.2 Instrumental analysis

Scanning electron and binocular microscopes were used for visual examination for the detection of residues (See Appendix A). Elemental analysis included Energy-dispersive X-ray analysis (EDXA) in the SEM to detect inorganic trace elements which are contained in the Groomstick and Fourier Transform Infrared Spectroscopy (FTIR) to detect organic composition, namely the functional groups found in natural rubber, *cis*-1, 4-polyisoprene. Backscattered images taken from the SEM and elemental analysis using EDXA were performed on uncontaminated (control) substrates and compared with those being tested. Spectra of the possibly contaminated surfaces, uncontaminated substrates and Groomstick were obtained from FTIR. These spectra were compared so as to identify any deposited residues.

#### 4.3 Groomstick applied at varying temperatures

The manufacturer of Groomstick advises that the product should be stored under room temperature and between polyethylene sheets (Picreater Enterprises Ltd 1999). Despite these instructions, it has been found that many conservation laboratories store their supply in the refrigerator. This is possibly due to the nature of natural rubber, *cis*-1, 4-polyisoprene, which has a very low glass transition temperature, enabling it to flow at room temperature. Refrigerated Groomstick would be less tacky than an un-refrigerated supply. A less sticky material would be less likely to attach to the surfaces that are being cleaned.

##### 4.3.1 Temperature selection: Discussion

The exposure of test samples of Groomstick to varying temperatures was performed in order to determine whether or not this would have any impact on potential eraser residues deposited. Realistic temperatures of 9°C (refrigerator temperature), 23°C (room temperature), 30°C and

40°C, a potential temperature in some countries and an unrealistic temperature of 50°C were selected.

### 4.3.2 Observations of Groomstick applied at various temperatures

It was expected that Groomstick when applied above room temperature would leave residues on the surfaces of the substrates. With the exception the flexible chromatography paper, it was observed through visual, elemental and FTIR spectroscopy that no contamination was found on any other surfaces. It was however observed that applying Groomstick at temperatures above 30°C resulted in a more elastic and tacky product.

## 4.4 Aging

### 4.4.1 Heat aging – Discussion

Groomstick is advertised as having an “Ever-lasting’ service life” (Picreater Enterprises Ltd 1999). In general, natural rubbers do not have good long-term chemical stability as they are susceptible to oxidation. Fig. 2 shows samples of Groomstick of unknown age, with typical signs of oxidation. Degradation of vulcanized rubber may result in tackiness and/or pastiness, discoloration and presence of an outer film.



Figure 2. Groomstick samples of unknown age showing typical signs of oxidation.

Following German standard (DIN 53508) for aging soft vulcanized rubber, test samples of Groomstick for thermal aging were exposed to the action of dry heat at 70°C for 24, 48 and 72 hours and 7, 15 and 28 days.

#### 4.4.2 Observation of thermally aged samples

It was observed that large visible clumps of all thermally aged Groomstick were found on all flexible chromatography paper. Groomstick thermally aged for 28 days, left residues on both Silicon Carbide and #1 chromatography paper. The residues of Groomstick found on silicon carbide paper could not be detected under the binocular microscope, but were easily discernable under the SEM at x100 magnification (Fig. 3). Qualitative analysis using EDXA identified the presence of titanium on both silicon carbide and Whatman's #1 chromatography paper. Silicon was also detected on the chromatography paper (Fig. 4).

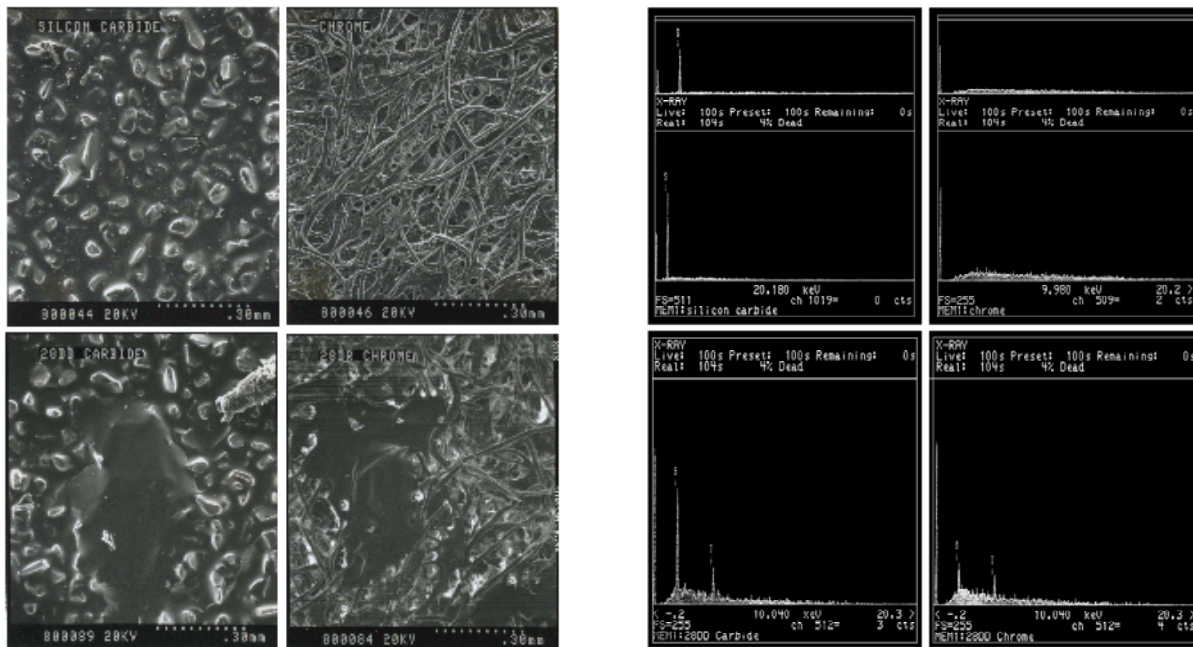


Figure 3 (left). Observation of thermally aged Groomstick. SEM photomicrographs (clockwise from upper left): Silicon carbide control (100x); chromatography paper control (100x), applied by tamping; 28 days heat-aged on chromatography paper (100x), applied by rolling; and 28 days heat-aged on silicon carbide (100x), applied by tamping.

Figure 4 (right). Observation of thermally aged Groomstick: EDXA spectra (clockwise from upper left) Silicon carbide control; chromatography paper control; 28 days heat-aged on chromatography paper, applied by tamping; 28 days heat-aged on silicon carbide, applied by tamping.

#### 4.4.3 Light aging: Discussion

Like the heat aged samples, Groomstick samples for accelerated light aging, following British Standard Institution (BS 1006:1990) for *Color Fastness to Artificial Light: Mercury Vapor Fading Lamp Test*, were exposed for 24, 48 and 72 hours, and 7, 15 and 28 days (BS1006:1990). Additionally, Groomstick pieces were aged under natural light on a windowsill and dark-aged at room temperature in a cupboard at 23°C for 28 days.

#### 4.4.4 Visual observation of light-aged samples

It was found that all artificially light-aged Groomstick produced a skin-like film. There were no significant changes found with the dark aged sample. Groomstick exposed to 28 days of natural light had the same physical appearance as the sample that was artificially light-aged for 7 days (Fig. 5).



Figure 5. Left, Groomstick exposed to 28 days of natural sunlight; right, Groomstick control.

#### 4.4.5 Observation of application of light-aged samples

Dark-aged Groomstick did not impart itself onto the test substrates, however all light-aged samples with the exception of the glass filter paper contained residues (Fig. 6). The Groomstick was found to be too tacky for the glass filter paper, pulling surfaces away. Clumps of Groomstick and transparent and/or translucent reflective films were observed with the aid of a binocular microscope, and some of the residues were visible without magnification. Traces of titanium and silicon were consistently detected using EDXA; absorption peaks containing functional groups including alkanes, double bonds and OH, typical of vulcanized rubber, were found on the FTIR spectra of all potassium bromide discs, indicating the presence of Groomstick (Fig. 7).



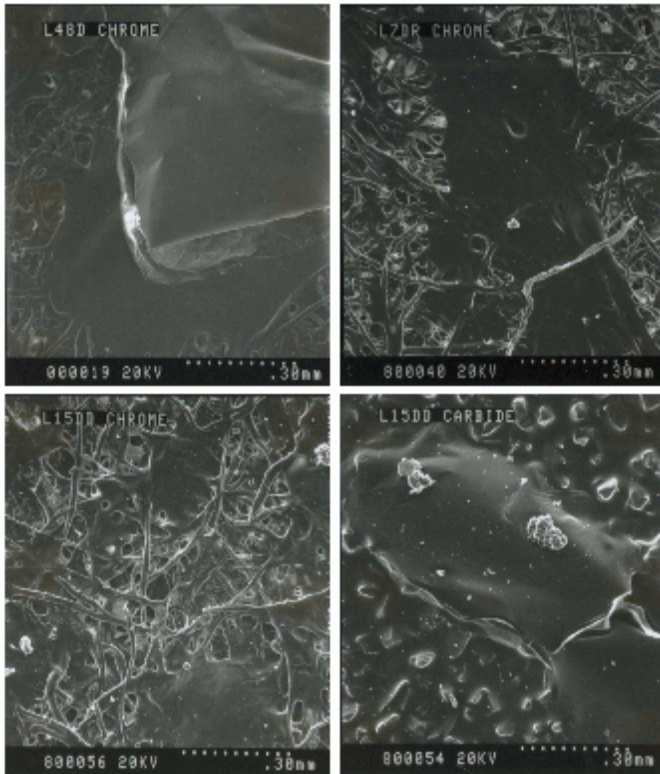


Figure 6. Observation of light-aged Groomstick. SEM photomicrographs, clockwise from upper left: 48 hours of artificially light-aged on Whatman's #1 chromatography paper (100x), applied by tamping; 7 days of artificially light-aged on Whatman's chromatography paper (100x), applied by rolling; 15 days of artificially light-aged on silicon carbide (100x), applied by tamping; 28 days of naturally light-aged on Whatman's #1 chromatography paper (100x), applied by tamping.

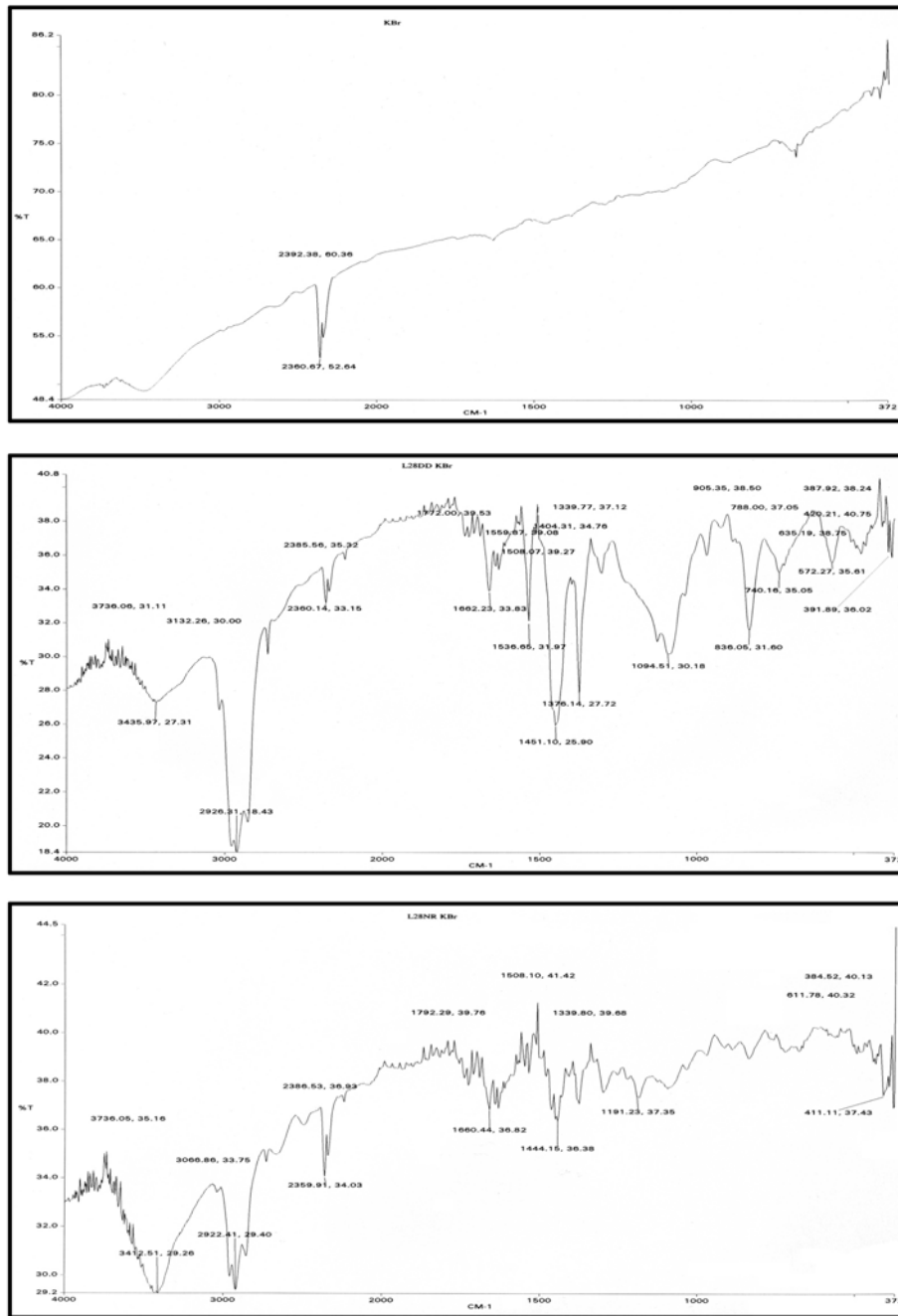


Figure 7. FTIR spectra of light-aged Groomstick. Top: KBr control, Middle: spectrum of 28 days artificially light-aged sample on KBR disc, Bottom: spectrum of 28 days naturally light-aged sample on KBR disc.

#### 4.4.6 Groomstick of unknown age

No preparation was required for the Groomstick pieces of unknown age labeled no. 1 and no. 2

#### 4.4.7 Observation of samples of unknown age

It was found that sample no. 2 of unknown age resembled Groomstick that was artificially light aged at 28 days.

Sample no. 2 of unknown age also imparted the same type of residues on the test substrates as Groomstick that had been artificially light-aged. Sample no.1 of unknown age did not appear to leave residues. It was also observed that the Groomstick samples of unknown age had functional groups found on the FTIR spectra similar to the artificially light-aged samples. Due to the control panel malfunctioning during analysis, trace elements could not be determined on EDXA.

### 4.5 Selected particulate matter

Four types of particulate matter were selected to contaminate erasers: (1) mold *Aspergillus niger*, commonly found in temperate climates on museum objects derived of cellulose, plant materials and other organic materials; (2) soot obtained from the interior surface of a glass candleholder; (3) lanolin (hydrous wool fat), often found in hand creams and lotions, was selected to imitate oily residue that might be found on bare hands; and (4) dust obtained from a nearby air-extraction unit.

#### 4.5.1 Observation of substrates cleaned with Groomstick contaminated with particulates

Dust, soot and mould were transferred from Groomstick to substrates. Dust was found on the surfaces of substrates having a topography. Soot was observed on the flexible chromatography paper and KBr discs (Fig. 8). Peaks found on the soot spectrum were found on contaminated substrates. Mold was observed upon application with the naked eye on most substrates. Contaminated mold substrates undetectable with the naked eye were confirmed under high magnification and FTIR spectroscopy. The transfer of lanolin on substrates could not be determined conclusively on visual examination or through FTIR analysis.

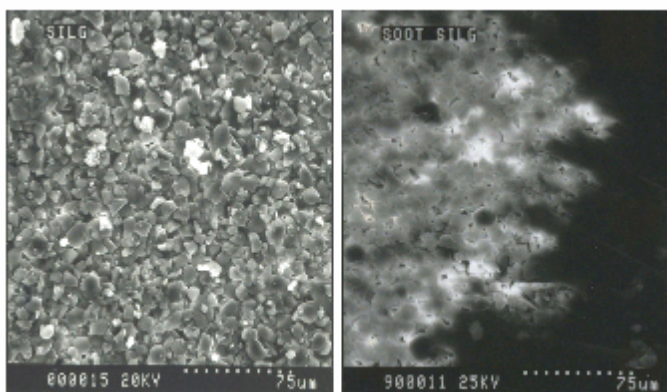


Figure 8. Left, Flexible chromatography paper control (400x), Right, soot observed on the flexible chromatography paper (400x).

#### **4.6 Observations of aged test substrates following application of fresh Groomstick**

No Groomstick oxidization residues were found on aged test substrates, with the exception of the flexible chromatography paper. This was the only substrate with residues that were visible during the application of Groomstick. The clumps that remained after aging appeared as yellow/brown rings around the gray mass of Groomstick.

#### **5. Review of test substrates**

It should be noted that the glass filter paper and flexible chromatography paper might not have been the ideal testing substrates. The surface of the glass filter paper lifted too easily, clinging to the Groomstick when applied, and it was readily disrupted on handling. All applications of Groomstick, even when fresh, had a marked tendency to stick to the flexible chromatography sheets.

#### **6. Conclusion**

The Groomstick investigation carried out in this project showed fairly conclusively that it has the potential to leave residues behind. However, the nature of the deposited residues will vary.

We can conclude that Groomstick is temperature dependent, as its ability to 'tack' to a surface increases with a rise in temperature. This is especially noticeable with surfaces that have topography. The rougher the surface, the more likely the warmer Groomstick will stick to it. Smooth surfaces, such as the pressed KBr, were less likely to retain a residue, as there is nothing for the Groomstick to grab or hold on to.

Despite the slight changes in working characteristic found in thermally aged Groomstick, only the substrates with irregular surfaces retained residues, and only after 28 days of heat aging. In contrast, with both artificial and natural light aging residues were found on both irregular and smooth surfaces even at 24 hours of exposure. It is unclear how much dark aging will actually affect Groomstick. Given its potential to degrade quickly in light, the product should be stored where exposure to light is minimal.

Soiling held in Groomstick has a great potential to transfer on to cleaned surfaces. It should be noted that if Groomstick is used to remove superficial matter, it should not be reused. However, the finding in this study that Groomstick has the potential to leave residues behind does not preclude its use for the cleaning of artifacts. What should be considered is temperature at which it is applied. Clearly, the suitability and efficiency of this product and its application must be evaluated on an object-by-object basis. In the end, Groomstick is worthy of remaining in our toolbox but the conservator's judgement is always paramount.

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## **Appendix A**

### **A. Methods of Analysis and Examination**

The purpose of this appendix is to provide an overview of the methods of analysis used during the project for the examination of residues Groomstick. The capabilities of each technique and the specifications while running the equipment will be presented.

#### **A.1 Stereomicroscope**

The Vickers Stereomicroscope with a built-in illumination consisting of a pair of x10 eyepieces and objective lens providing a x20 magnification was utilized for the initial examination of the substrates tested.

#### **A.2 Scanning Electron Microscope – Energy Dispersive X-Ray Analysis**

The Hitachi Model S-570 scanning electron microscope, equipped with a Mamiya camera was employed for examining and photographing all substrates, tested and untested. A beam of electrons at 20 kV is directed at the sample striking the atoms presented on the surface to approximately 30mm and 75 $\mu$ m in depth. Detecting the resulting secondary electron or backscattered electrons creates images.

Energy dispersive X-ray analysis, the analytical facility on the SEM was used to detect inorganic elements contained in Groomstick, which may have imparted on the substrates tested. The samples are bombarded by electrons or x-rays; the x-rays emitted are characteristic to the elements presented. The intensity will depend on how much of those elements are present. No bonding information is provided.

### **A.3 Fourier Transform Infrared Spectroscopy (FTIR)**

Organic functional groups were identified on tested and untested substrates using the Perkins Elmer 2000 Fourier Transform Infrared Spectrometer. The FTIR is a form of absorption spectroscopy that is concerned with the vibrational molecules. When a sample is placed in a beam of infrared radiation, the sample will absorb radiation at frequencies corresponding to molecular vibrational frequencies. Different functional groups will absorb at characteristic wavelength. Diffusive reflectance was employed as this provided little or no sample preparation. Substrates were placed on the plane mirror, at a resolution of 4 cm<sup>-1</sup> and scanned 50 times and set to infrared region of the electromagnetic spectrum: 400cm<sup>-1</sup> to 372cm<sup>-1</sup>.