Integrated Methodology for the Evaluation of Cleaning Effectiveness in Two Russian Icons (16th–17th Centuries)

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ABSTRACT This article covers a methodology for evaluating the effectiveness of cleaning two Russian icons. The icons belong to a group of five from the same iconographic school, dating from the 16th to 17th centuries. An integrated and complementary approach to varnish and overpaint involved microscopic techniques (optical and scanning electron microscopy) and colorimetry (CIE L*a*b* system). The materials and techniques used in these icons have been characterized previously. Cleaning revealed extensive overpainting that had not only dramatically changed the original appearance, but also the meaning and attribution of one of the two icons. The analyses carried out were useful in determining the extent of the overpainting and led to a better assessment of the results and effectiveness of the restoration. Microsc. Res. Tech. 73:752–760, 2010. © 2009 Wiley-Liss, Inc.

INTRODUCTION

In current conservation practice, the original state of the work is of primary importance with the object’s integrity being respected and preserved as much as possible. Part of the evaluation of the effectiveness of cleaning is based on the need to establish the original chromatic equilibrium and to identify the original paint by distinguishing past interventions which distort the image, such as overpainting (Perusini, 1990). Difficulties arise when some layers have suffered irreversible physical–chemical alterations. Furthermore, disequilibrium can result where cleaning has been inconsistent, resulting in some areas that are fully cleaned with others remaining as they were. The overall system of intervention (method and cleaning agents) must be chosen according to the chemical and physical nature of the materials to be removed and the sensitivity of the original materials (Brandi, 1977; Brunetto, 2000; Perusini, 1990).

The act of cleaning has been subject of discussion and controversy (Brandi, 1949; Gombrich, 1963; Philippot, 1999; Rees-Jones, 1962; Rhyne, 2006; Ruheemann, 1968) which continues to this day. One of the key issues has been the evaluation of “patina,” a problematic concept regarding what is or is not original to the surface.

The aim of the treatment reported in this article was to preserve the “olifa” layer while removing disfiguring overpaint from two Russian icons. The cleaning of Icons is usually deemed necessary for removing not only old and altered varnishes, but also past interventions such as overpainting that have completely changed the meaning and attribution of these artworks. Many icons have not only been overpainted but also covered with a thick and darkened “olifa.” “Olifa” is the name for a typical varnish found on Russian icons. It is based on boiled linseed oil with the addition of a few grams of cobalt acetate 3% (in use for Russian paintings since the 18th century, Sendler, 2001), or 7–8% litharge. These driers were added to accelerate the polymerization of the oil (Lobefaro, 2003; Popova et al., 2003; Sandu et al., 2006a,b). The treatise of Dionysos from Pourna (Hetherington, 1996) mentions another recipe used in the monastic workshops at Mount Athos: the linseed oil was “boiled” and vegetable resin, such as pine, mastic, or sandarac was added. In many cases in the past, contemporary taste at that time resulted in drastic interventions involving the removal of precious original layers, along with the overpaint (Lobefaro, 1996).

A traditional method for cleaning ancient icons, reported in various technical treatises, is to use mixtures of organic solvents applied by swabs or brush. In many cases mechanical means, such a scalpel, were also employed (Cremonesi, 2000; Koklova, 1996). Solvent mixtures in wide use have been based on ethyl alcohol, acetone, and low aromatic hydrocarbons in various proportions. The solvent and/or solvent system is tested carefully before use, in microscopic areas primarily along the edges of the painting (Koklova, 1996). The essential issue for treatments described here was...
the choice of solvents or solvent mixtures which are able to solubilize the darkened and aged varnish and overpainting without acting upon the original layers.

The effect of cleaning with organic solvents has been mainly studied on oil paintings, and in the last decades several papers have reported the action of solvents on other materials, such as animal glues, casein, egg, and vegetal gums (Burnstock and Learner, 1992; Cremone, 2000; Khandekar et al., 1994; Michalski, 1990; White and Roy, 1998; Wolbers, 1992). However, the evaluation of cleaning on icon painting is still a new area of research and an integrated analytical approach, using microscopic and colorimetric techniques combined has not been reported to date.

In the last decades, several techniques have been proposed for the evaluation of the cleaning effectiveness in polychrome works of art, ranging from microscopy on cross-sections (performed before and after the intervention) to macroscopic, spectroscopic, reflectographic, colorimetric, and/or profilometric characterization of the surface (Aucouturier and Darque-Ceretti, 2007; Brunetto, 2000; Daniela et al., 2009; Learner et al., 2007; Matteini and Moles, 1984; Realini et al., 1998; Wei et al., 2005, 2007; White and Roy, 1998; Wolbers, 1992; UNI Normal, 2001). For example, optical (OM) and scanning electron microscopy (SEM) observations of cross-sections of paint samples provide information on the morphology and appearance of the materials present in various layers of the paint/ground composite. The effect of solvents could result in solubilization or penetration of dissolved materials through cracks, lacunas or interruptions in the paint laminae (Pinna et al., 2005; van den Berg et al., 2008). The application of FTIR and micro-FTIR/ATR spectroscopy, confocal Raman microspectroscopy, reflectance spectroscopy (RS, FORS), and colorimetry for the characterization of materials and evaluation of restoration treatments have already been reported for the diagnosis and study of paintings (Barbiroli and Raggi, 2000; Cordaro et al., 2000; Khandekar et al., 1994; Lange et al., 1993; Learner et al., 2007; Oleari, 1998; Sandu et al., 2002, 2006a,b, 2008). Other noninvasive techniques, such as microprofilometry and atomic force microscopy (AFM), have been useful tools for comparative examination of pictorial surface before and after cleaning (Aucouturier and Darque-Ceretti, 2007; Wei et al., 2005, 2007).

The results reported here are obtained from the application of three complementary techniques—optical microscopy (OM), scanning electron microscopy (SEM), and colorimetry (CIE L*a*b*) for the evaluation of the effectiveness of cleaning. Two icons belonging to a group of five from Northern Russia (16th–17th centuries) were cleaned. The first icon represents Michea (Icon 1) and the second, before cleaning was identified as S. Geremia but after cleaning was revealed to be depicting Moses. Full results regarding the identification of the materials, artistic technique, and the description of the state of paint layers have been reported elsewhere (Sandu et al., 2009), but in brief the following pigments were present on both icons: red, yellow, green and brown earths/ochres, verdigris, and lead white. The gesso grounds consisted of gypsum and animal glue and the saints halos were covered with silver leaf. The paint layer binder was identified as egg or possibly an egg emulsion with oil. An oily varnish ("olifa") covered the original paint layers (Sandu et al., 2009).

The cleaning method consisted of removing overpainting with Turpentine Essence. Overpaint removal
took place after the paint layer had been consolidated with isinglass (produced from the swim-bladder of sturgeon), as detailed in Sandu et al. (2009).

MATERIALS AND METHODS

Paint samples were taken from the same areas before and after cleaning tests to establish whether the "olifa" layer remained intact. As noted above, the goal of cleaning was to remove only the uppermost layers of varnish and overpaint such that this protective layer was left undisturbed. The analysis of the physical and optical properties of the layers present before and after cleaning was carried out by both light microscopy and SEM.

Colorimetric measurements were used to quantify the colorimetric parameters (CIE \(L^*a^*b^*\) 1976) of representative areas both before and after cleaning.

Analytical Methods

Optical Microscopy on Cross-Sections (OM). Tiny samples taken of the paint and ground layers were embedded in polyester resin (Mecaprex SS) (Table 1). After curing for approximately 12 h, the resin blocks were cut and polished to reveal the paint/ground composite in cross-section. Cross-sections were observed under a Nikon Eclipse E600 binocular microscope (4× to 40× magnification), in both visible and ultra violet (UV) light. Images were acquired with a Nikon DXM1200F digital camera. The block of filters used for UV fluorescence was B-2A type (excitation radiation at 330–380 nm—EX, observation at 420 nm—BA).

SEM-EDX Analysis of the Cross-Sections. For the morphological characterization of the paint/ground samples and for energy-dispersive X-ray microanalysis, a SEM—VEGA II LSH Scanning Electron Microscope (TESCAN—Czech Republic) coupled with an EDX—QUANTAX QX2 detector (ROENTEC, Germany) was used, working at less than 1 × 10⁻⁵ Pa vacuum pressure, at 30.00 KV voltage. The working distance varied between 11 and 20 mm (16.6 mm for EDX analysis) and the magnifying power was between 78× and 1,000×, with a scanning speed between 200 ns and 10 ms per pixel. Eight cross-sections were analyzed with this method (Table 2), each had been coated with a thin layer of graphite.

Colorimetry (CIE \(L^*a^*b^*\)). For the colorimetric measurements a Minolta Chroma Meter CR-200, with
a Xe lamp and six Si photocells for measuring the tristimulus values was used. The measuring area has a diameter of 8 mm, the geometry was 0°/0°, the light source was D65. The data were reported in the CIE L* a* b* 1976 system (Barbiroli and Raggi, 2000; Cordaro et al., 2000).

Calibration was carried out before each set of measurements using a pure white standard (calibration values: $L = 96.94$, $a = 0.18$, $b = 1.89$).

To calculate color differences due to the removal of layers (dirt, aged varnish, and overpaint) measurements were performed before and after cleaning. To guarantee reproducible positioning of the colorimetric probe a transparent polyester sheet (Mylar®) template was prepared for each area and reference points from the paint below were traced on to each sheet. From the areas selected for measurement, a square (1.2 x 1.2 cm) was cut out of the Mylar® template to allow direct instrument readings of the paint surface. The surrounding excess Mylar® served to protect the paint surface from contact with the measuring head of the colorimeter. To test the reproducibility of the measurements, three sets of data for each area were acquired.

**Sampling, Treatment, and Analytical Procedure**

After cleaning, six samples of paint were taken for evaluating the effectiveness of the overpaint removal (1S1a, 1S2a, and 1S3a from the icon of S. Michea and 2S1a, 2S2a, and 2S3a from the icon of S. Geremia—Fig. 1). The data obtained were compared with data from five samples taken from the same areas before cleaning (Sandu et al., 2009).

Colorimetric measurements were performed on both icons on eight areas (labeled from A to H) covering the entire chromatic palette (Fig. 1). For each area, three sets of data were acquired and the average values were calculated together with the standard deviation from the mean (Barbiroli and Raggi, 2000; Cordaro et al., 2000; Oleari, 1998; Sandu et al., 2002).

**The Cleaning Treatment**

Treatment included the following steps:

1. **Localized consolidation** of the ground layers was achieved with a solution of 5% isinglass in water (wt/wt) brush applied warm (50–60°C) over Japanese tissue paper. This was repeated several times on small areas, water was allowed to evaporate, then heat and some pressure was applied to the tissue/paint using a hot spatula (ca. 60–80°C) until the area was completely dry.

2. **Paint consolidation** was carried out with a warm (50–60°C) 10% solution of isinglass in water (wt/wt) applied using a cotton pad over several Japanese tissue papers. The tissues were replaced several times (with renewed moistening with the isinglass) in
order to soften the painting layer without allowing the isinglass to cool. Once the paint had softened sufficiently, the area was pressed gently with a hot spatula (ca. 60–80 °C) until it was completely dry.

3. Restricting solvent access to the paint/ground composite cracks in areas to be treated with solvent (mainly those with overpainting) were treated with a 5% solution of isinglass in water (wt/wt). This solution was diluted to ensure increased penetration into the preparation layers. It was applied several times by brush at 50–60 °C. Once all previous applications were dry, a last application was made using a more concentrated solution (10%) at the same temperature. Residual glue at the surface was removed using a moistened cotton pad. It was felt that by running isinglass into the cracks, solvent penetration to the paint and ground layers would be restricted.

4. Poultice method for solvent application: Japanese paper and pieces of cotton were cut to match the shape of the areas to be treated. Solvent (rectified turpentine essence) was applied to the tissue/cotton
poultice by brush. The poultice was left in place up to 6–12 h with regular checks on progress, and with the addition of further solvent as needed.

5. Removal of overpaint: Mechanical removal was carried out with a scalpel in areas which had been exposed to the solvent soaked poultice. Using this method the paint layers along with the “olifa” layer were left intact, with the solvent/mechanical action acting only on the uppermost layers of dirt, varnish and overpaint.

This method can be used only on icons that still preserve the original “olifa” layer underneath later overpaint. Using this method, only the overpaint responds to the poultice by swelling and can then be removed safely by mechanical means from the paint/olifa surface. Figure 2 shows two details of the paint surface during the removal of the overpaint layers in icons 1 and 2.

RESULTS

The OM and SEM images of cross-sections obtained from the paint/ground samples were useful for comparing the sequence of layers present before and after cleaning as well as the morphological characteristics of the paint layers before and after the intervention. This allowed a close visual assessment of the effect of the solvent and poultice method on the original layers, and indicated that although treatment was efficient for the removal of the overpaint the original paint was not damaged. Although this evaluation involves microdestructive sampling, this was reduced to a minimum by taking samples from areas which were already damaged (edges of cracks or lacunas in the paint).

Colorimetry was used as a tool for quantifying changes in the appearance of colors, and for documenting the recovery of the original palette of the two icons.

DISCUSSION

Evaluation of the Effectiveness Using Microscopic Techniques to Investigate a Cleaning Treatment

In icon 2, in the upper right area close to the halo of the Saint, an uncleaned area was left to allow sampling of a microfragment in which both cleaned and uncleaned parts were present. The intention was to show in a direct way the level reached by the cleaning procedure and its efficiency in removing overpaint (Fig. 3).

Sample 2S3a illustrates the layers of overpaint and varnish on the left which have been removed on the
right. This sample also shows that the original layers remain intact after cleaning including the “olifa” layer which can be distinguished in ultraviolet light (Fig. 4). As noted above, the overpaint on this icon hid an entirely different image.

The “olifa” layer was found on all the icons which were analyzed belonging to the group of five icons. The remaining layers on the right confirm that the cleaning agent and method used for the removal of the varnish and overpaint layers was effective in dissolving only the unwanted layers without damaging the original layers, including the thin “olifa” layer (Fig. 5).

The ground layer in icon 2 preserves its original appearance, including the morphologic and granulometric characteristics, as it can be observed in the sample 2S1 (Fig. 6).

The same observations about the ground layers morphology and granulometry apply to samples from icon 1. The cross-section of a sample taken from the brown background (1S3) at high magnification (SEM, 1,000×) shows an image of the ground after the treatment very similar to the one before cleaning (Fig. 7).

Colorimetric Assessment of the Changes/Recovery of the Original Chromatic Palette

The colorimetric data confirmed that after the treatment the pictorial surface of the two icons gained brightness, color saturation. From a chromatic point of view, the original paint, rediscovered after the removal of the overpaint layers, is made up of fewer colors, with clearer hues. Furthermore, in icon 2, as noted previously the removal of the overpainting changed the attribution of the figure because the original inscription was revealed (Fig. 8).

After cleaning, the original paint displays chromatic values completely different from those of the overpaint. The background is not brown anymore but yellow ochre; the garments of the Saint acquire more saturated tonalities. $a^*$ values (chromatic axis of green-red) decrease for all areas with the exception of B and D areas of icon 1 and A, B, D areas for icon 2, respectively. The $b^*$ values (chromatic axis yellow-blue) increase after cleaning for all the measured areas in icon 1 and for A, B, D, F, and G areas in icon 2 (Fig. 9).

The $L^*$ values (lightness) tend to increase after cleaning, with some exceptions such as C and G areas of both icons or B and D in icon 2. $L^*$ values of the C areas (gilded halos of the Saints) decrease of about 5 units (DL1 = −4.13, DL2 = −5.12), thus indicating a decrease in the brightness of this area after treatment, due to the removal of the varnish. In other areas (as B, D, F in icon 2) the $L^*$ values are less affected by cleaning (Fig. 10).

Fig. 8. Detail of the Prophet’s face in icon 2 before and after cleaning, showing the change in the representation and attribution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Fig. 9. Colorimetric data of the eight areas (A–H) on icon 1 and 2, before cleaning (black circle diamond) and after cleaning (gray triangle).
The analytical results led to the following conclusions:

- The cleaning did not affect the original layers of ground and paint—the granulometry of the "gesso" at high magnifications and the aspect of the original layers show the same characteristics for samples from the same areas taken before and after treatment.

- After cleaning, the original paint revealed was very different from the overpaint; for example, the background is not dark brown anymore but yellow-ochre (this being the background in all the five previously analyzed icons), while other areas (such as the garments of the Prophets) acquire more saturated, brighter hues.

- From a chromatic point of view, the original paint found after overpaint removal is composed of a smaller number of colors: mainly yellow and red ochre, white, green, and silver leaf.

- The pictorial surface of the cleaned icons acquires brightness and luminosity, characteristic of the original palette used by the iconographer(s).

- In icon 2, the removal of overpaint changed the significance and attribution/dating of the figurative representation, the "original" Prophet (dated from 16th century) being Moses and not Geremia (Ieremia).

As a general consideration the ideal for conservation/restoration treatments is to have close collaboration with expertise derived from the conservator, art historian/curator, and conservation scientist.

In this case the integrated approach for the evaluation of the cleaning procedures gave good results at more than one level. At the microscopic level, it was possible to confirm that the cleaning procedure had no visual effect on the original layers; the extensive colorimetric campaign which was used to monitor the level of cleaning also permitted a complete and accurate determination of the original palette; and finally, the set of colorimetric data acquired after treatment will be of potential use in the future should monitoring of color change be carried out.

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