The cleaning interventions of icons and old gilded decorative frames represent a great challenge for the curator and the restorer. This type of restoration treatment requires an interdisciplinary approach in order to respect the mandatory experimental protocols: the assessment of the conservation state, developing the cleaning solutions by applying washing tests, that are compatible with the nature of the dirt deposits and with the original materials, and finally the monitoring of interventions through appropriate selection of methods and interdisciplinary techniques of scientific investigation. Cleaning interventions that require organic solvents are highly toxic for the operator, and that is why nowadays, traditional cleaning processes that make use of plant extracts and aqueous extracts of plants are studied more and more. Also, because the cleaning process touches the integrity of the noble patina, and in cases of surfaces that are gilded directly on the ground layer (boles) or on other painting layers, that act differently upon wash, there is the risk of exudates, of advanced softening of the painting layer, of peeling the gilded areas, of material losses, of dirt and some color components getting scattered etc. Washing tests require mandatory differentiated protocols for the two gilding cases presented in the paper. This paper presents a study on using natural, water based systems (infusions, extracts, decoctions) for cleaning dirt deposit from the surfaces of two type of gilding cases. Cleaning solutions by applying washing tests, that are compatible with the nature of the dirt deposits and respect the mandatory experimental protocols: the assessment of the conservation state, developing the cleaning solutions by applying washing tests, that are compatible with the nature of the dirt deposits and with the original materials, and finally the monitoring of interventions through appropriate selection of methods and interdisciplinary techniques of scientific investigation. Cleaning interventions that require organic solvents are highly toxic for the operator, and that is why nowadays, traditional cleaning processes that make use of plant extracts and aqueous extracts of plants are studied more and more. Also, because the cleaning process touches the integrity of the noble patina, and in cases of surfaces that are gilded directly on the ground layer (boles) or on other painting layers, that act differently upon wash, there is the risk of exudates, of advanced softening of the painting layer, of peeling the gilded areas, of material losses, of dirt and some color components getting scattered etc. Washing tests require mandatory differentiated protocols for the two gilding cases presented in the paper. This paper presents a study on using natural, water based systems (infusions, extracts, decoctions) for cleaning dirt deposit from the surfaces of two type of gilding encountered on an old wooden icon. An organic alcohol (95%) based solution, slightly alkalinized with a water ammonia solution (25%) that was compatible with the varnished gildings, was used as a reference system. SEM-EDX, micro-FTIR and CIE L*a*b* colorimetry techniques were implemented.

Keywords: icon, old wood, cleaning, aqueous extracts, micro-FTIR, SEM-EDX, CIE L*a*b* Colorimetry

The icons that are part of the cultural heritage, especially those involved in liturgical activities, are affected by dirt and soot deposits, in the form of thin layers, mostly of organic composition, which suffer from deterioration and degradation evolving effects caused by microclimate, microbiological factors, and by the human factor, through improper manipulation, display or preservation-restoration processes. Deposits found on the surfaces of icons can come from accidental splashes of natural products (wax, paint, bitumen, asphalt, paraffin, glue, wine etc.), or from over time solidified dirt of insect excrements or from different particles dispersed into the atmosphere (aerosols, bio aerosols, dust, products of burning candles, lamps, censers etc., found as tars, soot, ash and other particles present in the smoke/smog).

These deposits that often darken the polychrome layers, making the iconographic image illegible, are continuous re-formed structures, the result being a heterogeneous layer, composed by partially degraded organic materials, hard to define (waxes, vegetable oils, paints, tars/ hydrocarbons, fats etc.) and various inorganic disperse systems (dust, lime, ash etc.). The nature, structure and extension of these deposits differ from icon to icon, being influenced in their formation by the type, the texture/microtopography and by porosity of the varnish. This explains the fact that we can find areas with adherent dirt deposits, others areas where the dirt reaches and interacts with the painting layer and others areas where the dirt is clogged or cornified or suffer from blisters, uneven cracks that affect the aesthetic aspect of the icon [1, 2].

It is a known fact that over time the dirt passes from non-adherent layers (easily removed by wiping, vacuuming or blowing) to adherent dirt deposits, especially when the soot suffers oxidative clogging or thermal cornifiation (not mixed pigments) with uniform deposits and specific deteriorations and degradations, will be squared out through investigations done in order to authenticate the painting and to assess its conservation state. Single colour areas (not mixed pigments) with uniform deposits and specific deteriorations and degradations, will be squared out through photographic images or mapping [3, 5-6]. Cleaning tests have been studied with great detail in relation to elaborating protocols for the selection of chemical agents. Solubility tests with solvents are the most usual as they allow the solubility parameters of the layers, which are to be removed, to be established. In view of these tests, the solvent or

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mixture which presents the most adequate parameters for dissolving a given material, with as little interaction as possible with the original pictorial structure, can be chosen [27-31].

Until today, the range of solutions involved in cleaning has widened significantly, from the aqueous or organic solvents based solutions [10, 15, 18, 32], with or without surface additives [11], hydrogels [12], ionic liquids [10, 33-38] or enzymes [39-41], all the way to the strong invasive laser pyrolysis [21, 42-46].

During the last years the implications of noninvasive ecological cleaning systems were studied more and more. A particular role is that of plant extracts (saponins, colorless tannins, glycosides and chemical modified alkaloids), colorless vegetable extracts and green plants components, or colorless dry plants infusions etc. Besides the moisturizing effect, these have a good capacity of removing dirt [22-23, 47].

This paper studies the cleaning capacity of some water based indigenous plant extracts or colorless infusions, by comparing them with organic solutions often used in cleaning old icons, which have a toxic effect on the restorer.

The cleaning test, small squares with identical or similar layers were selected, for both types of gilding: golden pigments applied directly on the ground layer (bole) and on the paint layer. The cleaning capacity was analyzed through visible and UV reflectography, CIE L*a*b* colorimetry and IR spectroscopy.

Experimental part

The study was done on a XIXth century icon, depicting “Three Hierarchs Basil, Gregory and John” theme. Belonging to a private collection, the icon was painted in egg tempera on lime wood, in neo Byzantine style, by an anonymous painter (fig. 1).

Fig. 1. Icon of the Holy Three Hierarchs Basil, Gregory and John, XIXth century: a – Bolus gilded area, b – Gilding over the painting layer area

The icon has few characteristics: it is done from a single lime wood board, with crossbeams, with a thin layer of ground, bole on the halo area, and lighter colored earth colors (ocher) with egg based binder. The gildings were made with gold powder and not with traditional gold leaves, both for the halos and also for the garment of Saint Gregory. The gilding of the halos was done over bole layer, on Saint Gregory’s garment it was done over the paint layer.

Because of the technique used to create it, of countless and careless manipulations (the icon was initially a holyday icon used in church, and afterwards became a family icon), of improper storage and exposure, the entire surface of the icon is covered in dirt deposits with blisters and clogging, old age cracks, detachments, gaps, fly holes etc., all of them can be observed with the naked eye. Before applying the cleaning process, a good knowledge on the nature on used painting materials and varnish, of their state of conservation and also the consolidation of the polychrome layer are required.

Analytical techniques

The following techniques were implemented:
- SEM-EDX (techniques SEM, tipe VEGA II LSH RANGE and Detector EDX, tipe Quantax QX2) for structural analysis, elementary composition and for assessing the conservation state by correlating the results with
- Micro-FTIR spectrophotometer, used to analyze the functional groups that characterize the organic and inorganic compounds.

The cleaning effectiveness was evaluated in a comparative system, by observing with a magnifying glass and measuring the color, hue and lightness parameters using CIE L*a*b* colorimetry, with the help of LOVIBOND 300 Reflectance Tinctometer device, by comparing the washed surfaces with a new water based systems (CS) with those cleaned with a classic organic reference system (RS), often used to remove dirt from varnished gilded areas.

Portable Spectrophotometer Lovibond, Reflectance Tinctometer – 300 and the CIE L*a*b* were used to follow the colour modification, more exactly the way that the gilded surfaces have modified the parameters that give them their degree of light (L*) on the light coordinates: a* (green – red) and b* (yellow – blue). Initial measurements were done on the selected areas, used later as a reference both for RS and for CS. After the cleaning tests with CS1 – CS3, new measurements of the same areas were done in order to determine the colorimetric modifications that took place.

Cleaning systems and washing tests

As a reference system (RS) an organic alcohol based solution (52%), low alkaline due to a few drops of ammonia water solution (25%), was used because it is compatible with varnished gilded surfaces.

In order to obtain the synergic mixtures based on colorless vegetable extracts and dry herbs decocations supernatant, freshly prepared, the following cleaning systems were created (CS):
- CS1 – com silk decocation (50 %), pumpkin extract (25 %), white cabbage extract (25%);
- CS2 - com silk decocation (50 %), pumpkin extract (25 %), celery extract (25 %);
- CS3 - com silk decocation (50 %), pumpkin extract (25 %), carrot extract (25 %).

The com silk decocations were obtained by boiling 10g of dry plant (only the covered part of the corn husk) in 200 mL of distilled water, for 5 min, after which the colorless supernatant was extracted by centrifugation. The pumpkin, carrot and cabbage extracts were obtained by using a classic squeezing device, process that required the fine chopping of the vegetables and their centrifugation, in order to obtain the colorless supernatant. The celery roots were grinded really smooth and were then dispersed in distilled water, in a 1:1 ratio. After that the pulp was separated, the rest was used to obtain the supernatant by centrifugation. The five types of colorless supernatant were used to make the recipes described earlier.

In order to apply the cleaning test, both on the gilded halos, where the golden pigment was applied directly on the ground (bole), and on the garment of Saint Gregory, where the gilding process occurred over the painting layer, two areas were selected: one for testing the reference organic system (RS) and the other one for testing the water based systems (CS). The areas were bounded into squares by easily removable white color (aqueous dispersion of very fine chalk powder).
Fig. 2. Detail of icon with deteriorations of the paint layer: a – old age cracks; b – deep gaps; c – clogged dirt; d – degraded varnish.

Fig. 3. Deterioration of the painting layer: a – deep gaps; b – old age rough cracks; c – old age fine cracks; d – scratch; e – clogged dirt.

Fig. 4. Details of gilded areas: a, b, c – the halos of the Three Hierarchs; d – the garment of Saint Gregory.

Fig. 5. The areas from where the two sample were taken: a – halo, b – Saint Gregory’s garment.

The cleaning with RS was done by rubbing the area with a cotton swab with low alkaline alcohol solution, right after the area was slightly moisturized with the same solution. The cleaning with the three types of aqueous colorless dispersion was done on three other marked squares, in a similar manner. The only thing that differed was the fact that the rubbing was done for 10 cycles, in perpendicular directions, for a couple of seconds and the cotton swab was replaced every time.

**Results and discussions**

**Conservation state assessment**

The icon presents old age cracks, clogged dirt and evidences of intense use (gaps, wax, fat and lipstick deposits, scratches), all caused by the role of the icon (holiday and afterwards, family icon).

Through visible and UV reflectography, the following were observed:
- old age cracks (fig. 2a);
- lack of painting layer or gaps (fig. 2b);
- clogged dirt deposits (with blisters on some areas) on the entire surfaces of the painting layer (fig. 2c);
- partial lack or degraded varnish, as a result of an aggressive previous cleaning operation (fig. 2d);
- evolving deteriorations and degradations of the paintlayer (fig. 3): fine and semi-dynamic rough cracks, gaps, clogged dirt, scratches;
- the ground layer, based on red brown boles on the halos area and on ocher colored earth on the rest of the icon, is really thin (fig. 4);
- gold dust was used for gilding both the halos (fig. 4a-c) and the garment of Saint Gregory (fig. 4d).

In order to point out the structural aspects of the painting material used and to determine their elementary composition, two samples of 0.2 cm² were taken from the two areas studied (the halos and the garment of Saint Gregory), carefully not to damage the aesthetic aspect of the icon (fig. 5a-b).

Picture 6 presents the EDX spectra, the corresponding SEM microphotography’s and the data tables regarding the concentration of the chemical components.

Based on the chemical composition found in the EDX spectra it was determined that the two gilded areas were done using gold dust, mix with silver, and the ground layer of the two areas was done with colored earths, based on Si, Al and Ca/Mg. The halo ground layer contains a lot of Pb (minium mixed with colored earth), while the ground layer of the second area (garment) contains Fe, Ca, Ba, S, and Pb (colored earth, mixed with white barium and calcium sulfates). The C found in the two samples is attributed to the smoke deposits on the gilded area and to the elements found in the binders composition (egg for the gold pigment and animal glue for bole and ground layers).

The picture 7a and b shows the FTIR spectra of the same two samples analyzed through SEM-EDX.

The FTIR analysis of the two samples have confirmed the presence of corresponding peaks for the chemical compounds identified through SEM-EDX in gilded areas and ground layer specific groups (bole and painting/ground layer) (table 1).

The presence of these compounds confirms the gilding technique used: the gold layer was applied with a brush over a thin layer of red ocher clay, mixed with egg white and honey. The gold powder was prepared also with egg white and honey, until an undifferentiated mass was obtained. Afterwards, a resin based solution was applied over for smoothing.

**The effectiveness of cleaning tests**

The cleaning tests were done on small surfaces, of about 1 cm², squared out with an easy-removable white color (fine grounded charcoal dispersed in water). The reference system (RS) was applied first (figs. 8a and 9a), followed by the cleaning systems CS1 – CS3 (figs 8b-d and 9b-d).
Fig. 6. EDX spectrum of the sample taken from the gilded area: a - the halo, b - the garment

Table 1
REPRESENTATIVE PEAKS AND SPECTRAL BANDS OF THE CHEMICAL SPECIES IDENTIFIED IN THE SAMPLES ANALYZED BY MICRO-FTIR

<table>
<thead>
<tr>
<th>Type structure</th>
<th>chemical bands (cm⁻¹)</th>
<th>Theoretical</th>
<th>Spectral</th>
<th>Peak present in sample (cm⁻¹)</th>
<th>Peak present in garment sample (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicate</td>
<td>860–1175</td>
<td>947.61; 1064.75; 1197.38</td>
<td>924.47; 1068.54</td>
<td>1166.78</td>
<td></td>
</tr>
<tr>
<td>Aluminate</td>
<td>800–920</td>
<td>-</td>
<td>-</td>
<td>835.59</td>
<td></td>
</tr>
<tr>
<td>Sulphate and sulphide</td>
<td>570–680; 960–1030</td>
<td>-</td>
<td>-</td>
<td>623.66; 696.51</td>
<td></td>
</tr>
<tr>
<td>Carbonate</td>
<td>670–745; 800–890; 1040–1100; 1320–1350</td>
<td>1333.28; 1362.61; 1461.93</td>
<td>1316.84; 1465.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb(II, IV) as oxides and carbonated</td>
<td>660–685</td>
<td>684.49</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(II, III) as oxides</td>
<td>700–715</td>
<td>-</td>
<td>-</td>
<td>712.49</td>
<td></td>
</tr>
<tr>
<td>Aque and hydroxy complexes (coordination and crystallized water)</td>
<td>2850–4000</td>
<td>2862.71; 2942.64; 3427.39</td>
<td>2863.07; 2943.71</td>
<td>3440.31</td>
<td></td>
</tr>
<tr>
<td>Binder (egg protein identified by amide I and II)</td>
<td>~1547; 1621–1690</td>
<td>1596.68</td>
<td>-</td>
<td>1524.62</td>
<td></td>
</tr>
<tr>
<td>Varnish (Dammar – by ester groups)</td>
<td>~1265; ~1750</td>
<td>1742.05</td>
<td>-</td>
<td>1744.83; 1277.78</td>
<td></td>
</tr>
<tr>
<td>Tar and fats, as carboxyl and carboxyl groups</td>
<td>1950–2050; 2550–2750</td>
<td>1998.15; 2662.71</td>
<td>2602.15; 2704.72</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The reference cleaning (RS) was done with an alcohol solution, low alkaline that is often used in cleaning old varnished gilded areas, which had a quick effect. After the moisturizing stage, the removal was done with only one swap of the wet cotton swab. The picture 10 presents the comparison of colorimetric data obtained from the two gilded areas.

During the cleaning process, it was observed that all three used systems have a gradual moisturizing and cleaning effect of the dirt deposits, along the 10 washing stages, fact that assure an optimal dirt removal (fig. 11).

If the cleaning of the bole gilded area is constant over all 10 stages, in the second case, when the gold is over the painting layer, the rate of the removal process varies completely. This is attributed to the fact that the bole layer was completely dry when the gilding process occurred, which lead to a weak adherence of dirt, while the painting layer was not dry enough, which permitted the dirt to follow the texture of the layer, fact that ensured a better and differentiated adherence of the dirt. Figure 12 shows the colorimetric data of the two gilded areas, which allows the evaluation on the cleaning process effectiveness.

The C2 system turned out to be the one with the most efficient and non aggressive action, for the patina, the gilding for the cracked spots, on both gilded areas.
Conclusions
In order to clean the gilded surfaces of an icon with two different types of gilding, on bole (the halos) and on the painting layer (the garment of Saint Gregory), three synergic freshly made mixtures based on colorless supernatants obtained from vegetable extracts and dry herbs decoctions (CS) were used. Their efficiency was compared with the one of an alcohol based solution, low alkaline, with a few drops of 25% water ammonia solution.

By analyzing the washing effectiveness evolution chart over the 10 cycles, an almost constant variation of the cleaning rate of the halos, can be observed, while the evolution chart of the 10 cycles of the gilded area over the paint layer had a totally different removal rate evolution. This is attributed to the fact that the bole layer was completely dry when the gilding process occurred, which lead to a weak adherence of dirt, while the painting layer was not dry enough, which permitted the dirt to follow the texture of the layer, fact that ensured a better and differentiated adherence of the dirt.

By using visual analysis and CIEL*a*b* colorimetry for the two types of cleaned gilded areas, it was determined that the C2 system had the best results, ensuring a fast and efficient removal, without affecting the varnish, the gilded areas or the patina or causing cracks and exfoliations.

These types of ecological systems can be an optimal non aggressive cleaning alternative for gilded old wooden artifacts, and also safe for the restorer.

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