ECOLOGICAL CLEANING SYSTEMS FOR OLD ICONS PAINTED IN TEMPERA

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Abstract. Old icons, especially those involved in liturgical rituals are affected in time by external agents factors (temperature, humidity, light, pollution, microbiological attack, abrasion etc.), resulting changes of the appearance and of the structural integrity, dirt deposits, altered varnish and painting layer, cracks, material loss etc. In order to remove the dirt deposits, there are used cleaning systems with dry wiping, vacuuming, scraping, washing with organic solvents, ion exchange solutions, polyelectrolyte, surfactants, and so on, by enzymatic systems or by laser pyrolysis. The last two processes being considered aggressive and highly invasive, although they do clean very well adherent dirt deposits, which strongly degraded the varnish to total blackening (the iconographic image cannot be seen). Based on the literature in the field, regarding the nature of the materials used during the painting process and of the types and structures of the deposits, a series of alcoholic solutions of different concentrations were made, as such or basified, which were compared with ecologic synergic systems based on organic uncolored vegetable juices and decoctions from dried plants. The cleaning effectiveness was done by visual analysis and CIE L*a*b* reflection colorimetry, space proposed by the CIE (International Commission on Illumination) in 1976, was used. This technique permitting to determine by color deviations the critical point where the patina and polychromes layer.

Keywords: degraded varnish, deposits of dirt on tempera, wash tests, solvents, vegetable extracts, decoction of dried plants, CIE colorimetry reflection L*a*b*.

Introduction

To restore the aesthetics of an old icon, blackened in time and to improve the age patina "the golden halo" of an artifact [1-3] requires some cleaning procedures compatible and highly specific for adherent deposits. These operations consider a number of issues related to the value of the artifact, the age, the nature of the materials used in the making process, the effects of deterioration and degradation and the nature and aggressiveness of dirt deposits (loose, clogged - strongly adherent). These deposits lead to the darkened varnishes or bleaching of the paintings, along with the burns, blisters, varnish and paint layer warping, greatly affect the integrity and aesthetics, leading to their removal from the liturgical and museum circuit [4-6].

Cleaning dirt deposits includes dry physical and mechanical processes, wet physicochemical and enzymatic cleanings, or thermal processes by laser pyrolysis. The first group of methods is based on dust removal processes (vacuum), brushes, scraping (with knife), removal or dry polishing which is used for thick adherent deposits (wax, bitumen , paint and other fatty deposits accidentally splashed, or other type of contact etc.). The wet cleaning is applied frequently when using conventional washing solutions by using water or organic solvents in the form of a synergistic washing complex systems (emollients, surfactants or additives, surfactants, enzymes etc.) [7].

Lately, there have been increasingly studied the ecological systems based on uncolored fruit extracts and decoctions of dried herbs, freshly prepared [8-10]. The idea of using systems based on fresh colorless juices extracts (garlic, white onion, cabbage, zucchini, parsley, celery etc.) and decoctions of dried plants (corn silk, cobs containing alkali and furfural with moisturizing role, basil etc.) was often used in the past for cleaning carpets , upholstery and old icons blackened. In this regard, it was agreed a systematic reanalysis of them because they have a number of advantages related to the ecology of work (minimum aggression, high synergy, low cost, zero toxicity etc.).

Thus, the paper presents the results obtained by washing of old icons in tempera, using a series of synergistic natural systems based on extracts and decoctions. As a reference we used an aqueous solution based on alcohol, which was first optimized in relation to the old tempera painting, by varying the concentrations and slight alkalinisation or adding ammonia. For application, first wash test were performed on very small surfaces with representative degradation of the painting, with standard solutions, choosing the most effective formula. Then, wash tests were applied to systems based on natural extracts and decoctions. After every cleaning application processes the efficiency of cleaning was analyzed as well as the side effects on varnish and patina, using the visual and colorimetric analysis [11] by reflection CIE L * a * b *.

Experimental

The study is made on an icon of from XIXth century, from a private collection, representing the Three Hierarchs Basil, Gregory and John, made in tempera on lime wood, by an anonymous painter (Figure 1). The pigments used are colored earths blinded with egg yolk.

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Figure 1. Icon Three Holy Hierarchs Basil, Gregory and John (front/back).

By using visible reflectography, in UV and IR were observed on both the front and on the back a series of degradation and progressive deterioration, of the paint layer and of the wood panel from handling and careless or improper use or storage in unsuitable conditions, previously cleaned very aggressive, inappropriate, which led to the loss of varnish. Also other physical deterioration can be seen, cracking, wood plank separation, multiple and profound gaps in the paint layer, unevenness and small, recent hatch openings by borer insect attack (Figures 2 and 3).

Figure 2. Degradation of the paint layer and the substrate, no varnish on the right of the icon.

Regarding the dirt deposits, the paint layer were found adherent deposits, clogged are as on the golden cloak from the central area, yellowing and opacifying of the varnish, early micro fissures on the entire surface of the icon (Figures 1-3).

Figure 3. Cracks, separation, multiple and profound gap sin the paint layer to support wood nun even small.

Cleaning systems, washing tests

The washing tests were performed with cotton pads (100%) wound on wood sticks, soaked in solutions or mixtures of various solvents. For establishing the optimum cleaning standard system compatible with the old tempera painting, we studied the ability of washing small areas of homogeneous and uniform dirt, i.e. the same colors, with the following classical solutions based on ethanol or alkalinized:

E1 – aqueous 60% ethanol and 40% distilled water;
E2 – aqueous 70% ethanol and 30% distilled water;
E3 – aqueous 80% ethanol and 20% distilled water;
E4 – aqueous 90% ethanol and 10% distilled water;
E5 -100% absolute ethanol;
E6 - The aqueous solution obtained by mixing 6.5 mL distilled water with 2.8 mL ethanol and three drops of ammonia.

In order to achieve synergistic mixtures based on colorless vegetable extracts and of dried decoctions of fresh herbs prepared (which were previously selected and studied in [8-10]) were tested in the following washing systems:

S1 – 200 mL of 10g decoction of dried corn silk,
S2 – 10 mL juice zucchini,
S3 – 10 mL white onion juice,
S4 - 10 ml carrot juice,
S5 – 10 mL celery juice,
S6 – 10 mL cabbage juice,
S7 – 200 mL 10g decoction of dried basil,
S8 – 10 mL parsley juice,
S9 – 10 mL cucumber juice pulp (unshelled),
S10 – 10 mL broth Hustle wheat bran.

The extracts of succulent vegetables (pumpkin, white onion, carrot, cabbage and cucumber) were obtained by blending and then spinning them. The vegetables which are not so juicy (roots of parsley, celery) were finely milled and dispersed in distilled water in 1:1 weight ratio. Corn silk decoctions and dried basil were obtained by boiling 10 g of dry plant in 200 mL of distilled water for 5 minutes. From the corn silk only the cornhusk was used. Tests were conducted on very small areas, about 1cm^2, delimited and marked with special pencils Ceracoat type.

Evaluation of cleaning efficiency

The cleaning efficiency is highlighted by comparison system, by direct observation with a magnifying glass and by colorimetric CIE L*a*b* using a colorimeter LOVIBOND 300 Reflectance Tinctometer, by comparing the cleaned areas with alcoholic solution using the standard systems S1 - S10.

For graphical representation of colorimetric values of the samples analyzed the CIE L*a*b* space proposed by the CIE (International Commission on Illumination) in 1976, was used. The hue in this space (represented by basic colors: red, green, blue etc.), brightness or clarity (color ranging from black to white) and color (the color purity through its saturation, meaning its maximum brightness that appears for given added color), is analyzed on three axes: L*, a* and

b*. The axis 0X, noted a*, it represents chromatic variation from red to green (a* axis it refers to the chromatic red - a* > 0 and green - a* < 0), while b* represents the axis 0Y, the other two chromatic stimuli, yellow (b* > 0), and blue (b* < 0), and L* represents the axis 0Z, the brightness. This method of representation of color [11] by means of Cartesian coordinates is based on the consideration that no color can be red or green and yellow and blue at the same time (so it is assumed that there is a complementary red/green and blue/yellow). At the painting cleaning the basic principles of intervention were respected [12, 13], by testing the solutions on different types of deposits, and according to their state of preservation.

In this way, the colour parameters L*, a*, b*, h* as well as the colour differences ΔE [11-13] were determined.

The colour difference was computed with Eq.(1):

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b^2)]^{1/2} \quad (1)$$

where: Δ indicates the difference between the batch sample in the present case the tinctorial determinations as compared and a witness sample; ΔL represents the lightness difference (%) between batch and witness. If ΔL > 0, then the sample which reproduces (batch) is lighter than the witness; if ΔL < 0 the sample which reproduces (batch) is darker than the witness.

Results and discussion

After analyzing the conservation state of the icon the cleaning processes were done, initially by brushing and gentle aspiration, and then washing using various solvents, besides the usual and with some fruit juices and teas. For each system used, first a wash test was performed on a very small surface with painting representative degradation (Figure 4).

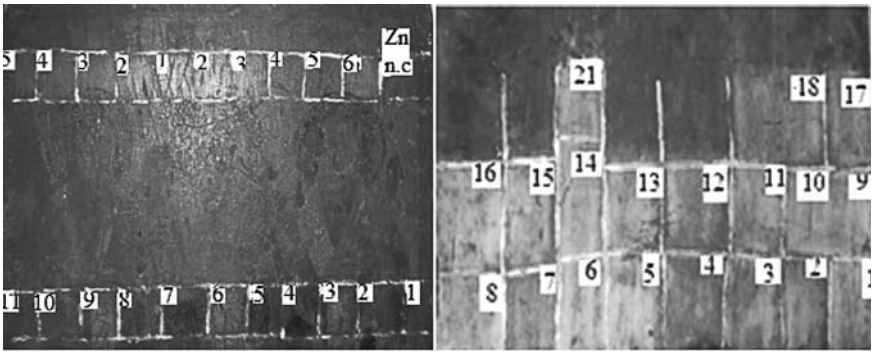

Figure 4. Washing tests (front /back) on small surfaces with aqueous alcoholic E1-E6 (top row), natural vegetable extracts and decoctions of herbs freshly prepared: S1-S10 (bottom row).

As mentioned, the wet cleaning operations, focused on two groups of systems:

-Five standard aqueous ethanol solutions (E1 - E5) with different concentrations from 60% to 100% (absolute ethylic alcohol) and the optimum solution E6 used later as a reference, which was obtained by basification with three drops of 25% aqueous ammonia solution E2 (70% ethanol solution).

-Seven uncolored vegetable extracts, two dried plants decoctions and a weak solution of lactic acid produced by the maceration wheat bran.

First of all the aqueous alcoholic solutions were tested, which are known in the literature for their cleaning properties on oil paintings but not on tempera. After each washing and after the surface was dried, the surface was inspected by direct visual observation or with a magnifying glass for increased comparing with the adjacent areas and that of the standard (E6), it was concluded that:

- E1 solution (60% ethanol) did not remove any adhering dirt, even in a greater period of time with 5 minutes.
- E2 solution (70% alcohol) removed easily greasy dirt and without affecting the varnish or age patina, in an emolliating time smaller than 2 minutes.
- E3 solution (alcohol 80%) permits removal of adhering dirt without affecting the varnish or patina, in an emolliating time of 3 minutes.
- E4 solution (90% ethanol) removed the less adherent in 4 minutes.
- E5 solution (100% ethanol) removed just the less adherent, in an emolliating time of 3 minutes.
- E6 standard solution removed all dirt adhesion, even the sturdy one and cleaning effect was better than other alcoholic solutions used without affecting the pigments, varnish and age patina.

It should be noted that no metal leaf was affected (Figures 5, a and b).

Figure 6 shows the reflectance colorimetry data obtained by the CIE L*a*b*on the six test areas with alcoholic solutions, confirming that the E4 solution (obtained by 80% E3 solution with ethanol, alkalizing it with three low drops of ammonia 25%) is the most effective, not affecting the varnish or age patina.

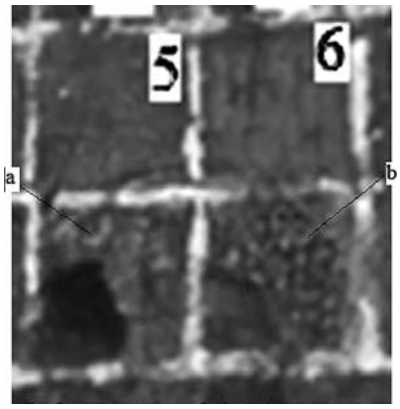

Figure 5. Details of areas cleaned using standard reference solution.

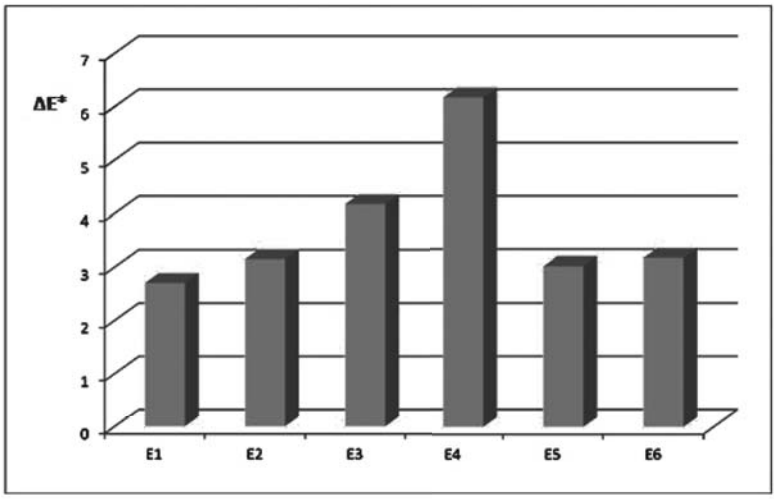

Figure 6. Colorimetric analysis CIE L*a*b* of the areas cleaned with alcoholic solutions E1-E6.

The cleaning efficiency of the ten natural systems was highlight ted by visual comparison with the standard clean areas and the good system efficiency was noted S3-S9 (Figure 7).

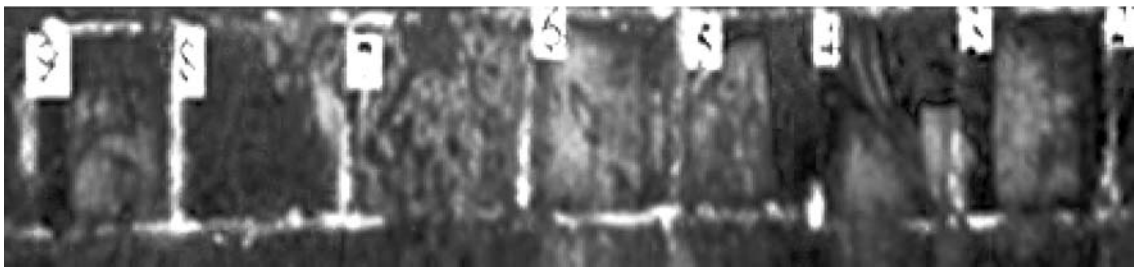

Figure 7. Details of the areas cleaned with natural extracts vegetables: S3-S9.

Figure 8 shows the reflectance data obtained by colorimetry CIE L*a*b* on the ten areas tested, washed with ecological systems, where it is clear that S6 - cabbage extract behaved most effective, then S3 system based on white onion extract, S4 - color less carrot extract, and S9 - cucumber juice gave a weaker result, and S7 -decoction of basil.

In the ecological systems - freshly prepared, used in the washing tests, is a very important observation to mention, about the behavior of these cleanings for a longer period of time and after second varnishing, is a subject for further research.

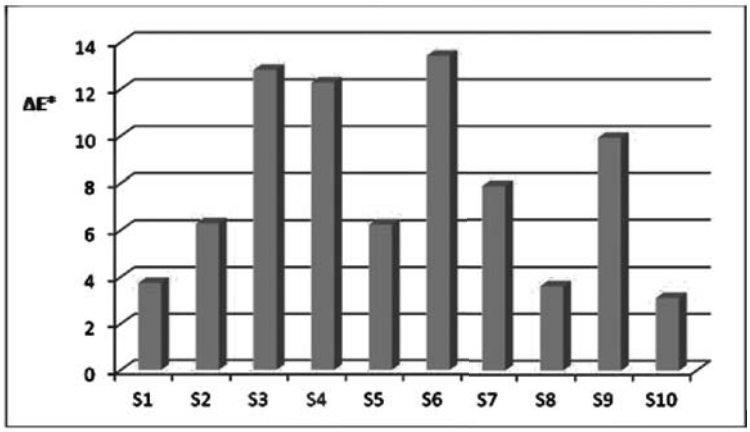

Figure 8. CIE L*a*b* colorimetric analysis of cleaned areas with ecological systems S1-S10.

Conclusions

To cleaning of the studied icons were used extracts of green plants and vegetables, dried herbs decoction that formed synergistic solutions, noted from S1 to S10 and a reference: the classical solution ethyl alcohol of various concentrations, or slightly alkalized E1 - E6. From the alcoholic solutions tested were chosen only the ones with effective cleaning on degraded varnish layer and deposits of dirt, which was alkalized with three drops of 25% ammonia (E6). Using visual analysis and the CIE colorimetric reflectance L*a*b* was observed that the best results were obtained with S6, S3, S4 and S9 systems, which provided: a quick and effective cleaning; paint layer, varnish and age patina were not affected; pigments have not changed color; detachments or flaking didn't occur.

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