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# **Research of new systems and procedures for cleaning old paintings**

**PHD THESIS SUMMARY**

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The doctoral thesis entitled "***Research of new systems and procedures for cleaning old paintings***" was elaborated on the basis of experimental data and studies on the diversification of physico-chemical processes and systems used for washing old patrimony paintings with deposits that affected the iconographic image, in order to capitalize them by reintroducing them into the museum circuit. In the substantiation of these studies was a complex critical analysis, on the basis of which was made a synthesis of the specialized literature regarding the current state of scientific research in the following fields:

- identification of pictorial materials and evaluation of their conservation status, along with the determination of the nature and structural characteristics involved in establishing the interactions with the substrate of unwanted deposits on the pictorial surfaces by involving modern methods of scientific investigation;
- selection of compatible cleaning systems for old paintings, which can be used in restoration practice, the study focusing on current materials and processes;
- methods and techniques involved in determining the effectiveness of cleaning interventions.

Also, in formulating the objectives and the issues addressed, it was taken into account the results obtained over time within our research team, especially at the "Alexandru Ioan Cuza" University of Iasi and the Evora University in Portugal.

**Chapter I. *Typology and structure of ancient paintings and evolutionary effects of deterioration of the physical state and degradation of the chemical nature of structural components***, a detailed presentation of the effects of deterioration and degradation, most often encountered in ancient paintings, is made, starting from the typology of these paintings, with a description of the structural components and materials involved in the commissioning, followed by the differentiated detailing of the results of the action of exogenous and endogenous factors on the structural-functional components and, respectively, on the existing materials, with the deepening of the aspects related to the deterioration and degradation of the icons on wood, from the simple forms to the complex evolutionary effects and the explicitness of the unfolding mechanisms.

**Chapter II**, according to the title ***Methods and techniques involved in the scientific investigation, preservation and restoration of old paintings***, takes into account the study of the scientific investigation of a painting by determining the characteristics of the artistic technique, the deterioration of the surface structures, the degradations of the surface structures, stratigraphic observations, the décor and reaching the current stage of the conservation state, these can be highlighted with the help of direct analysis what they mean without sampling (visual examination using magnifying glass, stereolupe and digital photofixing, UV, Vis and IR reflectography, reflectance transformation imaging (RTI), CIE L\*a\*b\* colorimetry, 3D scanning profilometry, X-

ray fluorescence, X-ray), as well as modern techniques of non-destructive and paradistructive analysis (microscopic type analysis on stratigraphic sections, optical microscopy by transmission, optical microscopy assisted by "staining tests", SEM-EDX, IR spectrophotometry, FT-IR and micro-FT-IR spectrophotometry, spectrophotometric analysis in UV-VIS, dynamic thermal analysis, PY-GC), finalizing with the preliminary investigation protocol, then proceeds to the elaboration of the methodology for applying the washing test, with the selection of areas with homogeneous polychromes and representative of old paintings.

**Chapter III** entitled *Evaluation of previous interventions of preservation-restoration and establishment of historical contexts in order to valorize a medieval church as a world heritage asset*, the Church of the Holy Archangels in Cicău, jud. Alba represents a historical monument whose age is lost in the mists of time, and the historiographical data record only two more important periods: the commissioning in 1495, with the realization of the interior frescoes and the transformations from the beginning of the XVIIIth century, with the exterior frescoes and the application of successive layers of lime.

Due to the way and attention paid to the preservation-restoration interventions, the monument represents a special case, with major damages brought both to the image of the church and to the way of approaching the safeguarding regarding the valorization of the national cultural heritage.

The modus operandi, in preserving frescoes by stopping the evolution of dynamic cracks and evolutionary gradients by encrusting, then in solving some finishes and marker elements in the masonry structures, there will remain samples of notoriety more close to vandalism than to carelessness.

The presence of a very interesting iconostasis (from a single massive slab, trovant type), of many aggressive interventions or left over time undefined and of much older polychrome layers, makes the monument to impose new scientific investigations, especially related to the authenticity of the artistic elements, cult and the technology of putting into operation.

Involving three modern analysis techniques, optical microscopy (MO), electronic scanning microscopy coupled with X-ray spectrometry (SEM-EDX) and differential thermal derivatography (TG, DTA and DTG), it was possible to confirm the year 1781 and the periods of application of the lime layer (with two purposes, of covering the outdoor frescoes in the reformed period and of periodic igenization, after certain periods of decay of the state of preservation. If by optical and electronic microscopy it was highlighted the state of preservation of the painting and finishing

materials taken into the study, from the elemental analysis data and, respectively, from the evolution of the two important characteristics (TG-% and DTG-%/min), a number of archaeometric (carbonation rate) and chemometric (difference in elemental concentration in C%w, evaluated by the formula  $\Delta C\% = C_{(i+1)} - C_{(i)}$ ), on the basis of which the periods of application of lime layers were determined. Thus, starting from the year of painting the outdoor fresco 1781 and by involving the two groups of chemometric and archaeometric characteristics, the following approximation was achieved: the first layer of lime was applied in ~1792, the second in ~1812, the third in ~1862, the fourth ~1912, and the fifth in ~1977, being a good framing for a period of 220 years.

**Chapter IV. *New ecological solutions with implications in the cleaning of a XIX century icon***, the evaluation of the washing efficiency of the aqueous extracts from st. John's wort powders, sage and licorice obtained in the four conditions (boiling, microwave, ultrasound and at room temperature) is presented on the icon made in fatty tempera, was made by CIE L\*a\*b\* colorimetry. Measurements of surfaces cleaned with natural extracts revealed the following:

- The sage supernatant obtained by ultrasonication proved to be the most effective (almost double compared to the one obtained with microwaves).
- The licorice supernatant with the active principles in the highest concentration was obtained for licorice in ultrasonication conditions, and the lowest for microwave sage.
- The supernatant of St. John's wort through its active components, extracted by ultrasonication and boiling allow a good softening, as well as washing.
- For all supernatants ultrasonication followed by boiling and under normal conditions is more effective than those with microwave extracts.

**Chapter V, entitled *Authentication and establishment of the patrimonial value of an interior fresco in order to change the iconographic system by elimination and repainting***, based on the expertise data regarding the authentication, the establishment of the state of conservation and the evaluation of the patrimonial characteristics/elements and of the patrimonial functions of the fresco from the "St. Spiridon" Church in the locality of Tiganași, jud, Iasi, for approval, by the Ministry of Culture and Cults, of preservation, with the professional restoration or its total elimination and repainting, the following conclusions are drawn:

- the fresco is relatively recent (29 years old), being made by a painter without a certificate of free practice approved by the Patriarchate of Romanian;

- the state of preservation in most iconographic registers is poor, with irreversible deterioration and degradation, some of which are already in precolaps;
- artistic technique is naïve, and the author used incompatible materials, some without artistic value for Orthodox iconography;
- the fresco has no artistic, cultural and historical value, which is why it must be replaced by a one made by a church painter authorized for heritage monuments, class A and B (level at which the edifice is classified as an architectural and historical system with an age of over 200 years), in order to improve the monumental value of the church settlement in order to raise the visibility of the community and to introduce the monument in the tourist circuit.

**Chapter VI. *Composition and process of wet cleaning of old paintings and varnish on a wooden support***, it is presented the elaboration and description of an invention regarding a composition and methodology for cleaning the polychrome artifacts and old varnish for the removal of semi-adherent or adherent superficial deposits, which affect aesthetics, the old patina, the washes, the layers of painting and the varnish. The process aims at valuing by reintroducing artifacts into the museum circuit. He went through two main directions in experiments: the assessment of the resistance to accelerated aging of some aqueous supernatants, obtained from dried medicinal teas from spontaneous flora and juices from mature native vegetable and fruit roots (applied in a thin layer on neutral and polychrome surfaces) and the optimization of recipes for cleaning dirt and other undesirable deposits on polychrome surfaces, using polynar compositions from the studied supernatants, gradually going from the dinar systems to those with more than five components.

Use an aqueous mixture of clear, freshly prepared supernatants from soap teas, basil, corn silk and chamomile, respectively from celery, parsley and horseradish juices mixed in a volumetric ratio of 1:1:1:1:2:2:2:2, which after stabilization is applied gradually on small areas from 1,0 to 4,0 cm<sup>2</sup>, by wiping with cotton wool sticks soaked in this mixture diluted with distilled water in a volumetric ratio of 1:1. Before starting the cleaning operation, prepare the seven clear supernatants from four dried herbal teas and three mature root juices, which were centrifuged, the first with 15,000 rpm and the others with 18,000 rpm, and after separation by decanting they were mixed gently, and then after stabilization they were diluted in a volumetric ratio of 1:1 with double distilled water. Also, before proceeding to the cleaning operation, depending on the size of the

surface, the chemical and physico-structural characteristics of the polychrome and dirt, a series of systems are prepared separately: for watering / softening, wiping / washing, devernising / revernising, with the first ones, the washing test is initially performed, and after establishing the stages and working times, the actual cleaning is passed. After removing the traces of supernatants, the cleaned surface dries, removes degraded vernisurilr and revernises. Finally, the behavior of the cleaning intervention will be monitored for a period of 6 months to one year, at intervals of 7 days, when it is studied by visual, colorimetric (CIE L\*a\*b\*), profilometric and reflective analyses in UV, vision and IR.

**Capitolul VII. *Impactul tratametului insetofugic a petrolului roșu de câmpeni la o icoană de sec. XVIII***, prin coroborarea tehnicilor OM, SEM-EDX, micro-FTIR și CIEL\*a\*b\* s-a studiat impactul tratamentului cu petrol roșu asupra lemnului policrom afectat de atacul xilofagic. Prin analiza OM și SEM s-a identificat specia insectei xilofage care a atacat suportul, precum și scăderea porozității lemnului în urma tratamentului.

**Chapter VII. *The impact of the insetofugic treatment of red field oil at an XVIII century icon***, by corroborating the techniques OM, SEM-EDX, micro-FTIR and CIEL\*a\*b\* was studied the impact of red oil treatment on polychrome wood affected by xylophage attack. The human and SEM analysis identified the species of the xylophagous insect that attacked the support, as well as the decrease in the porosity of the wood following the treatment.

From the EDX analysis, the retention of oil in wood was highlighted by increasing the concentration in C and O and by the presence of Fe. The micro-FTIR analysis confirms the penetration of the active principles of red oil through its characteristic peaks found in treated wood in the three fields:  $2850-2960\text{cm}^{-1}$ ,  $1350-1500\text{cm}^{-1}$  și  $950-600\text{cm}^{-1}$ . The CIEL\*a\*b\* analysis determined the chromatic deviation following the treatment, which proved to be insignificant for the human eye. Following the treatment, there was an increase in the conservationability of the wood by improving the wood fiber and the poor change in the color of the support that gives it a patina look.