The first operation in preservation and restoration of patrimony objects of painted wood, which present detachments of painting layer, is the preventive consolidation. This operation is followed by the definitive consolidation and the primary biocide. The present study focuses on the adaptability of the acrylic binder in the consolidation of damaged painting layer of an icon which is in collapse. The analyses were made using the following techniques: OM, SEM-EDX and CIE L*a*b* colorimetry. For this experiment there were used 5 painted wood samples from the icon under study. Two of them were coated by brush, with and without Japanese paper with an acrylic binder, and the other two with isinglass (used frequently as a traditional binder). A sample from the damaged icon was kept and compared with the other samples presented above.

For the calculation of the aging factor through thermo-oxidative was used the Arrhenius equation. The samples were kept for 12h at a temperature of 115°C, which is equivalent to aging at 20°C for one year. According to the colorimetric analysis, the best results were obtained on the coating samples with acrylic binder, without Japanese paper, and the intensity of the colour was modified with less than one unit, compared to the values recorded by the other samples.

Keywords: consolidation, collapse state conservation, painted wood, acrylic binder, isinglass, artificial aging, OM, SEM-EDX, CIE L*a*b* colorimetry.

Experimental part

Materials and methods

The experiments were performed on five old wood samples (3.5x3x2cm), taken from an icon painted in tempera with gesso, in collapse, from a personal collection (fig. 1). These samples were taken from different areas (fig. 2) that had a powdery pictural layer or partial detachments. Two samples, one with Japanese paper and the other without, were consolidated by applying with brush isinglass in distilled water. Other two samples were consolidated through brushing with a commercially available, reversible acrylic Binder [22]. In similar way, at a sample it was used Japanese paper and the other was applied with the brush the binder directly on the surface. Those four samples were subject to artificial aging through controlled heating in an oven with thermoregulation at 115°C, for 12 h, the equivalent of natural aging by one year, at normal temperature. Comparative, it has been used as a witness a fifth unconsolidated sample, which comes from the same area of the icon (fig. 2).

The analysis of pigments was studied using an optical microscope Zeiss Imager A1m, which has a camera attached AXIOCAM and specialized software. In addition, optical microscopy was used to evaluate certain aspects of the consolidation of the pictural layer of an icon which is in collapse, using isinglass and acrylic binder, by comparison to unconsolidated sample, using OM, SEM-EDX, artificial aging and CIE L*a*b* colorimetry.
of colour changes before and after the consolidation treatment of the paint layer.

The analysis have been made using a scanning electron microscope, type SEM VEGA II LSH, made by Czech TESCAN, coupled with EDX detector type QUANTAX QX2, made by BRUKER/ROENTEC, Germany. The microscope connected to a computer, has a tungsten electron filament, which can reach a resolution of 3nM to 30kV, with 30x zoom and a million X, accelerating voltage 200V to 30kV, scanning speed 200ns to 10ms for each pixel. Pressure is lower with 1x10-2 Pa. The resulted image can be formed with secondary electrons (SE) and retro diffusion electrons (ESB). QX2 QUANTAX is an EDX detector used for the quality and quantity of the micro-analysis.

The evaluation of discoloration was performed using LOVIBOND RT 300 (Reflectance Tintometer) spectrophotometer. This allowed the registration of each stage of chromatic deterioration, directly on the sample, before and after consolidation, through the CIE L*a*b* system. The obtained data was then transferred to the computer and processed, allowing a background to the discussions and conclusions on the results of investigations.

All the five curves of graphics were statistically processed through Microsoft Excel, using the method of Regression analysis, which allows the positioning of the tendency line, whose characteristics are presented in the top of each graphic.

The moisture degree of painted wood samples was measured with the help of a digital moisture device, Profi Scale DRY PS 7400.

**Results and discussions**

Initial, was studied the nature of the painting materials (pigments and binders), on the base on chemical composition EDX, the form, morphology and layout of chemical components in the pictural layer using OM and SEM.

In figure 3 we have the microphotogram OM of a representative area for the first four samples consolidated with binders used in this study, according to the experimental protocol presented above and which were analysed further and through the SEM-EDX method and CIE L*a*b* colorimetry. The witness sample (the fifth) was used only for CIE L*a*b* colorimetry after artificial aging.

From the microphotographs of those four consolidated samples (fig. 3), we can observe that the pictural layer is very fragile through the aging of the binder and blackened with dirt clogged. Chromatic deviations of the pigments is due to film of soot and tars deposit on the surface of painting. The elemental composition has been realized for the entire surface of SEM microphotograms (fig. 4).
Fig. 4. EDX spectra with microphotographs of the analyzed surfaces: 
a – sample 1, 
b – sample 2, 
c – sample 3, 
d – sample 4
Compositional data given in table 2 enables the determination of the chemical nature of the main pigments used in the icon. High presence of carbon and oxygen is attributed to the egg binder, dirt from burning candles and lamps, but also from carbonates, sulphates, phosphates, oxides and chemically bound water such as acquis-complex and hydro-complex crystalohydrates.

Thus, the following pigments have been identified:
- white lead: \(2\text{PbCO}_3\cdot\text{Pb(OH)}_2\), litharge (\(\text{PbO}\)) in samples 2 and 4.
- gilding with gold leaf, containing silver in the frame in sample 2;
- Green, obtained by mixing ultramarine blue (\(3\text{Na}_2\text{O}·3\text{Al}_2\text{O}_3·6\text{SiO}_2·3\text{Na}_2\text{S}\)) in samples 1, 2 and 3;
- brown, a mixture of red earth (\(\text{Na}_7\text{Al}_6\text{Si}_6\text{S}_2\text{O}_{24}\)) with ivory black (\(\text{C}\)) in samples 1, 2 and 3.
- yellow based on litharge or massicot (\(\text{PbO}\)) with grey earth with low content of \(\text{Fe}\) in samples 2 and 4.
- chalk (\(\text{CaCO}_3\)) and traces of silicates of atmospheric dust in sample 4.

Ivory black (\(\text{C}\)) used for the shadows and frame, can be found in all five samples overlapping tar and grease deposits. The presence of aluminium and silicates from atmospheric dust and carbon from low concentration deposits that are still noticed by the EDX, show that paint layers are affected by adherent deposits with which have interacted.

In the moment of brushing the film Binder, the colour was white, but after drying 30 min, it became colourless, and the isinglass which was initially translucent, after drying became colourless. On the sample one it was observed the formation of a little glossy film which increases the colour. In all cases, through consolidation, the detachments adhered very well to the support.

The four consolidated samples, along with the reference one, were introduced in an artificial aging room. The moisture of the wood measured at one millimeter under the preparation layer, before the consolidant was applied, was 0.6%.

For the calculation of the aging factor through thermo-oxidation, it was used the equation of Arrhenius: 
\[
\text{AAF} = \frac{Q}{10} \left(\frac{T_{\text{AA}} - T_{\text{RT}}}{10}\right) 
\]
where: 
- \(\text{AAF}\) is the aging factor in percent,
- \(Q\) is the rate of activation,
- \(T_{\text{AA}}\) is the artificial aging temperature,
- \(T_{\text{RT}}\) is the reference temperature.

\(\Delta t\) is the time of accelerated aging calculated by dividing the 12 h time (the duration of artificial aging) to AAF factor [23-25].

Chromatic modification resulting after artificial aging has been determined through CIE \(L^*a^*b^*\) colorimetry method, by reading the \(L^*a^*b^*\) values and the evaluation of DE from 3 to 3 h, an hour being equal to one month aging. At the end of artificial aging, the moisture of the wood measured in the same point with the initial one, was 0.6%.

Chromatic deviation was evaluated in the coordinates \(L^*\) a* and b*, in relation to the initial value for the same sample and in the same point (table 3).

The colour change was calculated for each colour coordinate (\(L^*, a^*\) and \(b^*\)) as related to its initial value on the same panel and in the same point. Finally, the total colour change (\(\Delta E^*\)) was calculated in each point, according to equation [26-31]:

\[
\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}
\]

where: 
- \(\Delta L^*\) is the luminosity change in the respective point after brushing the consolidantes and at different time intervals, until one year, comparative to initial value:
- \(\Delta a^*\) is the change of the red-green coordinate in the respective point consolidation of samples and at different time intervals, until one year (equivalent with 12 h by artificial aging), compared to initial value:
- \(\Delta b^*\) is the change of the yellow-blue coordinate in the respective point consolidation of samples and at different time intervals, until one year, compared to initial value:
The equation has the following form $y = ax + b$, where $b$ indicates the value of $y$ when $x = 0$ and $a$ is the regression coefficient. $R^2$, which appears on the graphics, is called determination coefficient, indicating the percentage from the dependent variable ($y$) estimated by explicative variable ($x$), through subsequent equation of regression. The more $R^2$ is closer to 1, the more the correlation between the two variables is higher [32, 33].

As we can see from figure 5, $\Delta E^*$ variations of sample one, consolidated through brushing with acrylic binder without japanese paper, at three hours (the equivalent of 3 months artificial aging), grew with 1.3 units, following that from 6 to 12 h, the colour to stabilize itself, until 0.46 units. For this sample, chromatic deviation is insignificant, her stability being confirmed also by the tendency line. Compared to the witness sample, sample one has intensified her hue with 0.45 units.

For sample two, consolidated through brushing with isinglass, without japanese paper, $\Delta E^*$ variations are oscillating. Chromatic deviation grows at three hours by one unit, at six hours grows with half unit, following at nine hours to drop by one unit and at twelve hours the growth starts resuming. Although the $\Delta E^*$ variations are insignificant, because they do not exceed two units, the tendency line shows us that chromatic deviation is growing. Comparative with the witness sample, the sample two suffers a chromatic deviation by 0.37 units.

$\Delta E^*$ variations for sample four, consolidated with japanese paper, were slightly decreasing. Chromatic deviation until 6 h grows by 1.70 units and then decreases in an insignificant way in the following 6 hours (6 months). Although we can observe slight decreases of the $\Delta E^*$ variations, which are insignificant, the tendency line shows us that chromatic deviation is growing. Comparative with $\Delta E^*$ variation at twelve hours of witness sample, sample four registered an intensification of the colour by 0.24 units.

For sample five, chromatic deviation is slightly increasing. An accentuated increase, by 2.14 units, can be
noticed at six hours of artificial aging. After twelve hours of artificial aging, chromatic deviation decreases until 1.39 units. The tendency line indicates a slight increase.

**Conclusions**

Applying the acrylic binder on wood painted samples, through brushing with Japanese paper, was carried out harder than without Japanese paper. In both cases of consolidation, with acrylic binder and isinglass – with or without Japanese paper - the detachments adhered to the support. The behaviour of the two types of consolidation has been analyzed colorimetrically during the gradual process of artificial aging from three to three hours, for twelve hours, equivalent to natural aging of one year, in normal conditions. All those four samples, consolidated with acrylic binder and isinglass, have not altered the physical aspect after artificial aging.

According to the colorimetric analyses, the obtained results on consolidated samples with isinglass in distilled water 5%, had an lesser chromatic deviation at sample four (with Japanese paper), comparative with sample three ($\Delta E^* = 1.74$). This confirms that through brushing without Japanese paper, it creates a film which intensifies the colour, in the absence of the Japanese paper.

Regarding the consolidation of the samples with acrylic binder, a smaller variation has been obtained on sample one, consolidated without Japanese paper ($\Delta E^* = 0.46$), comparative to sample two with Japanese paper ($\Delta E^* = 1.84$).

All the $\Delta E^*$ colorimetric variations registered after artificial aging by one year, at a temperature of 115°C, are under two units and they are insignificant for the modification of colours. The best results were obtained on the brushed sample with acrylic binder, without Japanese paper, the intensity of the colour modifying by less than half a unit ($\Delta E^* = 0.46$), comparative to the values registered on the other samples and the witness sample ($\Delta E^* = 1.39$), in conclusion, the acrylic binder can be used in preservation-restoration, offering better results than natural-organic binders.

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