Study Concerning the Influence of Acrylic Consolidating Agents on Gold Gilding and Schlagmetal

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*The first intervention realized in the case of art works with a precarious state of conservation is the consolidation of support and superficial layer. Generally for the puzzle-like painting layer the preventive consolidation is an urgent intervention, which will be followed, after a succession of interventions, by a definitive one. Furthermore, if the polychrome layer is pulverous, the binder will be applied over the entire degraded surface. In both of cases, the binder can damage the polychromy and gildings. For this purpose, this paper studies the influence of acrylic binders upon gildings with gold leaf and schlagmetal, respectively the manner in which these binders are applied and the effects they have upon them. For the experiments there were used samples of fir tree gilded with gold or schlagmetal or other imitative products that are on the market. After gilding the samples were coated with acrylic binders and put in the oven, for artificial ageing. The analysis were realized with optical microscope, SEM-EDX and spectrophotometer in CIE L*a*b* system.*

*Keywords: gilding, schlagmetal, acrylic adhesive Binder, artificial aging, SEM-EDX, CIE L*a*b* colorimetry*

The glitter of gold has fascinated men from ancient times. The conservation of gildings in time has led to the creation of art works with priceless value [1, 2]. The ecclesial cultural heritage comprises polychrome sculptures, icons or laic paintings gilded with metal leaves made of silver or gold [3-7]. The technological development allowed the manufacture of imitations of these noble metal leaves, and also the production of new materials for the modern paintings. Because these products have reduced the costs of gilding, they are used nowadays in preservation-restoration besides schlagmetal [5, 7-8].

The schlagmetal leaf (alloy made of copper and zinc) is used on a broad scale to decorate new art objects and redecorate old ones, being much easier to handle due to its thicknes [5, 6]. The gilding with oil based adhesives was adapted to schlagmetal and to various pigments used for gilding [5, 9-12]. Therefore, one of the modern materials used for schlagmetal gilding was mixtion, which is a viscous lake, based on linseed oil, massicot (PbO) and turpentine [5, 13-16].

Because gildings have a stratified structure, in which the metal leaf or the powder (pigment) must be compatible with the contact components, their behaviour in time is studied through artificial ageing processes. Therefore, these structures are exposed to extreme climatic conditions which lead to the alteration and microstructural destruction of component materials, whose evolution can be determined by means of certain chemometric characteristics [17, 18].

Depending on the material (organic or inorganic) the artificial ageing is made in ovens, at temperatures between 60 -110°C, in humid atmosphere (85-99% RH) or by exposure to UV radiations, for short periods, equivalent to long periods of time. The thermal procedures are more moderate and their effects can be remedied. At high temperatures processes of dehydration take place, which lead to structural changes. Also, redox, acid-base, and complexion reactions occur in the presence of oxygen from air at interfaces, depending on the type of component materials [17, 18].

This paper presents the behaviour of different commercial imitations of gold leaf, applied with acrylic Binder [19-20] on fir tree wood, at artificial ageing. They are compared to gold leaf.

Experimental part

In experiment there were used six samples of fir tree wood (20x20x30 mm), which were initially coated with a few layers of white ground. After drying the ground was finished with small grit sandpaper. In the case of Sample 1 (reference), mixtion with a drying time of 15'was applied by brush on the ground layer, after which immediately the gold leaf was spread on the surface. Sample 2 was gilded with schlagmetal produced by Maimeri, on the same type of mixtion as it was used for Sample 1. On Sample 3 was gilded with a imitation of gold powder (Treasure Gold, made by Renaissance Herts WD7 S.A) spread on the surface of the samples with fingers. A concentrated liquid dispersion, Dorure Liquide, produced by Lefranc & Bourgeois was brushed on Sample 4.

For Samples 5 and 6 it was used a mixture of different powders combined with Medium per bronzi solventi, made by Masserini S.R.L., ratio 1:1 in volumetric proportions. For Sample 5 the powder used was Bronzo in polvere made by Masserini S.R.L., while for Sample 6 it was used Doratura Tixe, produced by Cristoforo Tixe D'Arenzano S.R.L. After the mixtion cured under the metal leaf , half of each sample was brushed with a thin layer of water - based acrylic Binder, produced by Maimeri [6, 7], as a protection film, while the other half was not coated, being used as a reference.

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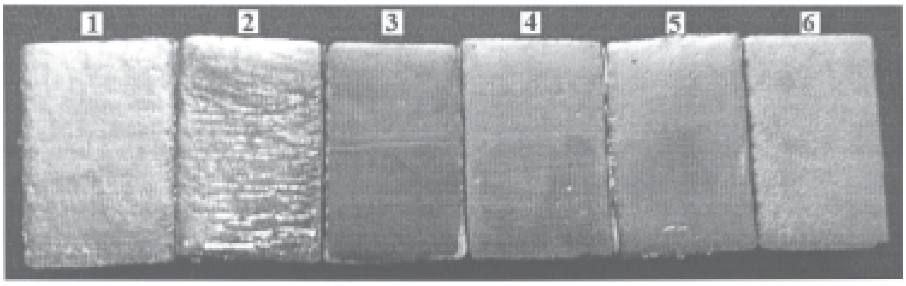

Fig. 1. The samples before aging engineering

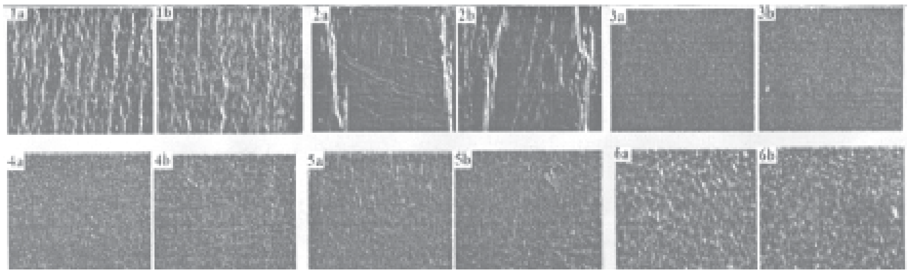

Fig. 2. The OM microphotographs of the samples: 1- Gold leaf, 2 –Schlagmetal, 3 – Treasure Gold, 4 – Dorure Liquide, 5 – Bronzo in polvere, 6 – Doratura Tixe, where a – the simple area and b – area with binder

After the acrylic binder dried, all the samples (fig. 1) were analyzed by means of colorimetry, and exposed to artificial ageing in a thermoregulator oven type Air Concept (FIRLABO), for 53h at 80°C (which is the equivalent of 4 months of natural ageing, at a temperature of 22°C). The colorimetric analysis of the samples was realized after 24, 48 and 53h of artificial ageing.

The samples surfaces were analyzed using a reflection microscope CARL ZEISS AXIO IMAGER A1m, with attached camera AXIOCAM and the elemental composition of the metal sheet and a imitation of gold leaf with a SEM -EDX, model VEGA II LSH, made by TESCAN Czech Republic, coupled with an X-ray spectrometer QUANTAX QX2, produced by BRULER/PROENTEC 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.

For calculation of the artificial aging factor through thermo-oxidative was used the Arrhenius equation: AAF = $Q_{10}^{[(T_{AA}-T_{RT})/10]}$. The accelerated aging time was done by dividing the desired time to the AAF factor [21].

The color changes were analyzed at 24h, 48h and 53h with a spectrophotometer LOVIBOND RT 300 (Reflectance Tintometer) spectrophotometer. The color change was calculated for each color coordinate (L*, a* and b*) as related to its initial value on the same sample and the same point. Finally, the total color change (ΔE*) was calculated in each point, according to [22-30], by equation:

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

where: ΔL* is the luminosity change in the respective point at different time intervals, by artificial aging, comparative to initial value:

$$\Delta L^* = L^*_{s.aged} - L^*_{initial}$$

Δa* is the change of the red-green coordinate in the respective point and at different time intervals by artificial aging, compared to initial value:

$$\Delta a^* = a^*_{s.aged} - a^*_{initial}$$

Δb* is the change of the yellow-blue coordinate in the respective point and at different time intervals, by artificial aging, compared to initial value:

$$\Delta b^* = b^*_{s.aged} - b^*_{initial}$$

s.aged – samples aged and initial – initial samples.

This allowed the registration of each stage of chromatic deterioration, directly on the sample, before and after brushing with acrylic Binder, 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 six 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 [31-32].

Results and discussions

In figure 1 it can be observed that the acrylic binder reduces the colour intensity for Sample 3 (Treasure Gold) and Sample 4 (Dorure Liquide). Using OM and SEM we studied the evolution of coatings morphology, of the chemical composition EDX and of the structure of metal sheet and imitations components after artificial ageing.

In figure 2 is presented the microscopic image (OM) for the six gilded samples, by comparison of the two areas (a - without acrylic binder and b - with acrylic binder).

The analysis by means of optic microscopy reveals a small change of colour and morphology of the samples' surfaces without acrylic binder (a) compared to the areas coated with acrylic binder (b).

In figure 3 is presented the SEM microphotographs of the six samples based on which the EDX spectra were obtained and the elemental compositions were evaluated.

From these microphotographs we can observe that the six samples have different morphologies and arrangements of structural components. From a morphological point of view, Sample 4 (Dorure Liquide) and Sample 6 (Dorature Tixe) present a certain resemblance.

The elemental composition EDX (table 1) reveals the fact that the most part of the studied gildings contain Zn, Cu, C and O, an exception being the Sample 3 (Treasure Gold) and Sample 4 (Dorure liquide), which also have Al in small quantities. None of these products made for gilding contains gold.

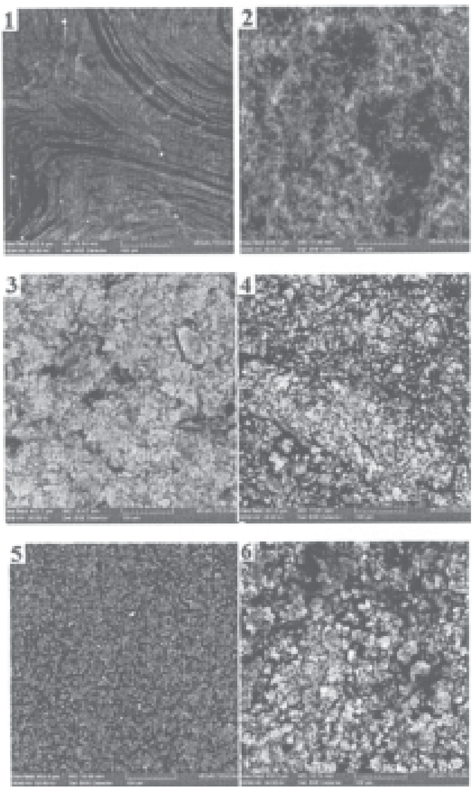

Fig. 3. The EDX microphotographs of the six samples (BSE 500X): 1- Gold leaf, **2** –Schlagmetal, **3** – Treasure Gold, **4** – Dorure Liquide, **5** – Bronzo in polvere oro, **6** – Doratura Tixe

Table 2 presents the colorimetric data in CIEL*a*b* system for all the 6 samples used in this experiment, made at every 24 h during the artificial ageing, with the exception of the last measurement, which was done after 5 hours, period imposed by the artificial ageing equivalent.

The ΔE* values can be seen in the following graphics in which it was pointed out the chromatic deviations. The results were used to obtain evolution graphics (fig. 4), to compare the chromatic changes for both areas of each sample (a – without binder, b – with binder), during exposure to artificial ageing.

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 [31-32].

We can ascertain that the gold leaf ages slowly and resists more in time. After thermo-oxidation ageing at 80°C, for 53 hours, we can observe that the chromatic deviation of gold leaf (fig. 4a) is insignificant for both areas, the registered values being smaller than 2 units. From this it can be concluded that the acrylic binder brushed on the gold leaf changes the gold hue. For Sample 2, with schlagmetal (fig. 4b), the ageing is very fast, after 53 h the chromatic deviation increasing to 20.53 units. It was interesting to notice that the area with acrylic binder coating has a chromatic deviation 4 units lower than the area without binder. The tendency lines for both areas of the sample are ascending.

Sample 3, with Treasure Gold suffered a chromatic deviation of 29.03 units on the original area, whilst on the area coated with acrylic binder, the chromatic change is 3 times smaller than the uncoated half (8.40 units). Sample 4 with Dorure liquid suffers a chromatic deviation smaller than 5.51 units, on the surface without acrylic binder, and on the half with binder the chromatic change increases up to 8.43 units. Sample 5 suffers a less significant chromatic change, of 2.77 units on the area without acrylic binder, the coated half recording a value with 2 units higher. On Sample 6 the chromatic deviation was 2.50 units on both areas, coated or uncoated with binder.

From the six graphics it appears that, after 53 h of artificial ageing by means of thermo-oxidation at 80°C, from the gold imitations samples, the smallest change (2.49 units) occurs in Sample 6, with Doratura Tixe. The highest chromatic deviations can be observed in Sample 3, with Treasure Gold (29.03 units) and sample 2, with schlagmetal (20.53 units).

In reference to the areas coated with acrylic binder, the highest colorimetric variations were recorded in Samples 2, with schlagmetal (16.60 units). The smallest variations were presented by Sample 1, with gold leaf, and, from the gold imitations, by Sample 6, with Doratura Tixe, 2.58 units.

Table 1
ELEMENTAL COMPOSITION OF LEAF GOLD, SCHLAGMETAL AND IMITATIONS OF GOLD

Sample	Elemental composition in weight percent (%)						
	Au	Ag	Cu	Zn	Al	C	O
1 Gold leaf	89.876	6.835	3.287	-	-	-	-
2 Schlag-metal	-	-	80.131	12.868	-	-	7.000
3 Treasure Gold	-	-	62.540	13.122	0.828	10.594	12.913
4 Dorure liquide	-	-	53.152	11.639	0.861	14.067	20.278
5 Bronzo in polvere oro	-	-	68.015	18.966	-	3.752	9.265
6 Dorature Tixe	-	-	61.756	8.902	-	19.054	10.285

Table 2
THE VARIATIONS CIE L*A*B* OF SIX SAMPLES DURING ARTIFICIAL AGING

Sample	CIE L*a*b*	Initial: Area without Binder	Initial: Area with Binder	24h: Area without Binder	24h: Area with Binder	48h: Area without Binder	48h: Area with Binder	53h: Area without Binder	53h: Area with Binder
1	L*	96.01	91.21	94.0	91.25	93.79	91.06	93.77	91.17
Gold leaf	a*	+5.58	+7.09	+5.67	+7.22	+5.84	+7.21	+6.01	+7.31
	b*	+37.0	41.78	+36.75	+42.08	+37.35	+42.21	+37.36	+42.17
2	L*	96.91	92.08	93.59	85.42	88.51	79.34	87.43	77.05
Schlagmetal	a*	+5.9	+7.81	+7.76	+11.25	+12.12	+13.46	+13.31	+13.89
	b*	+28.46	+30.78	+32.9	+36.41	+38.42	+41.87	+39.98	+43.37
3	L*	69.64	70.62	67.19	69.43	63.33	68.55	62.70	69.03
Treasure	a*	+12.39	+11.55	+14.63	+11.75	+16.19	+11.9	+16.49	+11.9
Gold	b*	+36.94	+37.48	+40.62	+38.69	+40.01	+38.81	+39.3	+38.5
4	L*	77.71	77.28	75.06	74.14	73.61	72.42	73.66	73.86
Dorure	a*	+9.6	+7.41	+10.99	+8.64	+11.93	+8.76	+12.27	+8.96
liquide	b*	+42.14	+36.11	+45.84	+39.73	+48.09	+39.60	+49.04	+40.14
5	L*	82.07	81.09	78.65	80.53	76.41	79,6	77.09	79.48
Bronzo in	a*	+6.31	+6.17	+7.19	+6.89	+7.45	+7.18	+7.28	+7.27
polvere oro	b*	+33.7	+33.81	+35.79	+35.29	+35.77	+35.74	+35.92	+35.78
6	L*	79.54	80.24	80.46	80.22	80.08	79.89	80.22	79.75
Dorature	a*	+10.51	+10.85	+11.19	+11.37	+11.23	+11.56	+11.28	+11.62
Tixe	b*	+30.44	+32.03	+32.53	+33.73	+32.66	+34.17	+32.81	+34.35

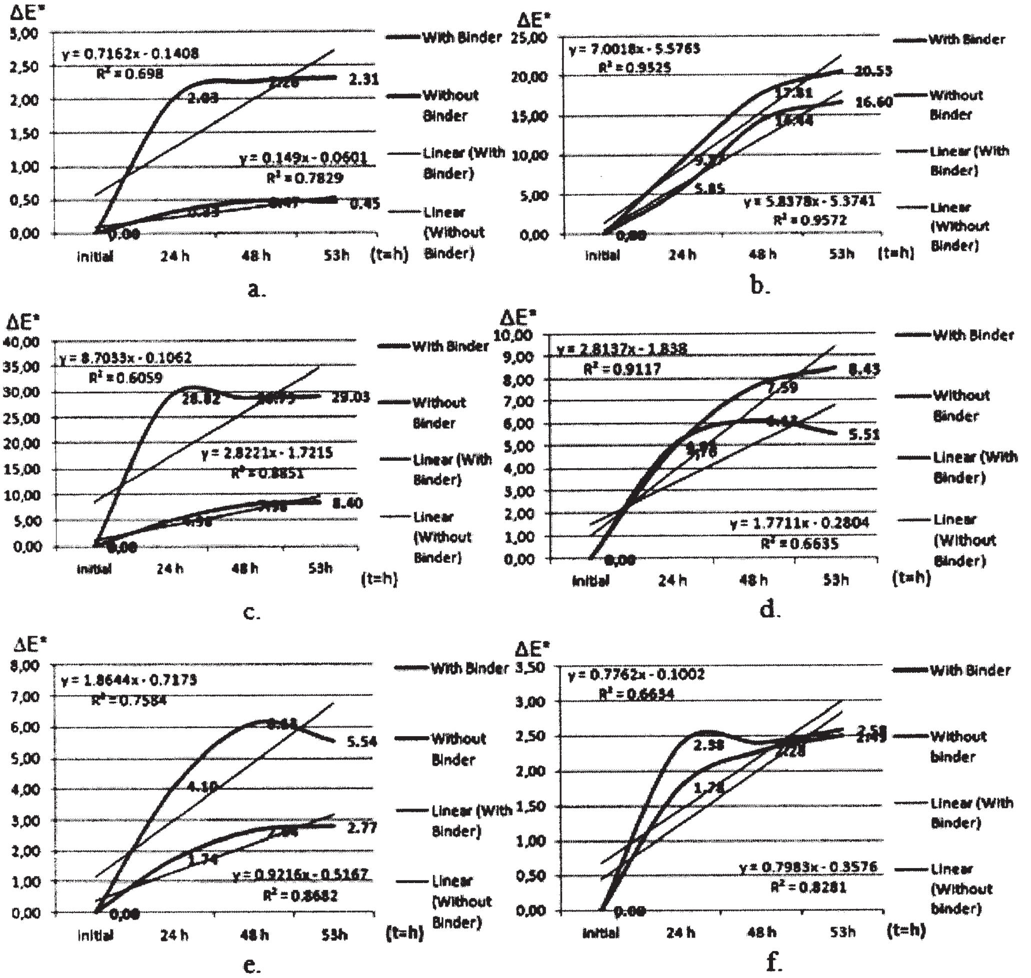

Fig. 4. ΔE* variations for the six sample during artificial aging: a. Sample 1 (Gold leaf), b. Sample 2 (Schlagmetal), c. Sample 3 (Treasure Gold), d. Sample 4 (Dorure liquide), e. Sample 5 (Bronzo in polvere oro) and f. Sample 6 (Doratura Tixe)

Conclusions

According to the results of OM and SEM-EDX analysis, the materials used as imitations of gold leaf do not have gold in their elemental composition.

From the results of this study it can be observed that the schlagmetal oxidizes the fastest, and between the other imitations, Treasure Gold suffers a higher change without binder (29.03). It should be remarked that the coating with binder of the Sample 3, with Treasure Gold, has lighten the colour compared to the original, whilst the binder applied on the other samples has darkened the original colours of the imitations. The gold leaf and, between gold imitations, Dorature Tixe age the slowest by means of thermo-oxidation during the considered period of time taken into study.

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