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BEHAVIOUR UNDER HIGH FREQUENCY PLASMA TREATMENT OF SOME PIGMENTS USED FOR PAINTING OF RELIGIOUS ICONS ON WOOD

Ghiocel Ioanid[1], Aurelia Ioanid[1], Dorina Rusu[2*] and Daniela Sălăjean[2]

[1]Romanian Academy, 'Petru Poni' Institute of Macromolecular Chemistry, 41A Gr. Ghica Voda Alley, Ro.700487, Iasi, Romania
[2]Cultural Heritage Restoration-Conservation Centre, National Complex of Museums 'Moldova', 1 Stefan cel Mare si Sfant, 700028, Iasi, Romania

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Abstract

In the last decades high frequency (HF) cold plasma has frequently been applied in the conservation of the cultural heritage. The removal of the smoke sediment from the icon's surface through cleaning treatments in plasma of HF using a gaseous environment of oxygen/argon is one of the various possible ways of application. The work is focused on studying three pigments: Cadmium yellow, burnt sienna and hydrated chromium green oxide. The variations of the surface appearance have been marked out through SEM analysis, followed by the measurement of the contact angle and chromatic measurements and also the compositional ones through SEM/EDX and FT-IR. The analysis did not marked out structural dramatic variations, the FT-IR spectra keeping the same characteristics before and after the treatment in plasma of HF while only a light increasing of the roughness can be observed on the surface.

Keywords: high frequency cold plasma, cultural heritage, conservation, pigments

1. Introduction

During last year's, researches concerning high frequency cold plasma (HF) have gained special attention due to its potential applications on sterilization, surface modifications (activation, cross linking, etching) and depositing of nanometric films, through unconventional synthesis of organic compounds or grafting.

In the conservation and restoration of cultural goods, high frequency cold plasma has been applied particularly on iron objects, since 1994 at National Museum from Switzerland [1]. Recent studies made by the researchers from the department of conservation of Museum of Art from Cleveland, by employing NASA technology, have emphasized the possibility of using HF cold plasma

* Corresponding author, e-mail: dorina.emilia@yahoo.com, phone: +40 232 213 296, fax: +40 232 218 383

under oxygen atmosphere, for removing of varnishes or smoke deposits onto painted surfaces [2].

Having in mind the newest regulations concerning environmental and worker protection, the replacement perspective of some harmful treatments (which utilizes biocides and organic solvents) with HF cold plasma treatments for decontamination and partial cleaning is not neglected. In this respect, for using such a treatment for the removing of smoke deposits accumulated onto icons surface we proposed to study the surface modifications which could be induced by the active species formed by oxygen plasma. The effect on some natural pigments has also to be studied.

As a rule, the icons on wood are painted in tempera. The paintings executed in tempera are encountered since ancient times, at Egyptians, Greeks, and afterwards the technique has been continued by the Byzantines.

The tradition of icons painted in tempera on wood was perpetuated during centuries; the technique and painting procedure are described in some manuals of painting, the so-called 'Erminii'. The support used for painting is the very well dried softwood (linden, fir, poplar, willow), onto which is applied a special ground, made of animal glue, chalk, some linseed oil or even honey or home-made soap to confer elasticity to the ground. In Middle Age egg tempera was most often applied. Gradually, this was replaced by oil painting and also applied for religious icons from Eastern Europe. Painting with egg tempera has revived during the XIXth century and it was largely applied [3]. Onto the ground a drawing is made and then the theme itself is painted. For tempera colours, an egg emulsion is used as binder, which confers freshness and resistance in time. After drying, the surface of painting is varnished [4].

2. Experimental

2.1. Materials and method

2.1.1. Sample preparation

The samples made of linden wood, of dimensions L = 3 cm, l = 3 cm and H = 1cm have been prepared following the traditional preparation technique of icons wood. Therefore, onto the surface covered with a ground of plaster and animal glue, two layers of pigments in egg tempera were applied. Tempera is the technique which uses emulsions of suspended pigments (organic or inorganic). Egg yolk is an emulsion formed of water, proteins, lipids, minerals etc. The preparation of binder made of egg yolk is done by its dilution in water in proportion of 1/3 (1 part of egg yolk to 3 parts of water) and the homogenization of the mixture.

Three natural inorganic pigments, most often employed in tempera technique for icons during the second half of XIXth century and XXth century, were taken into study:

- Cadmium yellow CdS·ZnO (Cadmium sulphide and zinc oxide) – yellow pigment,
- Burnt sienna Fe_2O_3 (Ferric oxide) – red pigment,
- Hydrated chromium green oxide: $Cr_2O(OH)_2$ - green pigment.

Yellow cadmium is a pigment which exists in nature as mineral (greenockite) in Scotland, Germany and USA, and it was prepared by the German chemist Friedrich Stromeyer in 1817 and introduced in painting in 1829 [4].

Burnt sienna is a pigment used for the preparation of red colours and is used since antiquity up to present.

Hydrated chromium green oxide is used since 1859 up to present. It is an intense pigment, transparent of blue green colour. Its chemical composition is 55.4% chrome, 42.5% oxygen, and de 2.1% hydrogen [5].

2.1.2. Technique

After drying in an oven at 35 °C for 10 h, the samples prepared in this way were treated for 1 h in HF cold plasma, at temperatures between 40 and 45°C [6]. The installation used for this purpose [7] is composed of a Pyrex cylindrical reaction vessel and in its interior are placed two stainless steel plan parallel electrodes, connected to an HF generator of 100 W power and 13.5 MHz frequency. The vacuum in the reaction vessel is assured by a rotating pump and maintained at the pre-established parameters (2×10^{-1} mbar) by means of a needle tap. Flow gas is adjusted by a flow meter to the value 6 l/h. A gas mixture composed of 10 % oxygen and 90 % argon was employed [2].

After fixing the samples in the reaction vessel, this is vacuumed up to an initial value of about 4×10^{-2} mbar, and afterwards the gaseous mixture is introduced adjusting the vacuum up to 2×10^{-1} mbar, and this value is maintained constant during the treatment.

2.2. Analyses

2.2.1. SEM/EDX analyses

The SEM studies were performed on samples fixed on copper supports. The coated surface was examined by using an Environmental Scanning Electron Microscope (ESEM) - Quanta 200 model, operating at 15 and 25 kV with secondary electrons in low vacuum. The Quanta 200 microscope is equipped with an Energy Dispersive X-Ray system for qualitative and quantitative analysis.

2.2.2. FTIR analyses

The IR spectrum of a substance is determined by the nature, number and relative positions of the atoms and functional groups. In FT-IR spectroscopy, the

spectrum is a repeated scanning of the sample over the radiation domain, a sum of individual spectra, while by using the Fourier transform mathematical function, the initial intensity-time spectrum is converted to an intensity-frequency spectrum [8].

Samples taken from the painted surface (emulsion of pigment on vaunted surface) were analyzed with an FT-IR (ATR) apparatus, type VERTEX 7, by attenuated total reflection.

2.2.3. Contact angle measurements

Measurements of contact angle have been done with a patented apparatus conceived at the 'Petru Poni' Institute of Macromolecular Chemistry, Iasi [9].

The contact angle represents the connection angle between the tangents to the liquid surface, in the contact point with the horizontal surface of the solid, measured in interior of the liquid [6]. If water is used as liquid, the hydrophilic/ hydrophobic character of the surface is determined. Values of contact angle higher than 90° indicate a hydrophobic surface and lower values indicate a hydrophilic surface.

2.2.4. Colour measurement

Evaluation of colour changes of pigments has been done by a POCKETSPECT COLOR QA^{TM}, illuminant D 65 device. RGB recorded values were processed by Easy RGB program and transformed in L*, a* and b* parameters for calculation of the colour difference in *CIEL*a*b** system.

Colour difference (ΔE*) is calculated with the relation (1) [10]:

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

where ΔL*, Δa*, and Δb* represent the differences between the final and initial values:

$$\Delta L^* = L_f^* - L_i^* \quad (2)$$

$$\Delta a^* = a_f^* - a_i^* \quad (3)$$

$$\Delta b^* = b_f^* - b_i^* \quad (4)$$

3. Results and discussion

3.1. SEM/EDX analyses

The superficial aspect of the painting layer dispersed in egg yolk (binder), deposited onto the ground layer is different according to the nature of pigment included in binder (Figure 1). All three types of painting layers present the morphology of a blend with the matrix constituted of the binder in which the pigment minor phase is distributed.

On the surface of the support containing the yellow pigment, individual grains of fine dispersed pigment and zones with small agglomerates can be

observed, randomly distributed within the binder phase, which has a continuous aspect.

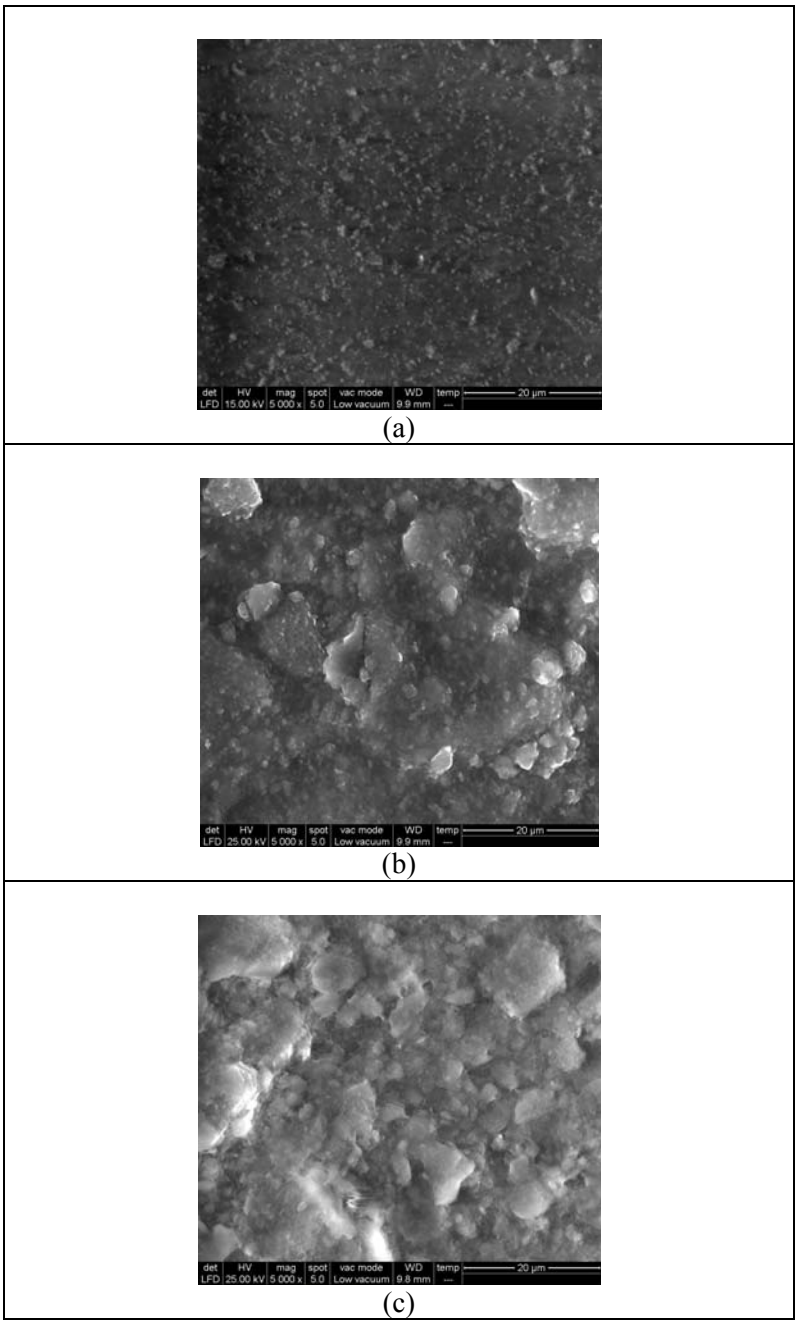

Figure 1. SEM images of studied pigments before treatment: (a) yellow pigment, (b) red pigment and (c) green pigment.

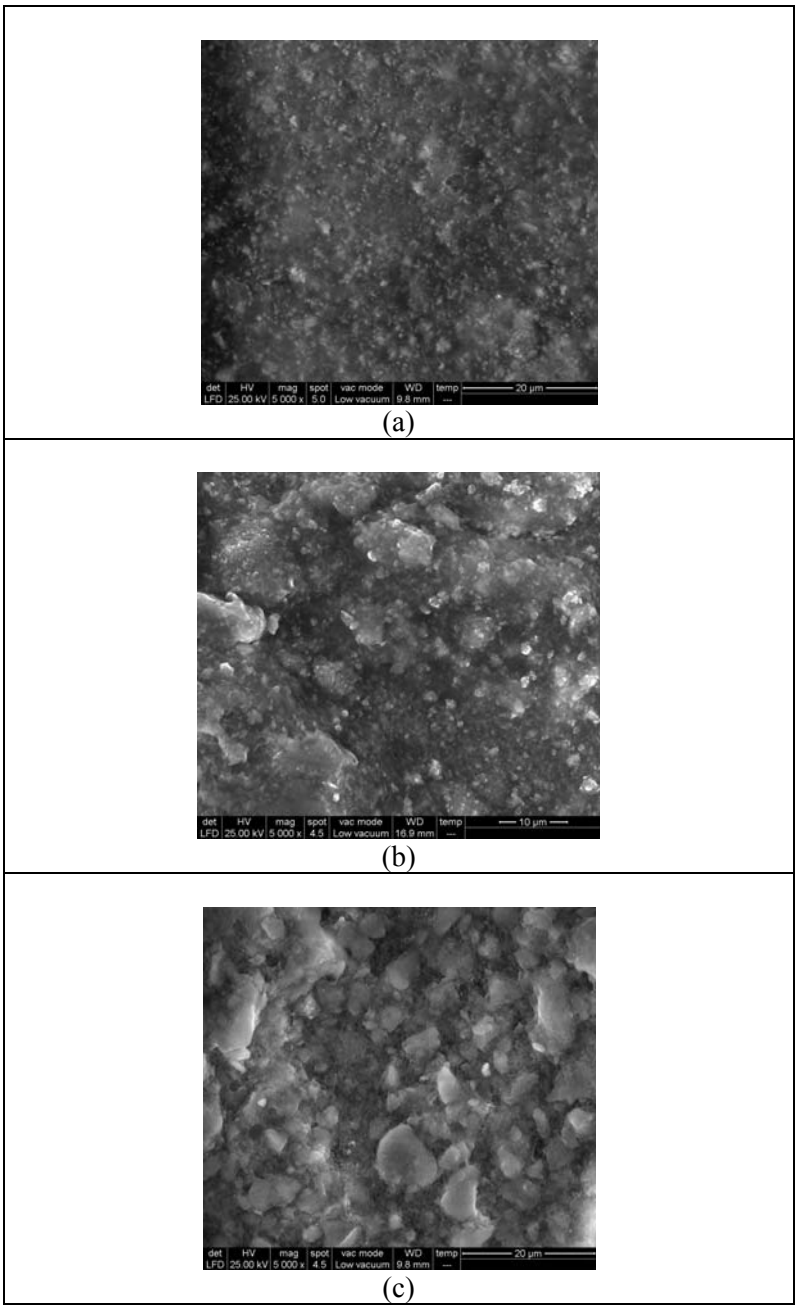

Figure 2. SEM images of studied pigments after 1 h of treatment in HF plasma: (a) yellow pigment, (b) red pigment and (c) green pigment.

The topographical aspect of the red pigment surface is granular. The grains of the pigment have a dense distribution with dimensions in the colloidal domain, representing individual units or compact agglomerates, included into the binder matrix with a porous aspect.

The particles of green pigment are individually distributed but also as agglomerates with micrometric dimensions. The binder has a discontinuous aspect, due to the presence of pores.

After the plasma treatment, (Figure 2) the aspect of the painted surfaces suffers modifications, in the sense that the surface painted with yellow pigment is not anymore continuous, the appearance of some pores is remarked, and in the case of the painting with red and green pigments an increase of porosity is ascertained, more visible in the case of the green pigment. This may be the consequence of a corrosion effect – at the nanometric level – of the binder, which incorporates the pigment grains in a way that leaves the surface grains bare (without binder). The mentioned transformations determine an increase of roughness. No modifications of the dimensions of the pigments particles are remarked.

Energy dispersive X–ray microanalysis was employed to obtain information on the elements present in the studied pigments (Table 1).

Table 1. Values of the mass percentages of the elements on samples surface.

Pigm. / **Elem.**	**Cadmium yellow: CdS·ZnO**		**Burnt sienna: Fe_2O_3**		**Hydrated chromium green oxide: $Cr_2O(OH)_2$**	
	After treatment Wt (%)	**Before treatment** Wt (%)	**After treatment** Wt (%)	**Before treatment** Wt (%)	**After treatment** Wt (%)	**Before treatment** Wt (%)
C	72.73	68.26	61.99	63.21	38.84	36.14
O	09.08	08.97	22.48	21.48	28.79	30.04
P	00.71	00.81	00.66	00.64	00.46	00.42
S	03.97	04.27	00.80	01.04	00.32	00.27
Ca	-	-	00.90	00.95	00.58	00.58
Cr	-	-	-	-	31.74	32.54
Al	-	-	02.01	02.14	-	-
Si	-	-	04.34	04.68	-	-
K	-	-	00.67	00.76	-	-
Fe	-	-	06.23	05.10	-	-
Cd	13.39	15.26	-	-	-	-
Zn	00.12	00.11	-	-	-	-

After the treatment in plasma there are no important compositional modifications for any of the used pigments. It is remarked the presence of the elements of each pigment: Cr, Fe, Cd, Zn in relatively high percentages and also the elements belonging to binder (egg yolk). Egg yolk is composed of water (52.9%), proteins (16.7%), lipids (26.7%), carbohydrates (2.6%), minerals (0.5%) and pigments (0.1%). The emulsions of the inorganic pigments in binder

are not homogeneous, therefore the concentration of the elements on the painted surface is not uniform and the values presented in Table 1 constitute the average of the measurements made in two different points.

Unlike burnt sienna and yellow cadmium – inorganic pigments, hydrated chromium green oxide – an inorganic pigment as well – has two hydroxyl groups in its composition, which may explain the increase in the mass concentration of oxygen, by 1.07 percentage, due to the formation of additional hydroxyl bonds. As regards the other elements it can be observed that the recorded values after treatment are close to the initial ones, which means the plasma treatment does not affect significantly the elemental composition at surface.

3.2. FTIR analyses

In Figure 3 are presented the modifications revealed by the FTIR-ATR spectra of the pigments treated in HF plasma. The initial spectrum is recorded with the colour of each pigment (yellow, red, green) and with black is marked the spectrum recorded after treatment. The analysis evidences the presence of the reflection bands characteristic to proteins of egg yolk. Therefore, in the range 3400–3332 cm^{-1} appear the asymmetric stretching vibrations due to primary amine groups N-H, and in the 3328–3250 cm^{-1} interval - the asymmetric stretching vibrations of the same primary amine. In the 1650-1590 cm^{-1} interval are present the deformation stretching bands of the secondary amines.

The absorption band located in 1090-1068 cm^{-1} is attributed to the stretching vibration of C-N from amine, while the band at 850-750 cm^{-1} is specific to oscillation of N-H group. Deformation bands specific to OH group from water appear in the 1640-1632 cm^{-1} spectral domain.

The absorption bands in 1680-1630 cm^{-1} domain are specific to the stretching vibrations of C ═ O group from amide I, and the bands located in 1570–1515 and 1305-1200 cm^{-1} to CNH group.

After the plasma treatment, in all three cases it is observed a decrease in the intensity of the deformation bands, specific to OH group from water, which suggests an elimination of water from egg yolk, under vacuum.

Amide I band at 1633 cm^{-1} corresponding to yellow and red pigments and at 1650 cm^{-1} for green pigment, as well as combined bands (stretching C-N, bending N-H), of amide II at 1570 – 1515; 1305-1200 cm^{-1} specific to CNH group are diminished after plasma treatment. These changes are a consequence of superstructure modifications of the binder, but in low limits, because the spectra do not present significant modifications.

Only in case of hydrated chromium green oxide the disappearance of the stretching band from 3275 cm^{-1} of the primary amines is noticed, while for the other pigments this band is diminished.

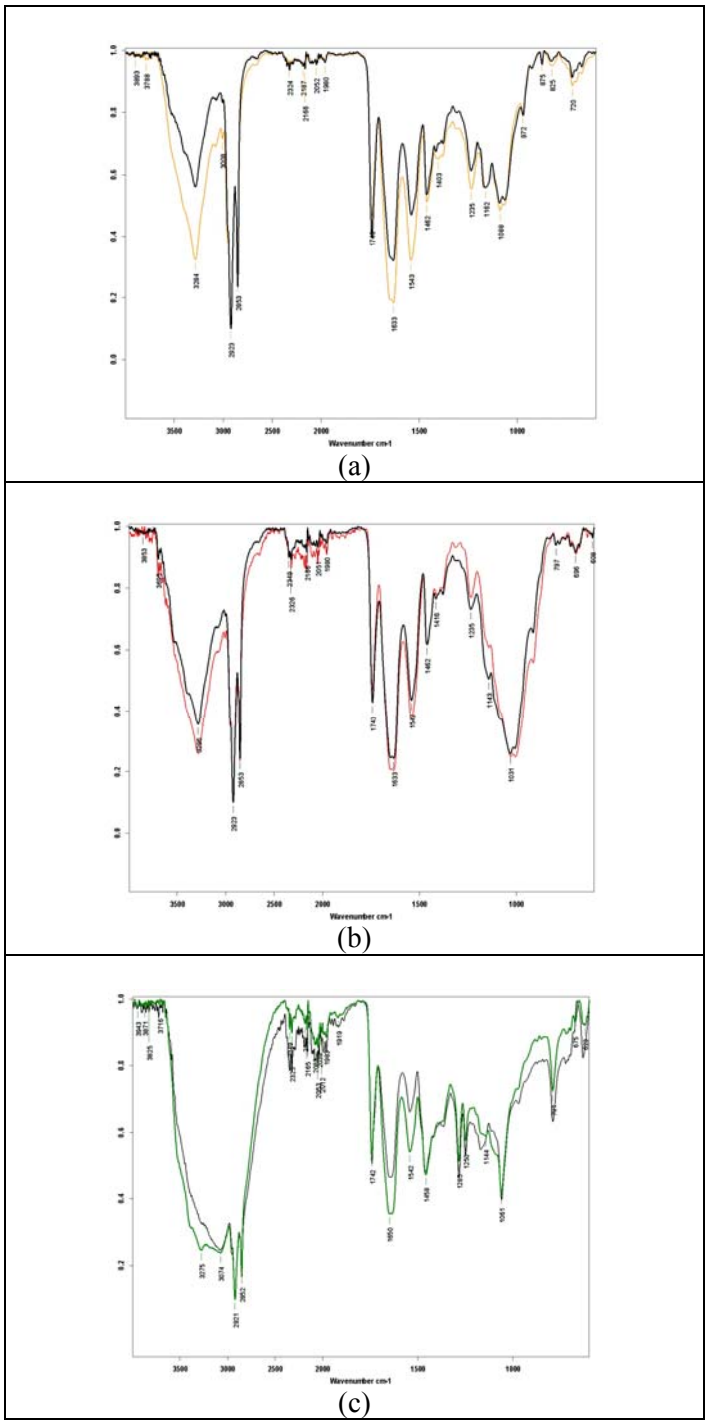

Figure 3. FTIR spectra of pigments: (a) cadmium yellow, (b) burnt sienna and (c) hydrated chromium.

3.3. Measurement of contact angle

It is well known that, the hydrophilic/hydrophobic behaviour of the polymers treated in HF plasma under oxygen/argon gas flow mixture as reaction medium, is modified in the sense of increasing of the hydrophilic character.

The values of the contact angle measured before and after HF plasma treatment indicate a different behaviour of the studied pigments. It is ascertained that, in the case of pigments which do not contain hydroxyl groups (burnt sienna and yellow cadmium) the contact angle increases from the initial average value of 48.2 to 59 in case of burnt sienna pigment and from 51.25 to 58.6 for yellow cadmium pigment. As regard to hydrated chromium green oxide, the presence of hydroxyl groups determine a similar behaviour of the polymers, the average value of contact angle diminishing from 72.75 to 20 due to the formation of hydroxyl bonds.

3.4. Colour measurement

Chromatic changes induced by active species formed into the used HF plasma are minor. Colour differences (Table 2) calculated according to equation (1), have low values, indistinguishable at a visual analysis.

Table 2. Chromatic modifications of the pigments.

Pigment	Initial			1 h treatment in oxygen-argon			
	L*	**a***	**b***	**L***	**a***	**b***	**ΔE***
Hydrated chromium green oxide : $Cr_2O(OH)_2$	9.156	-5.797	0.490	10.119	-6.052	1.163	1.19
Burnt sienna: Fe_2O_3	6.954	9.637	6.069	7.583	10.273	6.585	1.03
Yellow cadmium: CdS·ZnO	54.683	25.031	54.870	54.319	25.148	54.507	0.58

Therefore, from the data presented in the above table is concluded that the colour difference has the highest value in case of hydrated chromium green oxide - 1.19, probably generated by the presence of hydroxyl groups, followed by burnt sienna - 1.03 and yellow cadmium - 0.58. It is remarked that luminosity slightly increases in the case of dark coloured pigments (hydrated chromium green oxide, burnt sienna) and a decrease by 0.364 in the case of the yellow one, caused by the discontinuous aspect of pigment dispersion in binder after treatment, modification evidenced by scanning electron microscopy.

4. Conclusions

SEM images evidence a slight corrosion of binder during treatment which is leading to an increase of roughness.

After the plasma treatment there are no important compositional modifications for none of the studied pigments.

The aspect of the FTIR–ATR spectra recorded before and after the plasma treatment under oxygen indicates slight modifications of the binder's superstructure, but in reasonable limits.

As a consequence of the obtained results and taking into account that the HF plasma treatment can be controlled, it can be concluded that the modifications induced by the plasma treatment over the pictorial layer are insignificant and are produced only at surface (depth of few nanometres). Therefore, HF plasma can be taken into consideration as a partial cleaning variant for removal of soot accumulated at the surface of pictorial layer of icons.

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