Authentication of the Ancient Easel-paintings through Materials Identification from the Polychrome Layers

III. Cross - section Analysis and Staining Test

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This paper deals with the study of polychrome materials (pigments and proteinaceous or lipids binders) of the 18-th and 19-th centuries orthodox icons on wood or canvas support, belonging to some monachal and private collections in Moldova, by means of the " cross-section" - type microstratigraphical analysis, mixed with "staining tests", in order to determine the conclusive and exhaustive specific features or artifactometric attributes with implication in the authentication expertises (such as forgery attempts, incompatible chromatic reinstatements, inadequate exhibition or conservation, etc.). For the strictness of the authentication expertise, the experimental data are co-assisted or corroborated with those obtained by the pyrolytic gas-chromatography methods, with or without silylation, and the FT-IR spectrophotometry method, object of our two previous papers.

Keywords: old icons, polychrome layers, proteinaceous and lipids binders, pigments, vernis, microstratigraphy analysis by the means of "cross-section" and „staining tests", authentication expertise

The method of the microstratigraphic analysis allow the visualisation of the structure of a painting both on thin sections and on "cross-sections" ones, respectively, with the optical microscope or the stereolupe.

The method has been widely used from the 1960s in the analysis laboratories of the great museums and in the research institutes belonging to university centers all over the world. The information supplied by this technique have been gathered as database for samples collections which have practically formed the starting point in the documentation achievement / database for each analysed patrimony object, and which have been staying available for any subsequent research with more advanced means [1].

Generally speaking, the microstratigraphic analysis of a painting supplies metric data (the thickness of the layers / coating and the granulometry of the pigments), chromatic data (colour and the array of the pigments) and morphologic data (consecution of the layers and their continuity), information which can be complemented by microchemical reactions ("staining tests"), carried out directly on cross-sections, consequently allowing the authentication and the determination of the conservation state as well as the evaluation of the interaction between the various structural elements of the painting materials and their interaction with exogenous factors. Moreover, this technique allows the involvement of some complementary methods, by the co-attending or corroborating system, such as the μ-FT-IR and μ-Raman spectrophotometry, the reflexion and SEM – EDAX colourimetry, respectively, which supply very important additional information concerning the chemical composition, the distribution of the chemical elements, of the congruent structures, of the phases and interfaces, etc. [2- 4].

The analysis of the paintings by using the cross-sections method was devised by the chemist Laurie in 1914, and afterwards extended and improved in 1930 at the Fogg Art Museum, Cambridge, Massachussets [6]. At that time the waxes were used as mediums in order to include the samples, while the thin sections were obtained with a microtome. The waxes have been gradually replaced by synthetic resins, harder and more transparent. The method is being applied today in various laboratories such as the Central Museum Laboratory – Brussels, Belgium, London National Gallery, London University, Louvre Museum Central Laboratory, Rome Restaration Central Institute (ICCROM), etc., where polyesteric resins with induration at cold are used.

When taking into account the modern tendencies of applying the non-destructive techniques for the analysis of art works, the specialists insist nowadays more and more on the punctual samplings allowing the analysis of very small samples which do not affect the integrity, the aesthetics and the functionality of the object. The punctual sampling is obtained with adequate instruments, namely, the syringe needle, the lancet scalpel with a very sharp blade, etc. [7-10]. It is recommended that the punctual sampling should be carried out in second grade artistic and iconographic interest areas, minimally important, by implying cracks net, lacunar zones, craves or fly holes of xylophagic insects on the active painting surface. In the selection of the sampling area one should take into account the following aspects [11-14]: the state conservation of the painting, the thickness and the integrity of the pictural layer, the consecutive interventions in the active preservation and restauration process (consolidations, cleanings, repaintings, revernishings, etc.). The dimensions of the sample should not be less than 0.5 mm or bigger than 5.0 mm [1-3].

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The microstratigraphic method offers three main advantages:

- can be obtained from a small quantity of painting sample many useful information such as the consecution of the painting layers, the colour of the components, the granulometry, the thickness and the dimension of the pigments particles / powders, etc.;
- the pigments and the binders can be chemically analysed;
- the sampling of a small dimensions fragment allows the obtaining, under safe conditions, of some invazive interventions, which in opposite case could be dangerous for the painting; for example, the sample could serve as a support for the solubility tests in the selection of a solvent mixture for cleaning.

It is well-known that this method has also some disadvantages such as:

- a number and a quantity of samples cannot be obtained ad libitum in order to protect the painting;
- moreover, for a thorough study on the artistic technique or on the accomplishment procedure as well as on the aging process of the pictural material components, a series of samples which generally cannot be prelevated (sequential or extended series, respectively, both on the painting surface and in the deepness of the pictural layers) must be imposed by means of this method;
- there is a so called "statistic hazard quotient", which means that one cannot be sure that a very small surface of about 1 mm^2, necessary for prelevation, may be representative for the whole work, even if the eye perceives the zone as a homogenous one; that is why, under some situations, it becomes compulsory to study some adjacent areas, even identically polychrome, or to apply some other methods and techniques.

For this kind of complex studies the specialists appeal more and more to the non-destructive microendoscopic techniques, with optical fiber, which are directly applied in the crack, "roof upheaval" or in lacunary structures, co-assisted by the UV, Vis or IR reflectographic technique [15, 16].

In what the histochemical coloration technique on painting sections, also known as "metachromasy", is concerned, it was used for the first time in 1914 by Laurie [4, 5], then by Coremans who improved the method, by carrying out in 1959 the first analysis on the ultra-thin sections (20-30 m) [17- 19].

The study of the "in situ" binders, by means of the histochemical techniques on a big number of painting sections accomplished with samples prelevated during restaurations, has been devised and developed by Eibner, Ostwald, Coremans, Gettens, Thiessen and Plesters who have demonstrated that certain colorants such as methyl violet, methylen blue, Nile blue, etc., can mark out the lipids binders while the acid fuchsine-type colorants mark out the proteinaceous binders [16].

Another method, carried out and experimented in the Louvre Laboratories (Paris) and in the Rome Central Institute of Restauration in collaboration with the Michigan University and the Rome Institute of Embriology, consists in the usage of highly specific colorants on ultra-thin painting sections (4 –6) which allow the examination under transmitted light [1- 3].

In the painting layer the pigment can obstruct the perceiving of the analysed binders colour modification. This is the reason why light colour painted zones, containing less coloured pigments, are chosen. There must also be taken into account the physico-chemical modifications of the materials from the painting structure during the natural aging process. The complexity of the aging processes depends on the environmental agresivity, on the age, nature and durability of the materials as well as on their thickness [1-3].

Experimental Part

The Prelevation and the Processing of the Samples

The micro-samples selectively prelevated from old canvas and wood paintings belonging to various state and private collections, previously analysed by means of the pyrolytic gas-chromatography [20] and the FT-IR spectrophotometry [21] techniques, respectively, have been introduced into the transparent polyestheric resin, produced by Akemi®, with a methyl-ethyl-ketone peroxide-based intensifier; after the cold hardening into a 5x10x20mm flexible rubber formwork, the resin block with the sample has been extracted from its formwork and polished to the sample level (with abrazive paper of variable granulation, on the corresponding transversal section sample); then the surface including the cross-section sample has been smoothly polished. The samples prepared in this way have been preserved in exicators with $CaCl_2$ sic before being analysed on the microscope.

Microscopic Analysis and Staining Tests on Cross-sections

The experimental protocol has followed the specific steps of the cross-sections micro-stratigraphic technique (glossy or thick sections), namely, the microscope analysis and the applying of the colouring reactives for identifying both the binders and the pigments.

To visualise the pictural layer sections there has been used an Axioplan 2 Zeiss–type binocular microscope with optical fibres in transmission and reflection, with a MC80-type camera, at magnification powers of 10X, 20X, 25X, 40X and 50X, in Vis and UV.

To identify the binders, the pigments and the inert masses there have been used micro-chemical reactions with specific reagents such as HCl and KI for lead white, diluted HCl for calcium carbonate, AB3 for animal glue, Oil Red O for linseed oil.

The methodology for the histo-chemical colourings has followed the stages:

- colouring for a standard time period;
- washing with specific solutions for each type of colorant;
- visualising of the samples after the colouring procees on the stereoscopic microscope and the comparing of the examined sample colour with a reference sample, non-coloured, on the optical microscope at various magnification powers (10X, 20X, 25X, 40X, 50X, etc.) in reflected light.

Results and Discussions

On using the data from the specialized literature [1, 3, 22] there have been selected examples of specific histo-chemical analyses ("staining tests") for various traditional lipids and proteinaceous binders from the structure of old paintings (tables 1 and 2).

The data regarding the sections on the samples from the studied old paintings, obtained by means of the microscopic analysis as well as by the histo-chemical and micro-chemical colourings, respectively, are presented in Table 3. The obtained results are noted in a card indexed in the G414 file, representing the research documentation at the OPD Scientific Laboratory, Florence, and A003 at the Laboratory for Scientific Investigation and Preservation of Cultural Patrimony, the ARHEOINVEST Interdisciplinary Formation and Research Platform, "Al. I. Cuza" University, Iaºi.

Table 1

IDENTIFICATION OF THE LIPIDS BINDERS BY MEANS OF THE COLORIMETRICAL REACTIONS WITH SUDAN BLACK B, OIL RED O, NILE BLUE SULPHATE AND VANILLIN. TO ESTIMATE THE EFFICIENCY OF THE IDENTIFYING REACTIONS, THE FOLLOWING MARKERS HAVE BEEN USED: ABSENT BINDER (-), SMALL QUANTITY OF BINDER (±), REDUCED QUANTITY OF BINDER (+), VERY BIG QUANTITY OF BINDER (+ + +), RESPECTIVELY.

Binder	Oil Red O in isopropanol	Sudan Black B in alcohol at 70°C	Nile Blue Sulphate at 70°C	1% Vanillin in H_2SO_4
Gelatine	-	-	Blue	-
Egg-white	-	Traces	Blue	Red – violet
Yolk	+	+ +	Blue	Red – violet
Whole egg	+	+ +	Blue	Red – violet
Linseed oil	+ +	+ + +	Blue – red	Dark brown
Acacia gum	-	-	Blue	-
Natural resin	-	Soluble	Blue (traces)	Red – brown
Linseed oil and gelatine	+	+ +	Blue – red (traces)	Dark brown
Yolk and linseed oil	+ +	+ + +	Blue – red (traces)	Red – brown
Oil and egg-white	+	+ +	Blue – red (traces)	Red – brown
Linseed oil and resin	+	+	Blue – red	Red – brown

Table 2

IDENTIFICATION OF THE PROTEINACEOUS BINDERS BY MEANS OF THE COLORIMETRICAL REACTIONS OF THE FOLLOWING TYPE: REACTION WITH SPECIFIC AGENT, WITH ACID FUCHSINE AND AMIDO BLACK (AB1, AB2, AB3) SOLUTIONS, RESPECTIVELY, USING THE MARKERS: ABSENT BINDER (-), SMALL QUANTITY OF BINDER (±), REDUCED QUANTITY OF BINDER (+), VERY BIG QUANTITY OF BINDER (+ + +)

Binder	Identification of the proteins reaction with specific reagent based on copper sulphate (burette reaction)	Acid fuchsine in 1% water	AB1	AB2	AB3
Gelatin	++	++	+	+++	++
Egg-white	++	+	++	+++	+
Yolk	+ (-)	+	+++	++	+
Whole egg	+ (low)	+	++	++	+
Linseed oil	Soluble orange	-	-	-	-
Starch	-	++	+	+	+
Acacia gum	-	-	-+	-+	-+
Colophony	Orange	-	-	-	-
Linseed oil and gelatine	+	+	-+	++	+
Yolk and linseed oil	-	-+	++	+	-+
Linseed oil and egg-white	+	-+	+	++	traces

Table 3

PAINTING SAMPLES STRATIGRAPHICALLY-ANALYSED ON THE OPTICAL MICROSCOPE (IN VIS AND UV) AND BY HISTO-CHEMICAL COLOURINGS

No.	Data concerning the analysed painting (title, age determination)	Sample area	Photography conditions	Stratigraphic composition of the sample and other information
1	"St. Veronica Kerchief", wooden icon, 19-th century;	Decorative motif from the kerchief, pale red pictural layer ;	Vis, 20X; UV, 20X (09 blue filter, λ = 450 – 490 nm);	- ground from plaster and animal glue with black carbon dispersion; - red layer (vermilion ?); - vernis film;
2	"St. Veronica Kerchief", wooden icon, 19-th century;	Ochre yellow-silvery pictural layer from the kerchief	Vis and UV – 20X;	- ground from plaster and animal glue - red-ochre layer; - vernis film;
3	"Holy Virgin with Child on the Throne", wooden icon, 19-th century;	Upper right corner of the cloak, blue pictural layer;	Vis and UV – 20X;	- thick ground from plaster and animal glue; - blue-greenish layer (azurite?); - non-uniform vernis film;
4	"Holy Virgin with Child on the Throne", wooden icon, 19-th century;	Left leg of the throne, red pictural layer;	- Vis, 10X; - Vis and UV – 20X;	- thick ground from plaster and animal glue; - red layer (vermilion ?); - non-uniform vernis film;
5	"Holy Virgin with Child on the Throne", wooden icon, 19-th century;	Lower right corner, green-brown pictural layer;	Vis and UV – 10X;	- thick ground from plaster and animal glue; - ochre-browish pictural layer (terra?); - non-uniform vernis film;
6	"Holy Virgin with Child on the Throne", wooden icon, 19-th century;	Lower right corner, green blue pictural layer from the Virgin garment;	Vis and UV – 10X;	- thick ground from plaster and animal glue; - green layer (malachite?); - vernis film;
7	"Entering in Jerusalem", wooden icon, 19-th century;	Upper central edge, red pictural layer;	Vis and UV – 20X;	- ground from plaster and animal glue; - red layer (vermilion ?); - vernis film;

8	"Entering in Jerusalem", wooden icon, 19-th century;	Left area of the garment, green pictural layer;	Vis and UV – 20X;	- thick ground from plaster and animal glue with particles of black carbon or terra; - very thin green layer; - uniform vernis film;
9	"Entering in Jerusalem", wooden icon, 19-th century;	Lower right end, red pictural layer;	Vis and Uv – 20X and 40X;	- thick ground from plaster and animal glue with particles of black carbon; - red layer; - vernis film;
10	"Entering in Jerusalem", wooden icon, 19-th century;	Lower part of Jesus cloak, white pictural layer;	Vis and Uv – 20X and 40X;	- thick ground from plaster and animal glue with particles of black carbon and red; - white layer; - vernis film (cracks and craves of the pictural layer)
11	"Birth of the Holy Virgin", wooden icon, beginning of the 19-th century;	Ochre pictural layer, background;	- Vis, 25-40X; - Vis, 25X and 40X; - UV, 25X and 40X:	- white ground, based on plaster and animal glue; the part in direct contact with the pictural film contains terra (earths) and it is partially impregnated with the binder from the pictural film; - white-yellowish layer, based on lead white and ochres, done on two consecutive applications (70 µm thickness); - 4 vernis films among which two lightly pigmented with coal black; - thick wax layer, existing only on one part of the fragment;
12	"Entering in Jerusalem", wooden icon, 18-th century;	Preparation from the green background, lower right angle;	- Vis, 25X and 40X; - UV, 25X and 40X;	- white ground, based on plaster and animal glue; - yellow painting layer based on chrome yellow, lightly loaded with coal black (20 µm thickness); - thin vernis film with an intense white fluorescence;
13	"St. Spiridon", wooden icon, 19-th century;l	Green pictural layer from the saint garment;	- Vis, 25X and 40X; - UV, 25X and 40X;	- white ground, based on plaster and animal glue, the part in direct contact with the pictural part being impregnated by its oleous binder; - yellow-greenish thin painting layer (15 µm thickness) based on chrome green; - intermediary black layer based on Prussian blue and a small quantity of coal black; - 35 µm brown layer, based on yellow ochre and coal black; - light ochre final painting layer, based on lead white with ochre and scarce particles of red pigment; - vernis residue;
14	"St. Spiridon", wooden icon, 19-th century;	Red pictural layer from the saint garment;	Vis, 25X and 40X; UV, 25X and 40X;	- white ground based on chalk and animal glue partially impregnated with the oleous binder from the pictural film intensely fluorescent under the UV rays; - residues of red-orange painting layer, presented only on parts of the fragment; - thick layer of filmogenous material (wax?), loaded with various pigments with low UV fluorescence;
15	"Transfiguration", wooden icon, 19-th century;	Red pictural layer from Christ garment;	- Vis, 25X and 40X; - UV, 25X and 40X;	- white ground, based on plaster and animal glue, loaded with coal black and earths; - glue layer; - 15 µm thin layer of red-orange painting, based on red lead; - 5 µm thin and fragmentary yellow layer, based on an unidentified pigment (a possible „highlight"); - vernis layer with an intense white fluorescence;
16	"Jesus Christ, Teacher on the Throne", wooden icon, 19-th century;	Pictural layer from the area of Jesus halo;	- Vis, 25X and 40X; - UV, 25X and 40X;	- ground based on chalk and oil yellowish ochres; - gold foil on the sample parts; - 60µm semi-transparent layer based on oleous-resinous vernis; - yellow-reddish painting layer, based on lead white, a small quantity of yellow pigment and some vermilion particles only on parts of the samples; - oleous-resinous vernis film with an intense white fluorescence;
17	"Virgin Mary with Child", wooden icon, 18-th – 19-th centuries;	Green background of the icon;	Vis and UV – 50X:	- chalk (calcium carbonate) and animal glue; - 50 µ thick greenish pictural layer with scarce particles of blue and yellow pigment (Naples yellow?); - 20 µ thick vernis which penetrates deeply at the level of the cracks; - atmospheric deposit material without fluorescence in UV; (one can notice, in the pictural layer, a gilding residue or highlight accomplished with faked gold > probably a copper alloy>)

18	"Virgin Mary with Child", wooden icon, 18-th – 19-th centuries;	Red garment of the Virgin Mary;	Vis and UV – 50X;	- chalk (calcium carbonate) and animal glue; - 25 μ thick red layer, based on red varnishes with scarce yellowish particles; - about 5 μ thick red layer (late retouch); - (synthetical?) varnish-based vernis, red in Vis and white in UV; - air deposition matrial;
19	"Virgin Mary with Child", wooden icon, 18-th – 19-th centuries;	Garment of the Virgin Mary (decorative elements);	Vis and UV – 20X and 50X;	- chalk (calcium carbonate) and animal glue; - red layer based on pigment (inert mass) and red varnishes; - yellow layer (Orpiment or chrome yellow?); - irregular layer based on coal black; - thin reddish layer (retouch?); - white layer based on white pigment (titanium white or Litopon?); (the preparation is applied on a wooden-support canvas)
20	"Virgin Mary with Child", wooden icon, 18-th – 19-th centuries;	Icon edge;	Vis and UV – 50X;	- chalk (calcium carbonate) and animal glue; - 50 μ thick greenish pictural layer based on blue pigment and scarce particles of yellow pigment (Naples yellow?); - yellow-reddish layer based on red varnishes and yellow pigment; - white layer based on white pigment (titanium white or Litopon?); - vernis; (one can notice, in another area of the sample, the presence of a yellow layer above the greenish layer, without the white layer)
21	"Virgin Mary with Child", wooden icon, 18-th – 19-th centuries;	Icon edge;	Vis and UV – 50X;	- chalk (calcium carbonate) and animal glue; - irregular green pictural layer based on lead white, scarce particles of blue pigment and scarce particles of yellow pigment (Naples yellow); - thick yellow-brown layer based on yellow pigment, coal black with a varnish granule in middle; - thick layer based on red varnish; - vernis; - uniform and thin layer based on bitumen without UV fluorescence (forgery attempt?);
22	"Virgin Mary with Child", wooden icon, 18-th – 19-th centuries;	Red garment of the Virgin Mary;	Vis and UV – 20X;	- calcium carbonate and glue in two applications; - reddish pictural layer based on lead white and red varnish; - atmospheric deposit material which penetrates deeply some cracks; (the wooden support is also noticed in section)
23	"Virgin Mary with Child", wooden icon, 18-th – 19-th centuries;	Brownish garment of the Virgin Mary;	Vis and UV – 50X;	- calcium carbonate and glue; - blue pictural layer based on dark blue pigment (Prussian blue or Indigo); - thick vernis in which particles of gilding material are incorporated; - atmospheric deposit material which penetrates the superficial layers of the vernis;
24	"Virgin Mary with Child", wooden icon, 18-th – 19-th centuries;	Icon background;	Vis and UV – 50X;	- calcium carbonate and animal glue; - thin blue pictural layer based on lead white and blue pigment (Indigo and Prussian blue) and non-fluorescent red pigment; - thick vernis layer with whitish fluorescence; - two yellow fluorescent vernis applications with non-fluorescent stratified material (sandwich);
25	"Virgin Mary with Child", wooden icon, 18-th – 19-th centuries;	Icon bachground;	Vis and UV – 50X;	- calcium carbonate and animal glue; - thin pictural layer based on white and dark blue pigment (Indigo or Prussian blue) and non-fluorescent red pigment; - thick vernis layer with whitish fluorescence; - oleous-resinous vernis with yellow fluorescence;
26	"Weeping", canvas icon, 18-th – 19-th centuries;	Icon edge – red pigment;	Vis and UV – 50X;	- red earths, coal black and oleous binder; - basic chromatic layer, based on earths, coal black and lead white (in mimimum quantity); - thin red layer based on vermilion; - final vernis; (one can notice, in all sections of the canvas samples, the presence of a glue residue, probably used as an intermediary layer between the support and the preparation; one can also notice, at the glue level, the presence of the lead white)

27	"Weeping", canvas icon, 18-th – 19-th centuries;	Icon edge – metallic foil ;	Vis and UV – 50X;	- red earths, coal black and oleous binder; - basic chromatic layer, based on earths, coal black and lead white (in mimimum quantity); - oleous binder; - thin layer of oleous mixture, loaded with scarce red pigment granules; - metallic foil (silver?); - vernis with included atmospheric dust; (The preparation contains great particles of red earths .> the bolus has a finer granulometry >)
28	"Weeping", canvas icon, 18-th – 19-th centuries;	Icon edge – blue pigment;	Vis and UV – 50X;	- red earths, coal black and oleous binder; - basic chromatic layer with lead white and coal black; - oleous binder; - thin blue layer based on Prussian blue; - final vernis; (The preoaration contains calcium carbonate particles)
29	"Weeping", canvas icon, 18-th – 19-th centuries;	Icon edge – green-brown pigment;	Vis and UV – 50X;	- red earths, coal black and oleous binder; - basic chromatic layer with lead white and coal black; - oleous binder; - pictural layer based on lead white; - final vernis (one can notice the presence of thick lead white in the preparation)

Figures 1 – 29 present the photos of the sections in visible and ultraviolet lights, respectively, at various magnification powers (10X, 20X, 25X, 40X °i 50X) of the 29 samples prelevated from 14 orthodox icons on wood and canvas – the 18-th and 19-th centuries – belonging to monachal sites and private collections.

The observation in the diffuse light in open field has made possible the individualisation of the consecution of the polychrome layers and their morphological, granulometrical and optical characteristics.

The observation of the UV fluorescence has allowed the differentiation between various analysed binders and compounds. One knows that the fluorescence tonalities depend on the chemical nature of the materials and on their degree of aging. Generally speaking, the proteinaceous substances (proteinaceous binders) have a cold tonality fluorescence while the fat-type substances have a warm tonality fluorescence, between yellow and yellow-orange.

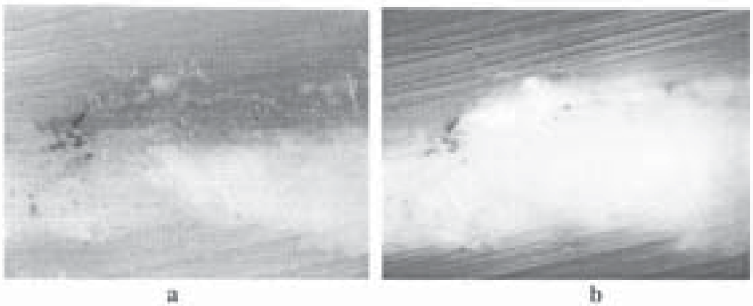


Fig. 1. Micro-stratigraphy of sample 1 (cross-section): a – in Vis; b – in UV

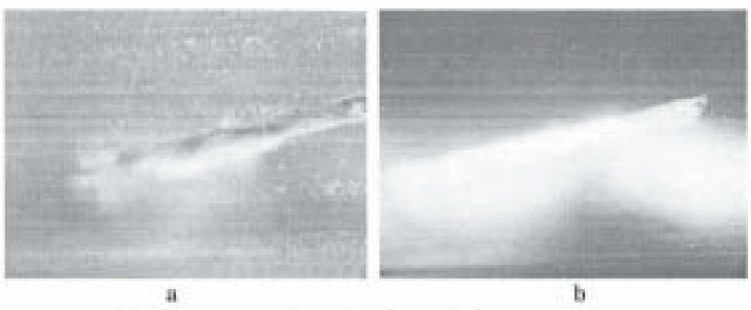


Fig. 2. Micro-stratigraphy of sample 2 (cross-section): a – in Vis; b – in UV

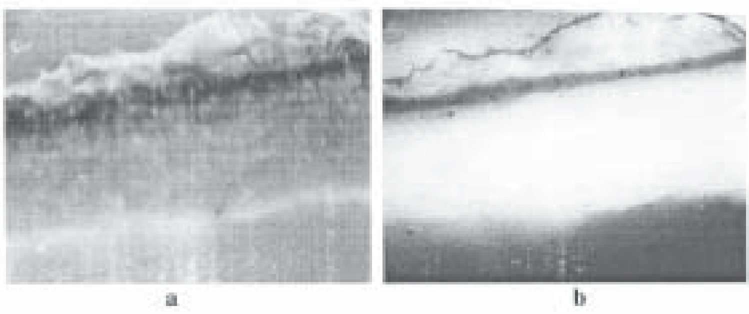
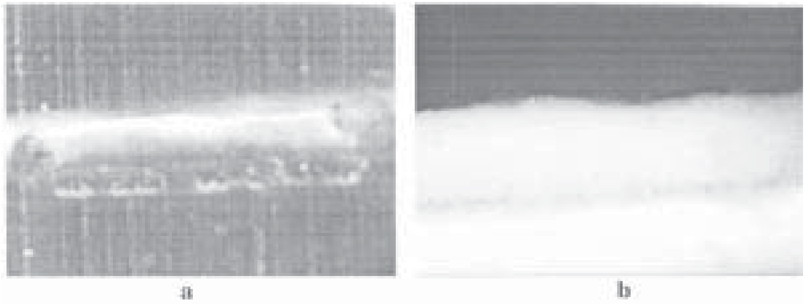


Fig. 3. Micro-stratigraphy of sample 3 (cross-section): a – in Vis; b – in UV



a b

Fig. 4. Micro-stratigraphy of sample 4 (cross-section): a – in Vis; b – in UV

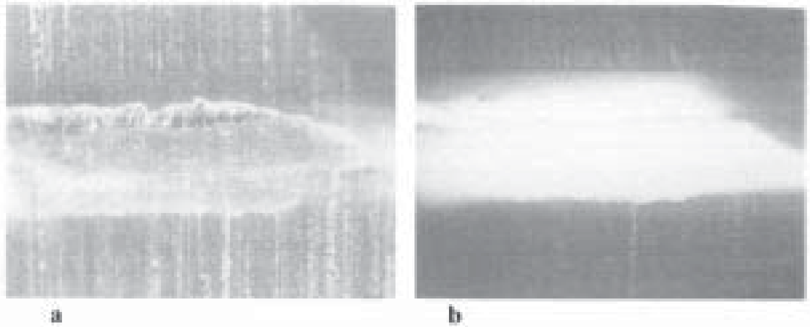


Fig. 5. Micro-stratigraphy of sample 5 (cross-section): a – in Vis; b – in UV

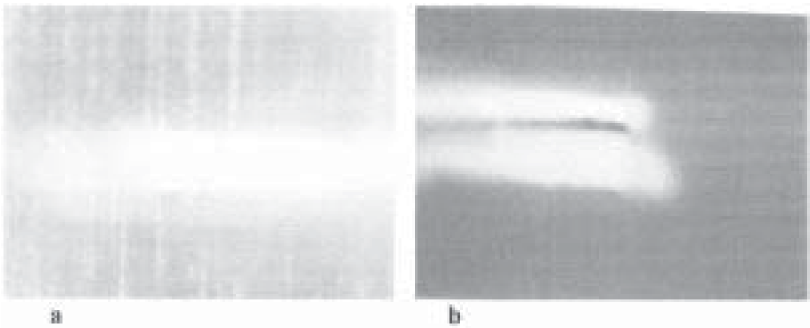


Fig. 6. Micro-stratigraphy of sample 6 (cross-section): a – in Vis; b – in UV

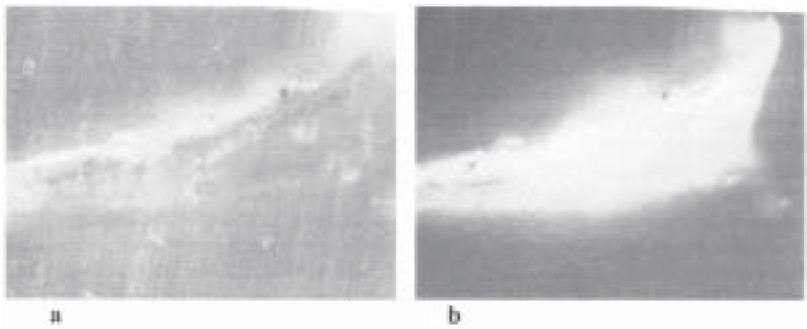


Fig. 7. Micro-stratigraphy of sample 7 (cross-section): a – in Vis; b – in UV

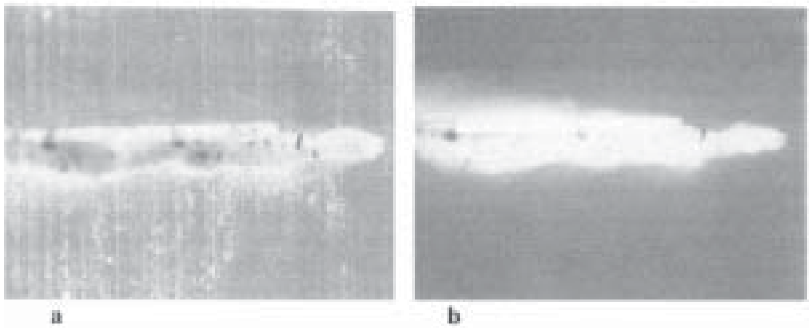


Fig. 8. Micro-stratigraphy of sample 8 (cross-section): a – in Vis; b – in UV

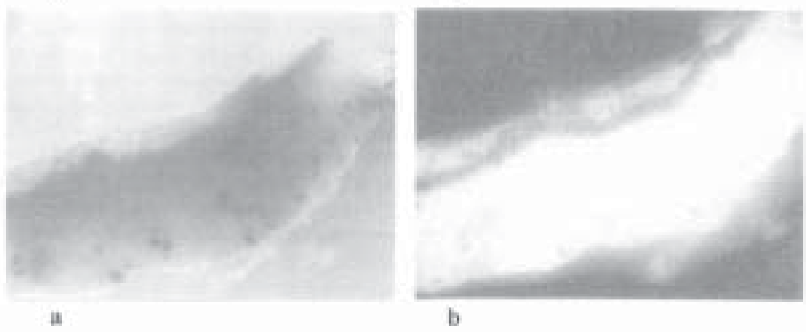


Fig. 9. Micro-stratigraphy of sample 9 (cross-section): a – in Vis; b – in UV

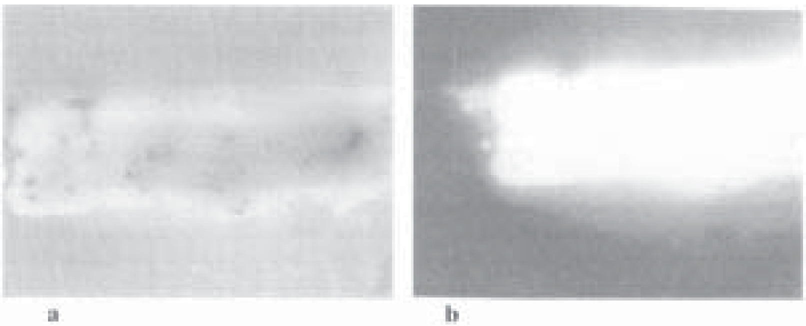


Fig. 10. Micro-stratigraphy of sample 10 (cross-section): a – in Vis; b – in UV

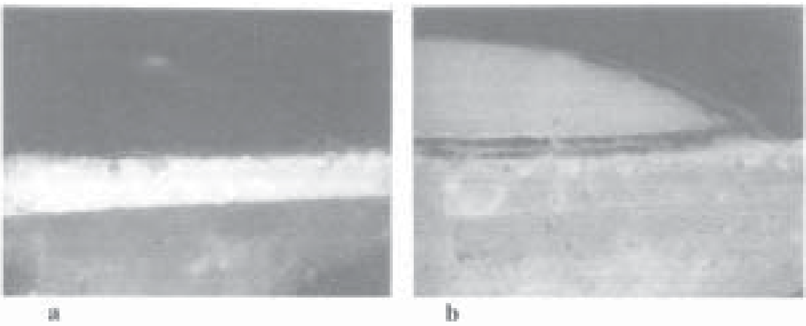


Fig. 11. Micro-stratigraphy of sample 11 (cross-section): a – in Vis; b – in UV

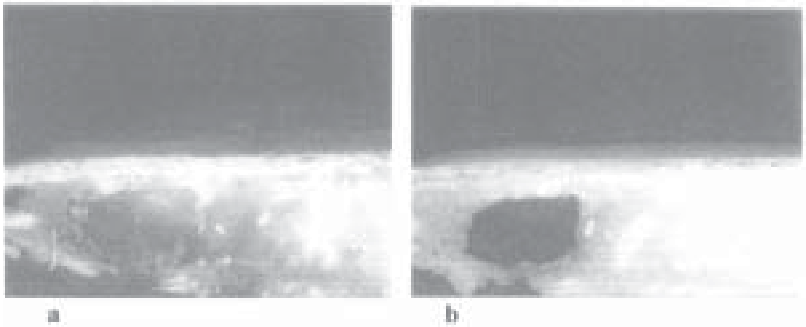


Fig. 12. Micro-stratigraphy of sample 12 (cross-section): a – in Vis; b – in UV

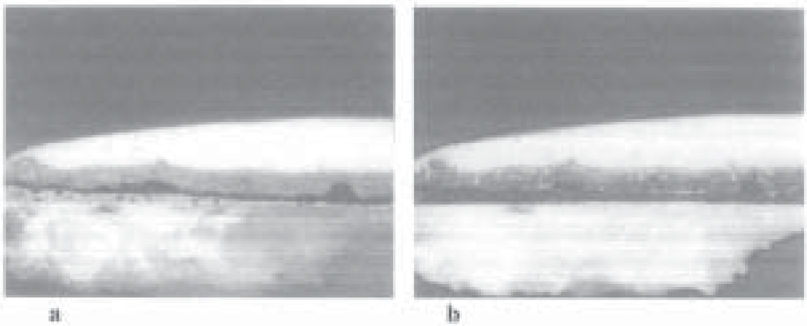


Fig. 13. Micro-stratigraphy of sample 13 (cross-section): a – in Vis; b – in UV

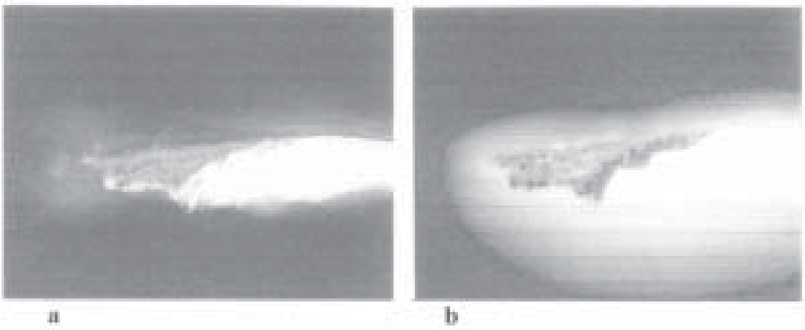


Fig. 14. Micro-stratigraphy of sample 14 (cross-section): a – in Vis; b – in UV

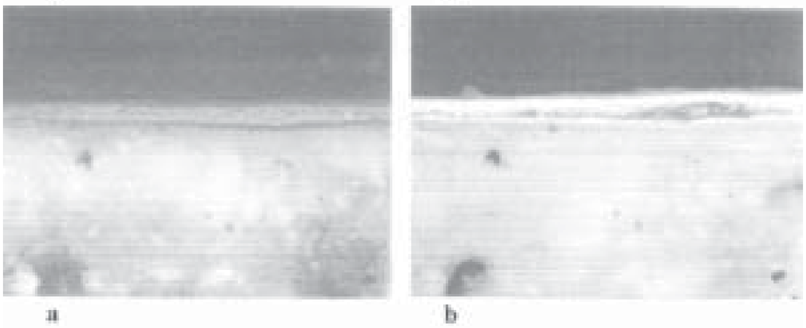


Fig. 15. Micro-stratigraphy of sample 15 (cross-section): a – in Vis; b – in UV

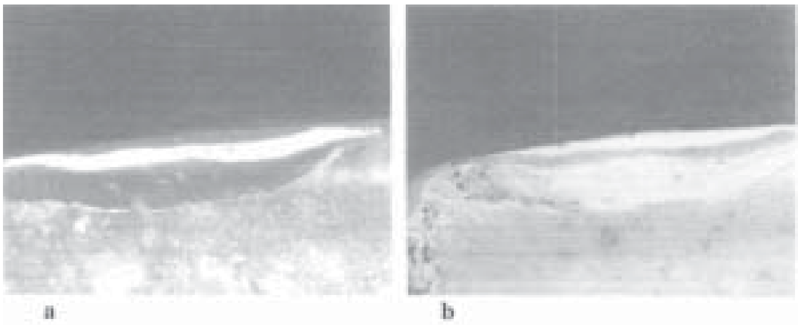


Fig. 16. Micro-stratigraphy of sample 16 (cross-section): a – in Vis; b – in UV

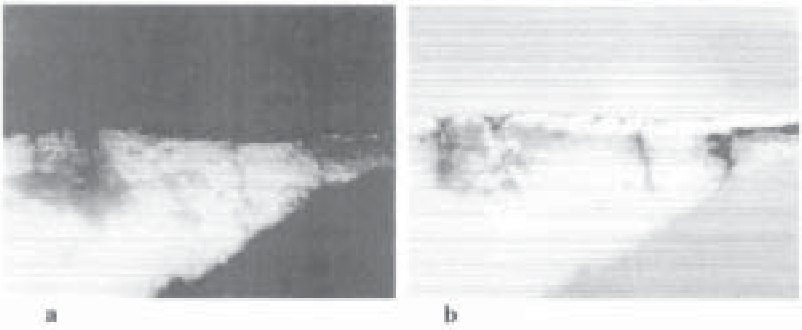


Fig. 17. Micro-stratigraphy of sample 17 (cross-section): a – in Vis; b – in UV

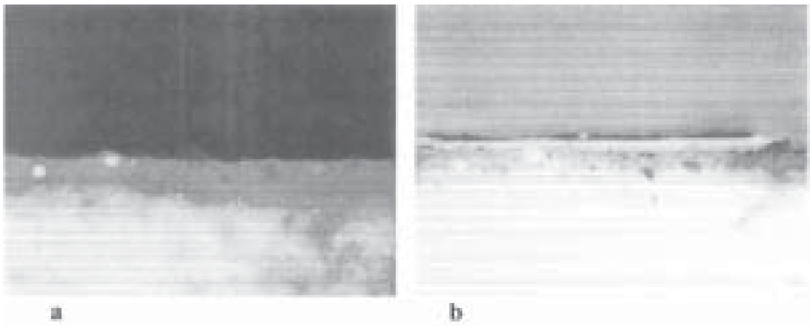


Fig. 18. Micro-stratigraphy of sample 18 (cross-section): a – in Vis; b – in UV

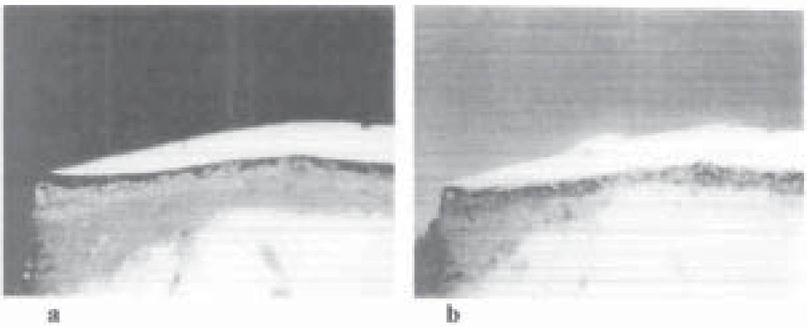


Fig. 19. Micro-stratigraphy of sample 19 (cross-section): a – in Vis; b – in UV

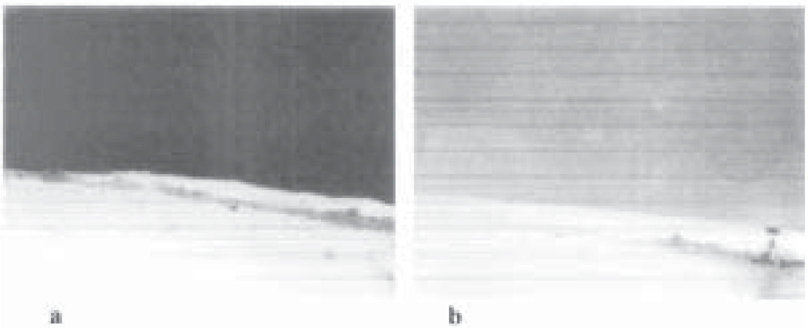


Fig. 20. Micro-stratigraphy of sample 20 (cross-section): a – in Vis; b – in UV

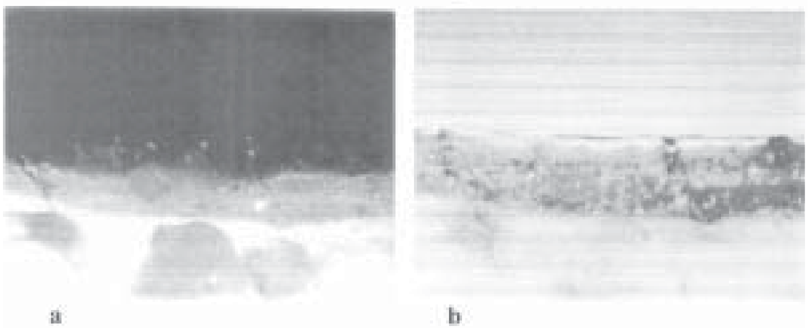


Fig. 21. Micro-stratigraphy of sample 21 (cross-section): a – in Vis; b – in UV

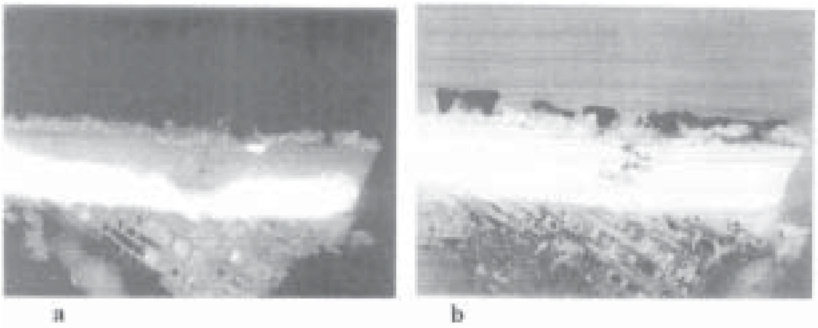


Fig. 22. Micro-stratigraphy of sample 22 (cross-section): a – in Vis; b – in UV

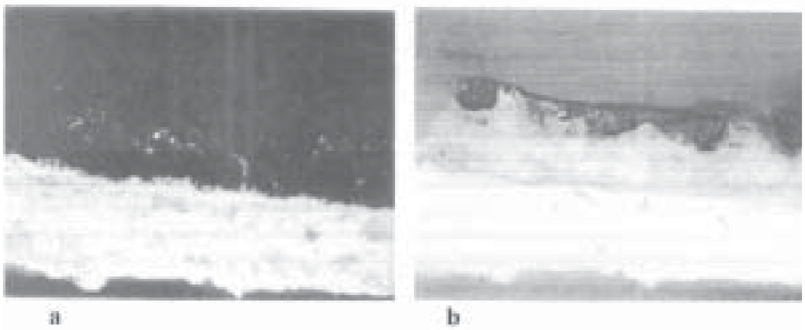


Fig. 23. Micro-stratigraphy of sample 23 (cross-section): a – in Vis; b – in UV

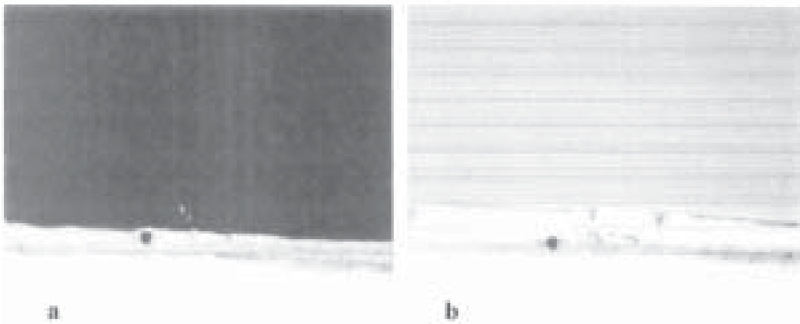


Fig. 24. Micro-stratigraphy of sample 24 (cross-section): a – in Vis; b – in UV

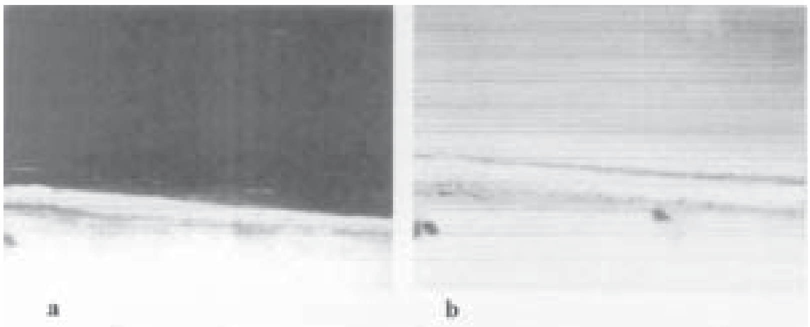


Fig. 25. Micro-stratigraphy of sample 25 (cross-section): a – in Vis; b – in UV

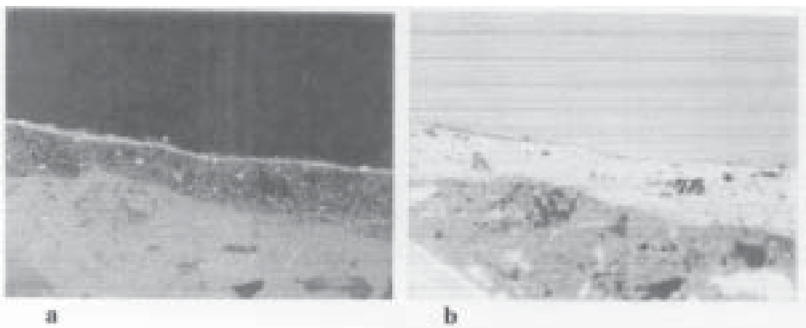


Fig. 26. Micro-stratigraphy of sample 26 (cross-section): a – in Vis; b – in UV

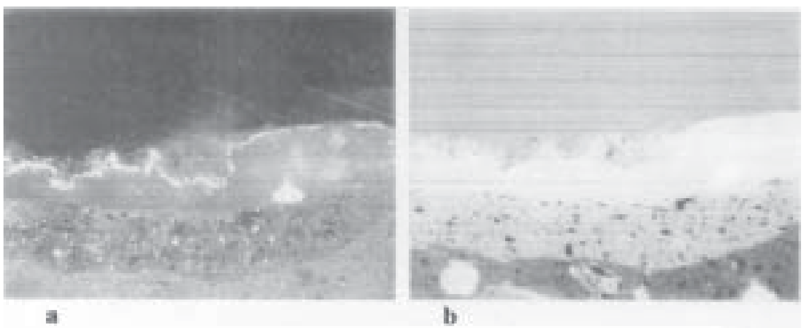


Fig. 27. Micro-stratigraphy of sample 27 (cross-section): a – in Vis; b – in UV

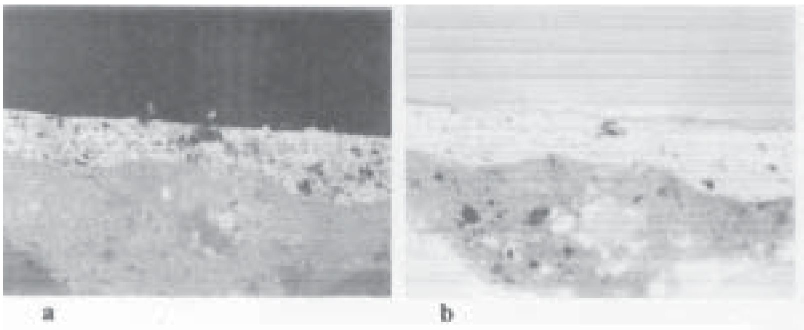


Fig. 28. Micro-stratigraphy of sample 28 (cross-section): a – in Vis; b – in UV

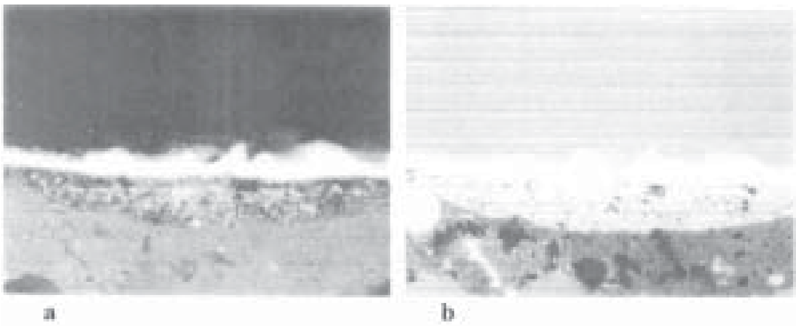


Fig. 29. Micro-stratigraphy of sample 29 (cross-section): a – in Vis; b – in UV

The stratigraphic photos from figures 1 – 29 are obtained in visible and UV lights, respectively, on cross sections which have been subjected to histo-chemical micro-analyses and are corresponding to the area for which the FT-IR spectra and the FT-IR-micro have been carried out. The data from these photos have been correlated with those obtained by the gas-chromographical analysis [20] and the IR spectro-fotometrical one [21] on the basis of which there have been rendered evident the nature, arrangement and the modifications undergone in time by the basic pictural materials, namely, binders, pigments and the filling materials from the preparations, respectively. Thus, there have been established the composition of the preparation layers which are from plaster or chalk powder for the wooden icons and from red earth and oil for the textile support icons, then the composition of the polychrome layer made up of proteinaceous binders in the case of the wooden icons and of lipids binders (some also containing mixion traces) in the case of the canvas ones, together with various pigments and varnishes from the 18-th and 19-th centuries. In the case of the vernises, this method has allowed, besides the establishing of their chemical nature (oleous-resinous, proteinaceous or resinous), the rendering evident of the conservation state (non-uniformity of the film, clogged residues, wax deposits, cracks / craves, etc), the forgery attempts (samples 19 – 21 and 24, 25), the gilding traces (samples 26, 27, 28, 29), faked gilding (sample 17), etc.

At the same time, there must be noticed the fact that no matter how much experience an analyst may have, he cannot be sure of his interpretation on an experimentally-obtained data system, by using a single identification method. This is the reason why he must by all means resort, in his authentication expertise, to the co-assistance or corroboration system between two or more methods from different analysis techniques. In our example, for the majority of the cases which have put identification problems, we have resorted to three instrumental methods, very different as technique and way of interpretation / estimation of the experimental results. Thus, for establishing some conclusive and exhaustive authentication characteristics or attributes (in the case of the pictural materials with a precarious conservation state due to an inadequate exhibition or storage, to forgery attempts or incompatible chromatic reinstalements) there have been corroborated the data obtained by micro-stratigraphy with those obtained by means of the FT-IR spectrophotometry and pyrolytic gas-chromatography, with or without silylation, published in two previous papers [20, 21], methods which have allowed precise identifications (for degradated binders, “highlights”, degradated red varnishes and pigments, etc.).

Thus, the majority of the data obtained by micro-stratigraphic analysis have been corroborated with those obtained by pyrolytic gas-chromatography, with or without silylation [20], by IR, FT-IR spectrophotometry and FT-IR micro, respectively, [21], data which have allowed arti-factometric or archeo-metric authentication estimations for the determination of the attributes from the open causal series such as material / artistic technique / accomplishment procedure technology or accomplishment procedure area / usage area / time impact / interventions / usage traces, etc.

Conclusions

The experimental data obtained by the micro-stratigraphic analysis, implying the “cross-section” and “staining test” techniques, on a series of icons on wood and canvas supports from the 18-th and 19-th centuries belonging to monachal and private collections from Moldavia (Romania), have allowed us to state the following conclusions:

- there has been succeeded, to a great extend, the identification of the nature, the arrangement and the modifications undergone by the main components of the preparation layers, the polychrome films and vernises; however, there have also existed some exceptions which, due to the precarious conservation of the pictural materials have made the analyses difficult;

- there have been established the causes of some degradation processes as well as the deteriorations due to the endogenous factors (for instance, the incompatibility between materials during the accomplishment procedure) and to the exogenous ones during the inadequate exhibition and conservation of the new materials, during some interventions of active preservation and incompatible restauration or even during some forgery attempts;

- regarding the preparation layers of the wooden icons from the 18-th and 19-th centuries, the plaster is the most usually encountered filling material which, as compared to the chalk powder, does not form deep early and old cracks despite the fact that it has a poor acid hydrolysis incompatible with the cellulosic supports; the wettability of the plaster gives the preparation a better elasticity and plasticity than in the case of the chalk powder which imposes, especially when used on the panels made up of more parts, the employing in the preparation of the "maruflated canvas", disposed on the entire surface of the panel or along the area where the parts are being glued;

- in the case of the clogged vernises, thinned or with adhesive deposists, the remains of the metallic pigments after the gilding have a somewhat stratigraphic continuity on the wooden paintings and are strongly divided into fragments on the painting on the coarse-threaded flax linen due to the fragility of the preparation, the polychrome film and the vernis under the elongation and compression actions of the canvas which makes it more difficult to identify;

- some old pigments from the structure of the pictural materials with profound deteriorations have also been difficult to identify due to their high degree of division, being shown in the micro-stratigraphy under the form of "highlights", of some clogged or chromatically degraded structures (for instance, the proteinaceous or lipids binders, red pigments and colorants) for whose identification there has been resorted to the corroboration with the data obtained from two other modern techniques, namely, the FT-IR spectrophotometry and pyrolytic gas-chromatography, with or without silylation, previously published in two different papers which form, together with the present paper, a co-assisting system of the experimental data allowing the drafting of a conclusive authentication expertise for the analysed icons.

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