

INDICATIONS FOR THE SELECTION OF RETOUCHING MATERIALS USED IN CONTEMPORARY PRACTICE

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ABSTRACT

The materials used by restorers have to fulfil the criteria of stability and reversibility. For retouching we use artistic materials adopted for this purpose (for example watercolors) and paints specially produced or handmade with selected pigments and resins - acrylic, polyvinyl acetate, until recently also ketone replaced by urea-aldehyde. Producers' positive assessment of the pigment or paint lightfastness and the estimation of the removability based on binder data and even on paint layers ageing test may not provide enough information for an infallible selection of materials to use. Sometimes unintended changes of appearance occur relatively shortly after the completion of the retouching process. Furthermore, in practice, we create the retouching layer-varnish system, more consistent than we assume, which has consequences not only for visual effect but for the removability of the retouchings themselves. It matters especially in the case of varnished retouching layers exposed to light.

Selected results of the research on contemporarily used retouching materials and the examination of some changed retouchings are presented to illustrate the indicated issues and facilitate the choice. They come from wider research conducted since the end of the 1990s, which had been continued up to now within the framework of partial projects

The investigation was based on accelerated light ageing accompanied by instrumental colour assessment and of structural changes imaging by SEM. The conclusions and hypotheses resulting from the removability tests and surface examination by OCT realized on varnished and unvarnished aged paint layers are included in this paper as well.

Keywords

Retouching materials; Paint layer lightfastness; Pigment photoactivity; Removability; Varnished retouchings

1. INTRODUCTION

The disturbance of the aesthetics and reception of the work caused by changes in the appearance of past additions or reconstructed parts of the paint layers of paintings or polychrome sculptures should never be the main reason for their re-treatment, but sometimes it just is. Each subsequent conservation treatment with the use of solvents, but also by mechanical means carries a risk for the original matter and, regardless of what we are inclined to believe - its depletion. Hence, in order to reduce the risk of interventions undertaken solely due to appearing defects of earlier reintegration we should act in accordance with the principles of modern conservation. It means that not only the separate materials used for retouching, but also the retouches themselves, should meet the requirements of high optical stability and reversibility (or more precisely - safe removability).

We have a wide range of materials at our disposal. [1] [2] [3]. Ready-made paints, currently specially produced for restorers, contain acrylic binders, polyvinyl acetate and urea-aldehyde resin, which has been replacing the ketone resin for some time. We also have hand-made paints made of mixtures of pigments with various water- or solvent-borne binders, or artistic

paints adapted for retouching - e.g. professional watercolors - or artistic crayons. We reach for various varnishes. The choice is not always obvious. This may be due to both - the lack of sufficient manufacturer information about the product, as well as occasional awareness or knowledge of users about the applied materials.

1.1. Choice of pigment palette

In any case, it is necessary to choose the paint / pigment palette that will ensure the desired visual stability of the retouching. The producer's promise of the 'highest lightfastness' of professional materials that we use may not be its guarantee.

We are not always aware that the materials we use are not characterized enough, mistakenly assuming that the lightfastness of a pigment given in the ASTM scale gives us a full range of information as to the behavior of the paint layer containing it under the influence of light. [4:141] [5]. Meanwhile, this is not enough knowledge and the lightfastness may not be the final selection criterion in some cases. The conviction of expected chemical inertia of the contemporarily used lightfast pigments must be reviewed. The visible effect of changes caused by pigments are the color shifts of retouching, whitening being one of the most striking manifestations. They were reported as early as 70 years ago as isolated cases [6] [7]. They were also signaled in later conservation literature [8], in reference to a simplified interpretation [9], which - presumably- did not act as a warning. My own observations of both changed retouching [10] and the cases of whitening reported in the studies of some paints [4] were an incentive to undertake detailed investigations aimed at explaining the causes and thus enabling conscious avoidance of the problem.

1.2. Final varnish choice and retouchings removability

The varnish applied to the surface of the painting, apart from the aesthetic functions and mechanical protection, hardly minimizes the negative effects of external factors.

Although it does not really protect the lower layer from UV and visible light, we know that the properties of the final varnish are important for the durability of the retouching features. It is not only about the immediate changes in the appearance that can be introduced by its application [4: 146-154] [5], nor is it

about its influence on the color stability in the ageing process.

We are inclined to assume that the varnish creates a separate distinct layer. However, the question arises whether this is the case with solvent-borne retouch layers varnished shortly after their completion. In this context, an important factor that a varnish may compromise is the removability of retouching. It could be crucial when they are made in the volume of the original layers (for example on abrasions up to underpainting or on damaged glazes).

. However obvious it might be, my experience to date has prompted me to illustrate the issues that are important for the conscious choice of materials with the results of the research below.

2. MATERIALS AND METHODS

2.1. Choice of pigment palette

As was stated in the introduction, the described issues are discussed in this text in relation to the currently used paints - ready-made or hand-made - used to the reintegration of lacunas in the paint layers of paintings and other polychrome surfaces. Nevertheless, the general guidelines for selecting pigments presented below apply to all colored retouching materials. Examples that illustrate them are taken from the investigation of several retouching case studies and from the research on retouching paint layers (mostly made with solvent-borne paints) performed over many years.

2.1.1. Preliminary choice

The method of pre-selecting pigments or retouching paints is to look at the standard-based evaluations of their lightfastness, taking into account different binders and pigment concentrations. If the assessment of the pigment producer and the paint producer do not coincide, and whenever the ready-made paint contains a mixture of pigments, it is advisable to familiarize yourself with the lightfastness of these components [11] [12]. This preliminary information will allow us to predict the possible behavior of the retouch layers when exposed to light.

2.1.2. Visual stability of the paint layers – selected examples

The results of the previous investigations [3], [4], on different retouching paints and a case study from

subsequent research [13] served to demonstrate the influence of the type of binder and the concentration of the chromatic pigment in the paint on the lightfastness of the obtained paint layer. An illustration of these issues was provided by the accelerated light ageing of the paint layers and their colorimetric assessment.

At the same time, the research provided data allowing to consider what rating of lightfastness can be satisfactory in painting conservation.

- The choice and preparation of the paint layer

The above-mentioned issues were illustrated with the use of paint layers with various binders, including the red imitating madder lake, (necessary on the palette), , and Prussian blue. Anthraquinone red pigment - synthetic alizarin crimson (PR 83:1) was used, as well as its monoazo substitute (PR187) called 'Azo Alizarin' and layers based on ready-made paints imitating its hue, containing quinacridone rose (PV19) in mixture with perylene red (PR 149) and ultramarine (PB29). They were tested in full strength and reduced with titanium white rutile PW6 (Kremer Pigmente or titanium white from ready-made paint sets). White was mixed into red in the same proportion by weight in the first series of tests and in the following series of tests [9],[2] until the reflectance (R) of the layer of 30-40% in a minimum reflection (see Figure. 1 in section 3).

Prussian Blue (PB 27) – its ammonium variety Ferric Ammonium Ferrocyanide (Kremer Pigmente, DE) was chosen to be examine in two different binders [13]. Layers were applied in full strength and reduced with rutile type titanium white as above. For Prussian Blue the layers extended with 'Chalk of Bologna' (Kremer Pigmente, DE) - natural inert mixture of gypsum and calcium carbonate (chalk) were made as well.

Examples of conservation paint layers have been selected to illustrate their lightfastness.

For the support of paint layers the glass plates were chosen – to exclude the influence of any absorbing material on the results of the ageing process. Half of the surface of paint layers was covered with varnish (see 2.3.21).

- Accelerated light ageing

Accelerated ageing of the series of paint layers, after their seasoning, was carried out in a xenon arc lamp ageing apparatus. Xenon lamps provided light true to the CIE D₆₅ illuminant and light filters blocking UV and IR radiation were used to simulate indoor daylight. Together with the samples, blue-wool standards (ISO R105) were aged – up to discolouration of 7 standard

of the 4th degree of the grey scale (ISO 105 A02). The radiation dose absorbed by the samples was 'converted' into exposure time under normal museum conditions, that is about 60-100 years (depending on the 200 lx/h or 150lx/h illuminance) [4] [14]. The Relative humidity in the ageing chamber was maintained at 60%.

- Colour and colour change assessment

Colorimetric measurements before and after ageing of paint layer samples were performed using spheric reflectance spectrophotometer using d/8° geometry, CIE illuminant D65, 10° standard observer, and with specular component included and excluded. Color changes was assessed visually and mathematically expressed using color difference ΔE CMC equation (one of the modification of ΔE^* CIELAB formula, introduced by the Color Measurement Committee of the Society of Dyers and Colorists, better correlated to visual assessment).

2.2. Changes of appearance – whitening

A survey conducted among conservators and then a review of the condition of retouchings carried out in the galleries of the main Belgian and Polish museums and several ateliers as early as in the 1990s, supplemented in later years each time when visiting permanent museum exhibitions, allowed to register, among other things, changes in retouching consisting in whitening.

2.2.1. Case studies of whitened retouchings

In the case of whitened retouching observed during the review, efforts were made to determine the time, technique and composition of the altered retouching. At the beginning, a query was conducted - a review of annotations and conservation reports as well as an interview in museum studios. The next step was to make macroscopic observations in VIS and UV followed by microscopic examination. The composition of whitened retouches in the selected cases was analysed [15] [16]. The elemental composition was determined spectroscopically (XRF) and the crystal structure of the pigments present in the sample was defined by X-ray diffraction (XRD). In individual cases, it was possible to perform GC-MS analyzes in order to determine the kind of binder.

2.2.2. Mock-up paint layers examination

The results of the whitened retouchings analyses were an incentive to conduct further tests on specially made

samples. All the more in view of the already noticed whitening of the aged layers of paints factory-modified with white, considered as screening and being the same ones as those found in the whitened retouchings [4: 158, 167]. Mock-ups were made to confirm the possibility of similar changes and to investigate them.

- Paint layers preparation

Pigments and paints were selected for testing and their pigment content was instrumentally determined by XRF and XRD analyzes.

The samples were made in such a way that it was possible to make observations at the fractured cross-sections. Light blue paint layers containing white pigments selected on the basis of the content of the whitened retouchings and mixed with cobalt blue (PB 35, Kremer Pigmente) in predetermined proportions, were applied to the substrate made of a chalk-containing ground, applied to a thick polyester foil and insulated with varnish. The painting layers were made with solutions of Paraloid B-72, dammar and ready-made paints - acrylic dispersion (Cryla Flow Artists') and gouache (Designers' Colour Extra Fine, Talens). Some sample surfaces were insulated with acrylic varnish made of poly isobutyl methacrylate (Acrylic Varnish Glossy, 114, Royal Talens, NE) and dammar varnish of own production. After three months of seasoning, the samples were subjected to accelerated ageing.

2.2.2.2. Artificial light ageing

Accelerated ageing was carried out in the manner and under the conditions described above in the ALPHA High Energy Xenotest (see 2.1.2)

2.2.2.3. Assessment of changes of appearance

Changes in the samples due to ageing were observed under microscope. and instrumental colorimetric assessment was made as previously described (see 2.3.).

2.2.2.4. An attempt to determine the nature of changes

In order to initially recognize the type of changes in the structure of binders contained in the whitened layers tested, comparative tests of several samples were performed. The FTIR spectra obtained from the batch of aged and non-aged identical resin film samples and paint layers were compared. Due to the small amount of research material and the content of

various polymers in the samples simultaneously, the research was merely indicative.

- Imaging of structural changes in whitened paint layers

Due to the limited possibilities of chemical analysis, it was decided that the changes observed visually, recorded by colorimetry and initially analytically confirmed, were to be visualized by means of a scanning microscope. Fractures were made of selected samples of the paint layers, not covered with varnish and varnished, both in original and aged areas.

2.3. Final varnish choice and retouchings removability

The stability and removability of conservation paints is generally tested without any varnish insulation layer to know the response to light ageing of the paints themselves [17] However, to finish retouching work we generally cover them with varnish. It was decided to compare the solubility of aged layers containing different pigments in masstone and reduced to tint, both unvarnished and varnished and to attempt an interpretation in order to draw practical conclusions.

2.3.1. Samples preparation

Paint layers obtained from various hand- and ready-made solvent-borne paints currently used for retouching were selected for the tests. Both layers covered by varnish and without unvarnished were tested. The selection of materials - paints and varnishes - was made on the basis of the available assortment and the popularity of use.

Paint layers obtained from pigment mixtures (Kremer Pigmente) were represented with acrylic copolymer solution Paraloid B-72, poly-vinyl acetate solution (type Mowilith 20), both in proportions based on previous experiences and the calculations of pigment volume concentration. The ready-made paints were ketone-based containing poly-cyclohexane (RestaurArte, Bresciani and Maimeri), acrylic-based poly-n-butyl methacrylate with poly-isobutyl methacrylate addition (MSA Golden), mastic-based paints (Restoration Extrafine Varnish Colors, Maimeri) and urea-aldehyde resin Laropal A81-based paints (Conservation Paints, Gamblin). Charbonell acrylic-ketone paints, long discontinued, were omitted in the text. The layers were tested in sets consisting of titanium white and nine different chromatic hues mixed with it and applied in masstone. The aim was to

create sets with identical hues and pigment composition, however, in ready-made paints, a given color was not always created by the same pigment [3] [4, 200-201]. (Tested hues are indicated on Figures 4. and 5.). Unpigmented films of binders and varnishes were also created. All samples were applied with a clean brush to glass plates in separate bands made one after the other had solidified. No attempt was made to reproduce the actual layout present in retouching [18] (mastic - isolation varnish - retouching / with isolated underlayer or without / - final varnish) but only the top layers to avoid additional factors influencing the interpretation. The varnish was applied on half of the surface of dry paint layers. For most samples polyisobutyl methacrylate (Acrylic Varnish Glossy, 114, Royal Talens) was used. For PVAc layers polycyclohexanone varnish (G. Berger's OF BEVA Finishing Varnish, CTS, formerly constituting a set with this binder) and for samples with Laropal A-81 (Gamblin) varnish of hydrogenated hydrocarbon resin RegalRez 1094 (Eastman) self-made, stabilized with Tinuvin 292 were applied. They were diluted in white spirit. After varnishing, the samples were re-seasoned.

2.3.2 Accelerated light ageing

After seasoning, the samples were subjected to accelerated ageing - in the manner and under the conditions described in section. 2.1.2.2

2.3.3. Removability tests

The determination of removability was supported by solubility tests performed initially on selected paint layers, briefly reported earlier [3] [4], and then on all aged ones, repeated twenty years later, after being stored non exposed to light. The tests were made in a comparative manner on the same aged layers without varnish and varnished. A set of solvents and their two-component mixtures was used for testing, creating a scale of increasing polarity (and 'solvent power'). It was inspired by the famous proposal of Robert Feller [19].

To bring the test results closer to the common conservation practice, white spirit was used instead of cyclohexane (a mixture of aliphatic and aromatic solvents with experimentally determined proportion; it obviously had an impact on the solubility parameters of the first steps of the scale).

Table 1 – Solvents and mixtures for removability tests

White spirit	toluene	acetone	Nr
100	-	-	1
75	25	-	2
50	50	-	3
25	75	-	4
-	100	-	5
-	75	25	6
-	50	50	7
-	25	75	8
-	-	100	9

Solvents were applied to the paint layers in the form of drops and the result was observed after 45s by applying a blotting paper. The time slot finally used in the protocol was determined after performing the preliminary tests as sufficient to make observations for tested layers with different solubilities. The tests were repeated many times, taking into account local differences in the thickness of the layers applied with a brush, which may affect the results obtained. Whenever it was necessary to extend the operation time, the application was repeated. It was assumed that - due to, among other factors, the non-absorbency of the sample substrate - the test results is not a direct determinant of the solubility of the actual retouch layers - especially its speed - but an indicator of removability limitations of the systems such as the tested ones.

In order to complement the observations and tests, the varnished / unvarnished boundary surfaces of the selected samples were analyzed by the optical coherent tomography (OCT) method.

3. RESULTS AND DISCUSSION

3.1. Choice of pigment palette

3.1.1 Preliminary choice and assessment of lightfastness of paint layers – chosen examples

The ASTM assessment for a given pigment in various binders provides preliminary data [20] - if available. ASTM rate for natural alizarin Crimson (PR 83) and its synthetic imitation (PR83:1) is III (i.e. fair) in oil and acrylic binder and IV (poor) in watercolors. The monoazo substitute (PR187) of those anthraquinone

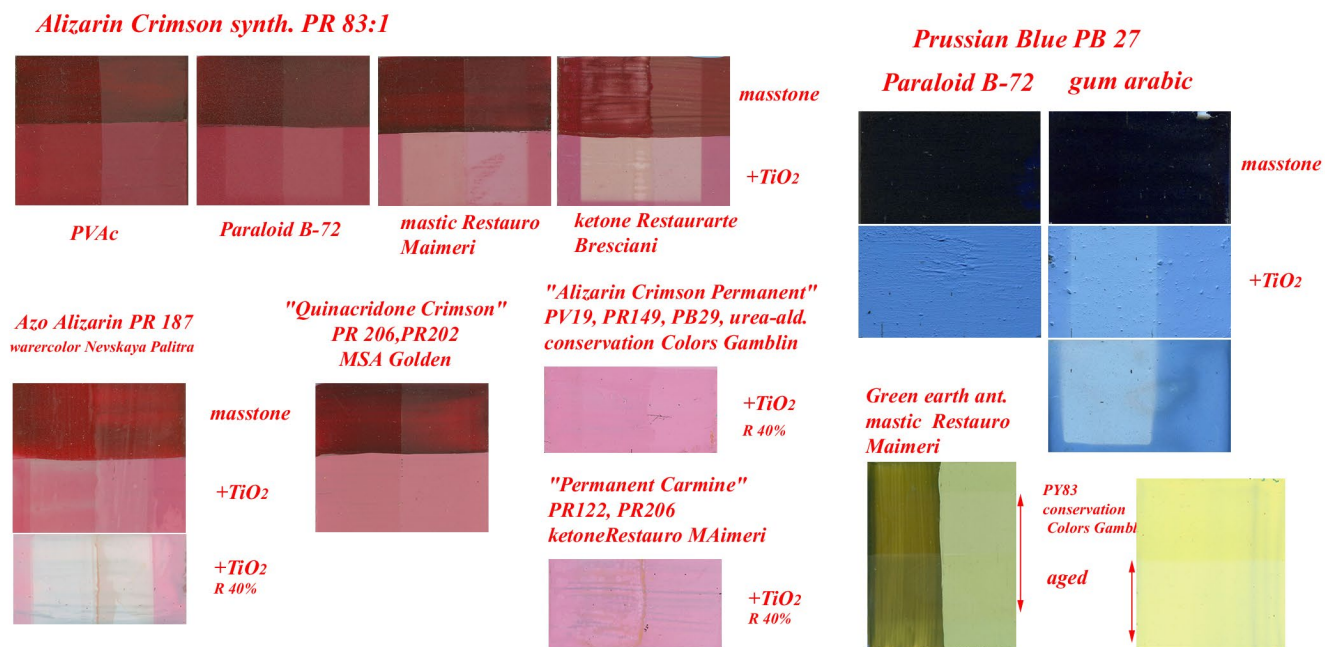


Figure 1 – Lightfastness of pigments in paint layers

pigments is assessed as II, but in some suppliers' websites it can achieve lower marks. Quinacridone pigment (PV19), is rated as I for oil and acrylic binder, II for watercolours, its rate can also depend on its hue (rose tints are less stable). What is signaled is the dependence of pigment lightfastness in the paint layer on the type of binder and its protective properties. The next step in the preliminary selection is to search for the data marked according to the Blue Wool Standard (BWS) eight-point step, taking into account the pigment concentration. And so, alizarin crimson achieves 7 in full tone, and only 5 in tint, while its synthetic counterpart PR 83: 1 - 7-8, 7-8, 6. For PV 19 it is differentiated - depending on the binder, from 8;8;8 to 6;6 [20]. In the case of mixtures of pigments contained in the ready-made paint, the comparison of their lightfastness allows us to assume how the color of the layer obtained from it may evolve when exposed to light. For a mixture of PV 19 and PR149 (perylene red), as long as PV 19 is used in a more durable purple variant, its shade may become dominant over time. In the case of Prussian blue, it is even clearer that stopping at the ASTM assessment, high (I) for various binders is insufficient, its instability at a lower concentration (in tints) is indicated by the BWS assessment [20].

The truth of these indications was confirmed experimentally [Figure 1]. As is demonstrated by the results of the ageing of paint layers containing synthetic alizarin, in full tone its durability in various binders used for retouching does not visually raise any objections, and the changes registered by colourimetry are very insignificant. When slightly reduced by the addition of the same amount of titanium white, the differences in lightfastness between layers with different resins become clear. [Figure 1] The layers with ketone and mastic binders turn out to be very unstable. Nevertheless, what is significant, there are also visible differences in lightfastness of layers with stable polymers - Paraloid B-72 and polyvinyl acetate – surprisingly to the disadvantage of the first, more stable resin. It is likely that the inconsistency results from a different interaction of the anthraquinone pigment itself with these polymers [21]. The comparison of watercolor layers containing PR 187 in various concentrations reveals its clear instability in light tint (reduced to R ~ 40%). The example of paint layers of Prussian blue with gum arabic and Paraloid B-72 confirms its high rating in full tone. However, reduction with titanium white makes the differences in the layers with different binders easily legible. [Fig. 1].

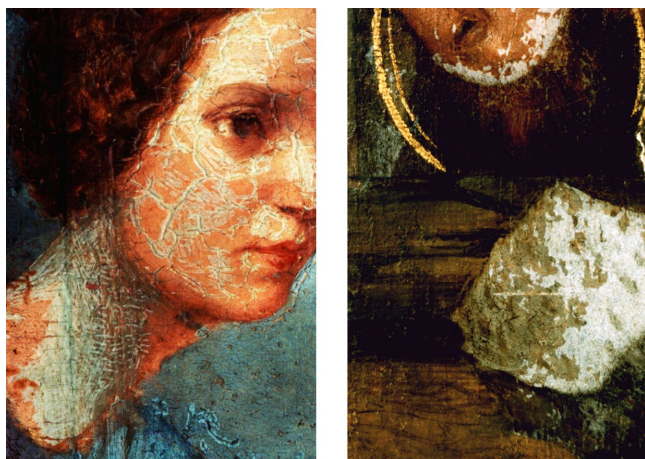


Figure 2 – Examples of whitened retouchings-fragments of paintings: W.K Stattler, Portrait of Potocki, National Museum Warsaw, phot. W Górski, A, Skowroński; Legend of St. Victor, n 13, Mechelen St Rombault Cathedral, phot. E.Szmít-Naud

When reduced with the ‘chalk of Bologna’ extender, it becomes explicit due to changes in the color properties of the pigment and possibly also of the binder. [13] The comparison of those two layers containing gum arabic confirms that titanium white, although strongly scattering light in the layer, nevertheless plays a screening role.

The conducted research also provokes reflection on the ratings of lightfastness presented by paint manufacturers. Among the presented examples, both professional artistic watercolor (Madder Lake Light Red) and conservation paints: Indian Yellow Permanent urea-aldehyde and Antique Green Earth mastic were rated the highest by the manufacturer. Meanwhile, the changes resulting from ageing are clearly legible, which in the case of red and yellow (PY83, diarylide yellow HR70) should be associated with their lightfastness. In the case of green earth, which is a mixture of lightfast iron earth pigments, the changes are greater in the layer without white. They probably result from the interaction of light on the paint components and from the interaction of iron pigments with the mastic binder [4: 116, 161].

Most likely the paint producer's rating simply corresponds to the assumptions according to which the highest lightfastness, i.e. I degree ASTM and 7-8 BWS, is given when changes reach $dE = 4$, and the rate II and BWS 6, i.e. ‘very good’, is accepted, [7] although it even means changes between $dE 4$ and 8. However, do we accept such a level of changes? Will

they actually not occur before the predicted time? Already in the classification proposed years ago (the first time in 1975) by Robert Feller [19], materials obtaining the 6th BWS degree were considered ‘intermediate’.

My research and observations confirmed that changes in the color of the samples in the vicinity of $dE\ CMC = 2$ are clearly visually noticeable (which corresponds to $dE^* ab$ formula from ~ 2 to 4.5 depending on the color parameters of a given pigment). They appeared on aged samples when the change of the BWS 7 standard became noticeable.

The current year will see the end of the research presently conducted by the ASTM Subcommittee with Golden Artist Colors, Gamblin Artist Paints and Natural Pigments with the aim of developing a new testing method for artist's materials [22]. Let us hope that they will bring new opportunities in this matter.

3.1.2. Changes of appearance induced by the lightfast pigments - case studies of whitened retouchings and mock-up paint layers examination.

Ultimately, the results of the overview revealed that whitened retouching accounts for almost 1/5 of all cases where unwanted changes in the appearance of retouching are noticeable. Conservation records and documentation allowed to establish that the whitening may occur very quickly after retouching is completed - after 2-3 years or even a year. The data on the technique of whitened retouching was more difficult to pin down, especially since corrections were made in some cases - sometimes to whitened retouchings themselves! Nevertheless, it was possible to conclude, based on the information about the materials used in the studios at a given time, that whitened retouching could be made with very different techniques, homogeneously or in combinations: with oil and oil paints combined with dammar or mastic, ready-made oil-resin paints, pigments with natural resins, later also synthetic ones, mastic paints, gouache and watercolor [15][16]. Observations made in situ occasionally allowed to notice the detachment of the varnish and chalking under it, but also whitening in the subsurface layer or in the entire thickness of the retouching without the loss in its cohesion. None of the whitened retouching was subject to permanent ‘regeneration’ with solvents or resin solutions. The gloss of the altered areas was varied. Unlike other retouching, the whitened ones showed in UV radiation gray, bluish

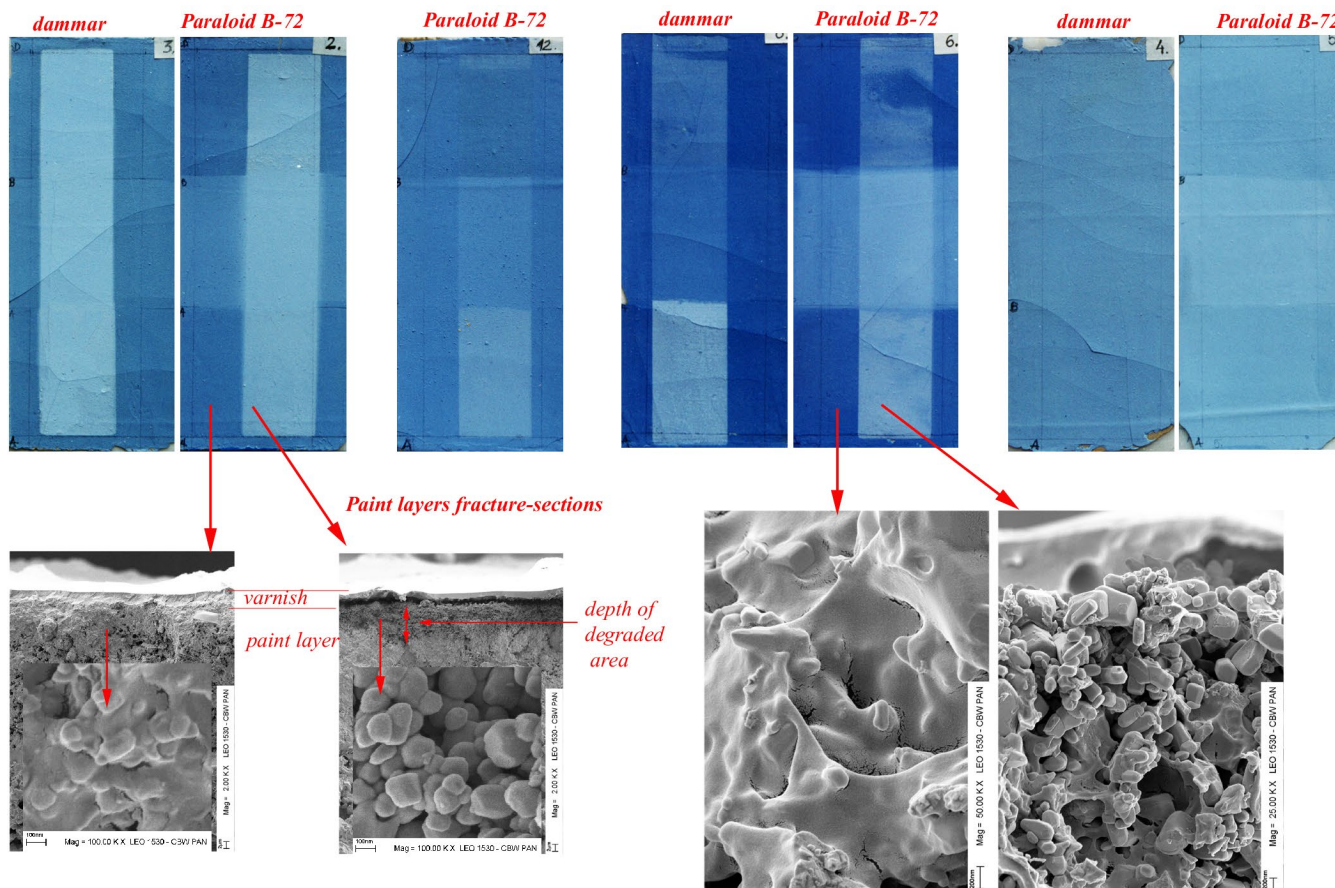


Figure 3 – Whitening of mock-up paint layers containing zinc white (PW4, and titanium white (PW6) rutile and anatase

gray or gray-violet appearance. Whitening occurred in the retouched parts of skin, sky, light robes and other light ones. Their pigment composition was examined in fifteen paintings. Apart from a small amount of color pigments adapted to the part of the retouched image, the analysis identified predominantly white pigments. The common feature in the composition of the whitened retouchings was the presence of zinc white (zinc oxide) and titanium white - titanium dioxide in the anatase crystalline form, sometimes both at the same time. They were sometimes supplemented with lead white and fillers - barite or chalk.

In the case of a retouchings containing zinc white (whitened after a year!), made with watercolors saturated with dammar varnish and another unchanged one from a dark part of the same image, it was possible to compare their spectrum in the infrared, which allowed to observe a difference suggesting the

occurrence of acid decarboxylation, indicative of the binder degradation.

The results of mock-up analyses revealed an intense whitening of the initially blue paint layers, containing titanium dioxide anatase and those containing zinc oxide in both binders, i.e. in Paraloid B-72 and in the dammar, both with and without varnish. In the varnished parts, the chalking at their contact with the paint layer was so strong that it caused the varnish to detach. In the samples with anatase, the dammar varnish was even flaking. However, it was generally noted that all whitenings are not exclusively superficial. Samples in which anatase was present in equal proportions with barite or with rutile titanium dioxide whitened less, regardless of the type of paint (acrylic or gouache). Barely visible but instrumentally recorded changes occurred where anatase was only an admixture to rutile. Colorimetrically assessed slight color changes in the sample with rutile only did not

consist in whitening. The comparison of the reflection spectra of the samples before and after ageing confirmed that the whitening is not a discoloration. The indicative results of comparative instrumental analyzes (FTIR) of both unaged and aged film of the resins themselves and of whitened paint layers containing them, exposed differences suggesting the occurrence of structural changes in the resins present in the whitened samples. The SEM scans of the fractures of several whitened samples clearly showed a loss of resin volume in the varnish layer at the contact with the paint layer, visible as an empty slit and the exposure of pigment grains below to a depth of several micrometers [Figure. 3]

The changes observed as whitening of the retouching in the bright parts of paintings, described already in the 1960s, were associated with the presence of zinc oxide in them and were explained by the chalking of oil binder and dammar and / or the fading of organic pigments in its presence [6] [7]. The studies described above distinctly illustrate the fact that also titanium white can cause them with greater intensity, and these changes are also subject to resins other than dammar, e.g. acrylic, also those with proven chemical stability, such as Paraloid B-72, which was confirmed by subsequent studies [23] [24]. It was not until relatively recently that the specific interest in the problem of whitening has been renewed in publications addressed to conservators [25], [26], however, already more than 70 years ago researchers working in the field of polymer chemistry dealt more widely with the properties of zinc white, then titanium white and their interactions with the environment causing or enhancing chalking of binders in their presence. The bibliography for this topic and extensive explanation were cited earlier [4:121-126; 166-171]). They can be summed up by the statement that both zinc oxide and titanium dioxide exhibit photocatalytic activity, inducing radical reactions leading to the degradation of binders. The reason for such properties of zinc white, not recognized by all, are the imperfections of the crystal lattice of this oxide and their degree, closely related to the production method. As a result, some varieties may not display them. [27: 42,44] [28] The fluorescence color of the pigment in UV may be an indication, but my own observations did not confirm the possibility of differentiating on this basis [4: 122-123]. In the case of titanium dioxide, both of its crystalline varieties (anatase and rutile) used as pigments show photocatalytic properties resulting from the semiconductor nature of this oxide and can

induce oxidative degradation. This activity is limited in various ways, including by treating the surface of the pigment. The rutile variety is modified in this way, and in the case of anatase, which is more photochemically active, the ability to cause chalking is even used in external 'self-cleaning' white paints. The effects of the above-mentioned mechanisms, perforce only briefly signaled, are confirmed by the results of the presented research. One may wonder about the fact that zinc oxide, considered to be less photochemically active than titanium dioxide and, similarly to it, strongly absorbing UV, is still used as a screening pigment and added to other paints. However, whitened retouching and mock-up layers could contradict the thesis about its protective effect, especially when it is present in a significant proportion. In addition, in the case of zinc oxide, due to its alkaline nature (pH 7.1-7.5), whitening can also be seen as an outcome of its reaction with the environment, i.e. with the components of binders and air pollutants. The result will be salts (including soaps), also white. Identifying the possible products of such reactions in the course of the described research was not feasible due to the insufficient amount of research material. Therefore, although the registered changes indicate the degradation of binders, the other mechanism cannot be excluded, either.

It should be noted that, although in the described cases, the changes in the appearance of the paint layers are striking, titanium and zinc whites are not the only reactive pigments or those showing photocatalytic properties present on our palettes, [4: 126][29][30], The possibilities for further research into the noticeable changes caused by these properties of the pigments in use have not been exhausted.

3.3. Removability of varnished retouchings paint layers

When varnishing the paint layers of individual sets of retouch paints, clear differences in absorption were visible. In order to insulate the surface, the layers of ketone paints required multiple varnish applications, while acrylic and mastic layers only two, and polyacetate and urea-aldehyde paints – a single one. Already during the research on the effect of varnish application on the appearance of the painted layers of these sets, the dependence of luster on the type of pigment and the addition of white, as well as the type of paint binder [4: 150-154] [5] was clearly visible in each of them. Varnishing and ageing did not blur those

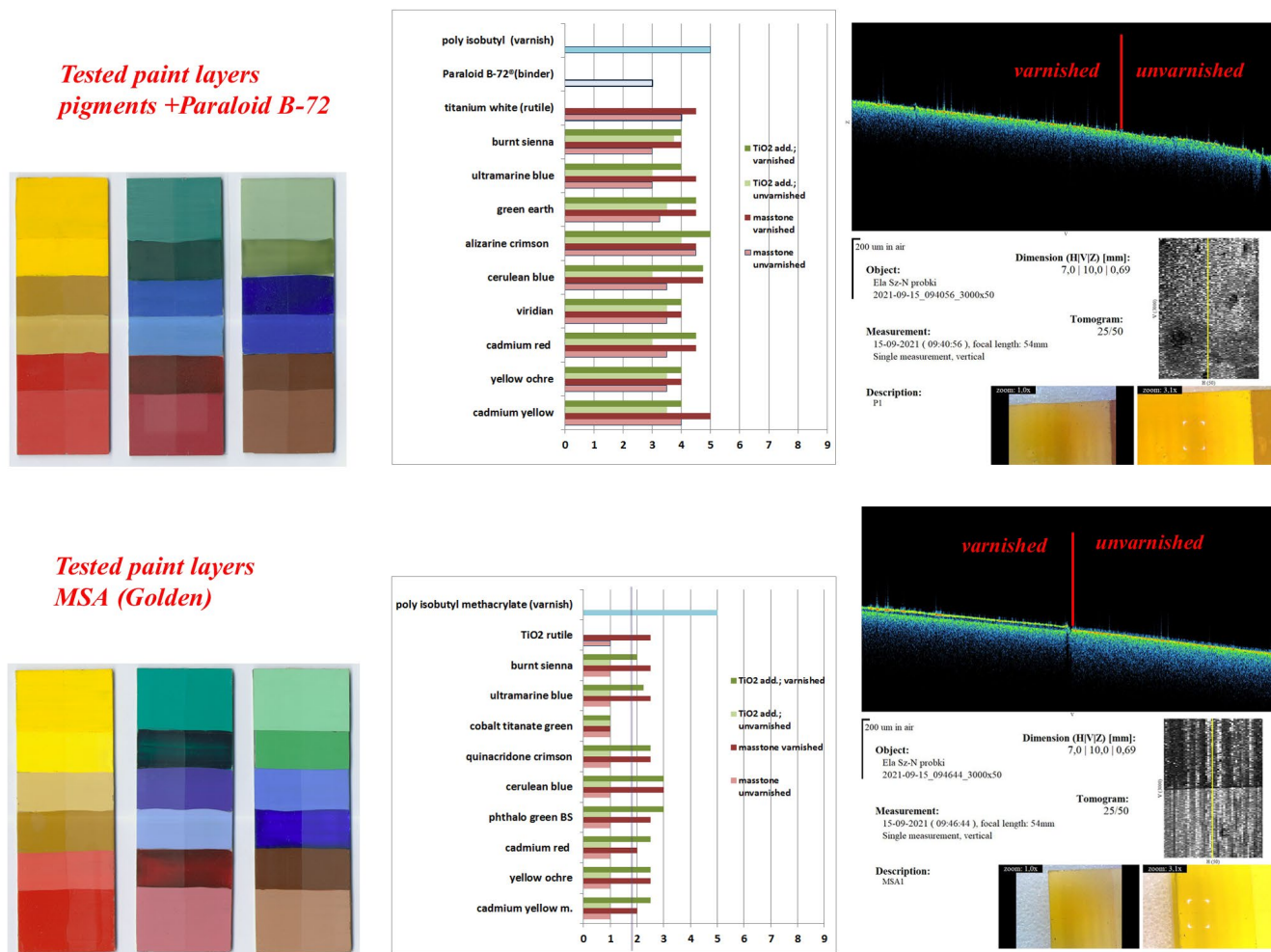


Figure 4 – Removability and surface OCT imaging of varnished and unvarnished paint layers - aged acrylic paints example

differences. It is not surprising that the unvarnished paint layers containing only titanium white (rutile), regardless of the binder resin, were less soluble in general, or even showed worse solubility than other layers in masstone.

From the point of view of the type of paint binders considered as a whole set, the most easily soluble of the discussed are the layers of MSA acrylic paints, then Gamblin urea aldehyde, layers with Paraloid B-72, slightly worse polyvinylacetate, then ketone and definitely the hardest - mastic. However, the removability of the layers not covered with varnish and varnished was not identical. The analysis of the test results showed that the application of the varnish may make it easier or more difficult to remove after ageing, as will be illustrated by a number of examples.

In the case of layers with Paraloid B-72 and MSA paint layers, the binder of which is poly butyl methacrylate, covering them with a ready-made varnish containing another acrylate – poly isobutyl methacrylate, resulted in a reduction of their removability compared to non-insulated layers. The initial solubility of both acrylic binders of these paints is different. Initially, dissolving poly butyl methacrylate does not require a high content of aromatic solvents. It was not required after ageing to dissolve the layers of unvarnished MSA paints, still soluble in white spirit, but it was necessary to add toluene to completely solubilize the varnished layers. In the case of Paraloid B-72 paints, a larger proportion of it was necessary to remove the varnished layers.

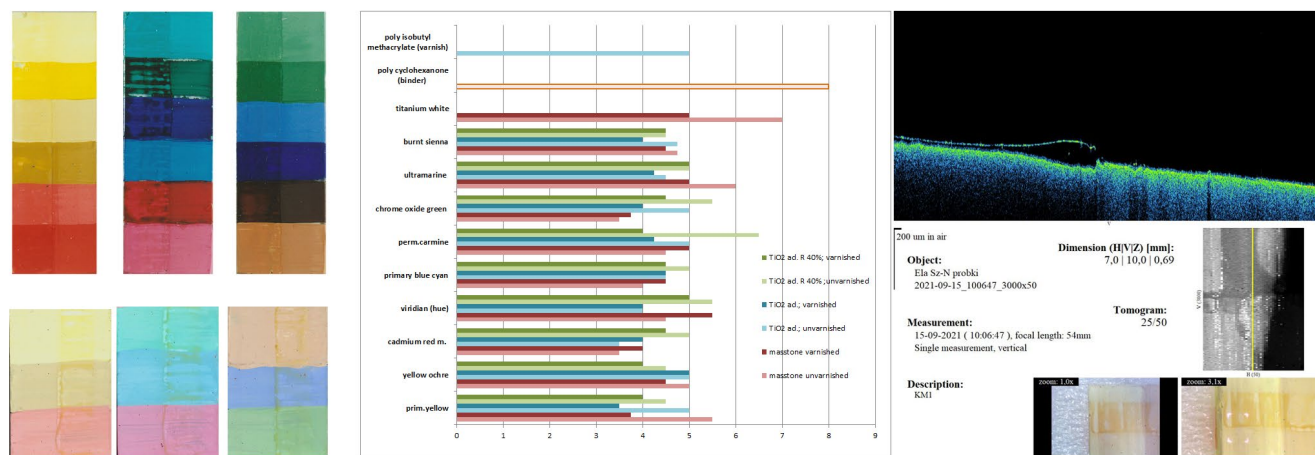


Figure 5 – Removability and surface OCT imaging of varnished and unvarnished paint layers – aged ketone paints example

According to the surface image obtained in the OCT, these are two different situations – the varnish seems to penetrate into the paint layer with Paraloid B-72 and to create distinct layer on MSA. However, it cannot be ruled out that its parts may penetrate into the paint layers, which visibly soften during the application of the varnish. The solubility of unvarnished layers of MSA paints in white spirit and the need to add toluene in the case of varnished layers, could indirectly indicate the use of stabilized resin in paints (which, however, is not confirmed in the manufacturer's information) and unstabilized poly isobutyl. Oversaturation of ketone paints layers with varnish containing isobutyl methacrylate resulted in the easier removal of varnished layers compared to non-varnished ones (i.e. lower toluene content). In the layers that have absorbed varnish to a smaller extent, the ageing effects of the ketone resin paint binder seem to have a dominant effect on solubility, resulting in its greater reduction.

A similar effect was achieved by applying a ketone varnish onto PVAc paint layers, although their absorbency was lower (they required double varnishing in individual cases). The OCT image suggests that the varnish, penetrating into the near-surface area, formed a thinner and less distinctive layer on top. All the varnished layers required slightly more toluene to remove than the unvarnished ones, and in one case the addition of acetone. It seems that the effects of ageing of the varnish ketone resin were dominated by changes in solubility due to aging by exposition to light (i.e. the prevalence of

methacrylate in the varnish. It is its solubility that has been reduced, although both resins are subject to cross-linking. Perhaps this condition was also influenced by the addition of turpentine oil in the ready-made varnish [31: 120, 128].

The opposite situation, i.e. paint layers with a binder resin less chemically stable than the one in the varnish, is illustrated by the example of ketone paint layers covered with an identical acrylic varnish. The layers of these paints were saturated with it before it finally formed a film on their surface, more regular on smoother tints (those with more white). polyclohexanone oxidation over polyvinyl acetate degradation)

In the case of mastic paint layers, covering them with a layer of acrylic varnish (as above) gave in OCT a surface image similar to the one described above, suggesting penetration into the surface of the paint layer. This resulted in often only slight differences in removability requiring, unfortunately, similarly to unvarnished layers, very polar mixtures (content from 50 to 100% acetone). It is possible that these differences would be more advantageous if the ready-made acrylic varnish (Acrylic Varnish Glossy, 114, Royal Talens, NE) did not contain turpentine oil, which could additionally catalyze the oxidation of the mastic.

And finally - in the case of some paints of the set, coating the layers of paints with Laropal A-81 stabilized varnish from RegalRez 1094 allowed to dissolve them in a mixture of white spirit with toluene (50:50), while unvarnished layers required a larger

proportion of toluene (and in the case of the aforementioned Indian yellow permanent even with acetone).

The performed study lead to conclude that if we apply a varnish that is less chemically stable in the ageing process (including additives in it) onto layers containing more stable resins, the limitation of the removability applies to this whole. It is illustrated by the examples of layers made of acrylic paints and PVAc. On the other hand, covering the retouching with a varnish containing a resin that is more stable than the binder resin improved its removability compared to an unvarnished layer. It was illustrated by the example of ketone paint layers, and was noticeable for the layers with Laropal A-81 conservation paints as well as those with mastic.

The described test results demonstrate that the characteristics of the resin (and possible additives) in the varnish applied to a dried, but recently made retouching layer, will visibly affect its removability in the long term. This cannot be interpreted as a simple dependence on ageing changes in the varnish itself as the final protective layer, because in the applied system used it does not form a completely separate layer.

In order to determine the nature and degree of changes and to confirm its interpretation resulting from this study, more extensive research and instrumental analyzes are required

4. CONCLUSIONS

When choosing materials for retouching, we obviously pay attention to their application features and the compliance of the obtained effect with the original painting. However, the properties that guarantee the long-term durability of the achieved visual results are equally important.

The first, obvious step in selecting materials is checking the lightfastness of the pigment or the ready-made paint. The examples of color changes in the paint layers recorded and illustrated here in confrontation with the normative assessments (ASTM, BWS) provoke reflection. I assume that in the case of all paints produced for conservators the lightfastness rates does not only rely on the table in the appendix of the ASTM standard but are the effect of the research. It may seem that the manufacturer's 'highest' lightfastness rating does not match the independent experimental

results because the changes presented here were noticeable and confirmed by colorimetry. The remaining question is what is the rate of changes that are willing to accept. Let us hope that the aforementioned research aimed at developing a new testing method for artist's materials will bring a reliable assessment of the materials proposed to us. While waiting for the results, I would postulate that when selecting pigments and paints for the conservator palette, one should give up those whose components of the BWS ratings in both masstone and tints are below 7, and in the case of available lightfastness tests for specific paints, consider those whose dE^*_{ab} does not exceed 4 (or calculated with improved dE formula is close to 2).

Excellent lightfastness turns out to be in some cases an insufficient selection criterion. White paints containing 'Chinese white' and anatase titanium white are a clear example of this. Recently more numerous publications on these particular properties of theirs may result in greater care in avoiding them in conservation applications.

It should be noted that the exposure to light and the level of air humidity necessary for the reactions in which both discussed white pigments take part, do not have to be extreme, as evidenced by whitened retouching in museum galleries. At the same time, the zinc white and titanium anatase themselves do not deteriorate. Although zinc oxide may not always have a photocatalytic effect, it is difficult to recognize what kind of pigment we are dealing with, and it can also cause changes due to salt formation. For the durability of the retouching, it is a safe solution to exclude from the palette of paints the ones containing zinc white (PW4) and titanium white (PW6) of an unknown type and to use a treated – and thus 'safe' - rutile variety that limits its photoactivity.

In addition to the properly selected components of the retouching paint itself, its properties are also determined by the varnish, usually applied very quickly after painting reintegration is completed. As a rule, we are inclined to treat the varnish as a separate film. Observations on unvarnished and varnished aged layers of retouching paints convincingly indicate that the retouch covered with the varnish is a system that should be treated inseparably. It is mistaken to assume that the changes in the solubility of the varnish and the retouch layer underneath can be considered independently. The varnish applied does not (only) work as a "filter". From the point of view of the safety of removing the retouching from the area where they

were applied within the thinned original layers, the above statements are utterly significant.

The examples discussed in this text, taken from many years of research on retouching materials, were not intended so much to present their assessment (which was done in separate earlier publications) but to focus using them on the aspects important for the conscious choice of retouching materials and their handling. I hope that the presented conclusions will provide the guidelines supporting optimal selection and use of retouching materials.

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NOTES

Artificial ageing: Xenotest 150S (Heraeus, Hanau – Germany) in Instituut Collectie Nederland, Amsterdam and in Institute of Dyestuffs of Łódź Polytechnic; Xenotest ALPHA High Energy (Atlas, USA), Department of Conservation and Restoration of Paintings and Polychrome Sculpture of Fine Arts Faculty, Nicolaus Copernicus University (NCU), Toruń

Colorimetric assessment: Minolta CM 2002, Instituut Collectie Nederland in Amsterdam, Macbeth 2020 Color Eye, Laboratory of Colorimetry, Institute of Dyes and Organic Materials, Łódź; SP-64 XRite, Nicolaus Copernicus University, Department of Conservation and Restoration of Paintings and Polychrome Sculpture of Fine Arts Faculty at NCU, Toruń

XRF: Energy dispersive X-ray spectrometer MiniPal PW 4025 (Philips Analytical) analysis: Adam Cupa, Department of Paint Technique and Technology of Fine Arts Faculty, NCU, Toruń

XRD: Tractor Xray Du Bois 404 Object Analyser. analysis: L. Maes, Département des Laboratoires, Institut royal du Patrimoine artistique (IRPA/KIK) Brussels; diffractometer Siemens D500, analysis: Stanisław Gierlotka PhD, Diffraction X Laboratory, Institute of High Pressure Physics Polish Academy of Science, Warsaw; diffractometer X HZG4/A, analysis: Jerzy Rauchfleisch, Laboratory of Instrumental Analysis, Faculty of Chemistry, NCU Toruń

FTIR : dr Marina van Bos, Département des Laboratoires, IRPA/KIK, Brussels ; Perkin – Elmer, analysis: dr hab Irmina Zadrożna, Faculty of Chemistry Warsaw University of Technology

GC-MS : GC: Varian 3400, capillary column DB-5. MS: Finningan ITS 40, analysis: Marina van Bos PhD: IRPA/KIK, Brussels ; GC- Hewlett-Packard HP-5890II, capillary column Ultra 2, MS: HP-5971A. dr hab Irmina Zadrożna, Faculty of Chemistry Warsaw University of Technology

SEM- Leo1530, column Gemini, analysis dr Adam Presz, Institute of High Pressure Physics Polish Academy of Science, Warsaw

OCT – optical coherence high resolution tomography, analysis: dr hab. Magdalena Iwanicka, Laboratory of Nondestructive Analysis, Center of Modern Interdisciplinary Technologies, NCU, Toruń

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