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TITANIUM DIOXIDE WHITES IN XX CENTURY WORKS OF ART: OCCURRENCES AND COMPOSITION STUDY

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Abstract

In this study, a representative set of 184 paintings created in the period from 1920 to 1990s was analyzed by portable X-ray fluorescence spectrometer (pXRF) to reveal the chronology and frequency of the use of titanium white pigment. The dataset included the works of American, European and Soviet artists from museums and private collections. Only in sixteen works TiO_2 was found, and micro-samples of the paints taken from these paintings were further investigated by polarizing microscopy (PLM), scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS), Raman and Fourier transform infrared (FTIR) spectroscopy. Some samples were also analyzed by gas chromatography-mass spectrometry (GC-MS). The experimental results showed that the use of titanium white in the first half of the 20^{th} century was extremely rare - it appears in the palette of artists closer to the 1940s, i.e. twenty years after the introduction of paint on the market. In Soviet artists' works the use of this pigment is observed convincingly from the 1970 onward and mostly in non-oil binders. Furthermore, the study highlights the chemical composition of titanium dioxide whites that changed throughout the 20^{th} century. The criteria for identification of composite titanium whites were revealed. The identified technological features of white pigment can serve as dating signs for more precise determining the time of paintings creation.

***Keywords**: Titanium white; Composite pigments; Chemical composition; Occurrences in works of art; Artists' pigments; XRF, SEM-EDS, GC-MS.*

Introduction

Titanium white is one of the most important pigments in determination the time of creation and the authenticity of twentieth century works of art. Titanium white was first produced in Norway in 1918 by a Titan Company A/S, and a year later the production of this pigment by Titanium Pigment Company started in the USA [1]. As an artists' paint, titanium white was first introduced in 1920 in the USA (F. Weber & Co.) [1, 2] and no later than in 1924 in Europe (Lefranc) (Fig. 1). In the USSR, artists' oil paints containing titanium dioxide was introduced much later - only in 1972[1] [3]. However, whether these dates can be considered as the beginning of the pigment's use in painting is still a controversial issue.

Since the start of the industrial production of titanium dioxide and throughout the 20^{th} century, the technology for its manufacture has improved and changed, which affected the quality of the paints. Some European and Soviet manuals on painting technique of the 1930s and later stated that certain properties of titanium whites "limit their application when they are ground in oil" [4], including the tendency of the paint layer to become both soft and chalky and its yellowing

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[1] For water-soluble techniques the pigment has been used since the late 1950s [3].

upon short ageing. The authors of the manuals recommended to avoid the new pigment or to use it cautiously [4-6].


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Suie calcinée	Bistre	» »	1 85	1 10	» »
	Bitume de Judee	4 20	1 85	1 10	» »
Carbonate de plomb (1)	*Blanc d'argent				
	* — — fluide	5 35	2 30	1 30	» »
	* — — épais				
	* — de plomb	5 35	2 30	1 30	» »
Oxyde de Titane non chimiquement pur	* — de titane	5 35	2 30	1 30	» »
Oxyde de zinc	** — de zinc	5 35	2 30	1 30	» »
— —	** — — siccatif	5 35	2 30	1 30	» »
Stannate de cobalt	**Bleu cæruleum	» »	10 40	» »	3 75
Cyanure de fer	* — de Chine	» »	5 30	» »	2 »
Aluminate de cobalt	** — de cobalt	» »	6 90	» »	2 50
— —	** — — foncé	» »	7 40	» »	2 75
Cyanure de fer, alumine	* — minéral	» »	4 65	» »	1 75
Silicate de cuivre et de chaux	* — de Pompéi	» »	3 90	» »	1 50
Cyanure de fer	* — de Prusse fin	» »	3 90	» »	1 50
—	* — — ordinaire	» »	3 20	» »	1 25
Colorant sulfuré, alum., silice	** — saphir fixe	» »	2 80	» »	1 10
Os calcinés	Brun de Bruxelles	5 85	2 50	» »	1 »
Oxyde de fer	** — de fer	» »	3 20	» »	1 25
Prussiate de cuivre	* — de Florence	» »	4 65	» »	1 75
Oxyde de fer, carbone, alumine	** — d'Irlande	» »	2 50	» »	1 »
Oxyde de fer précipité	** — de Mars	» »	3 90	» »	1 50
Bleu de Prusse calciné	** — de Prusse	» »	6 »	» »	2 25
Oxyde de fer	** — rouge	4 70	3 05	1 20	» »
Oxyde de fer, carbone	* — Van Dyck	4 20	1 85	1 10	» »
Carbone, fer, alumine	** — Vibert	» »	3 20	1 80	» »
	Carmin (de cochenille)	» »	6 90	» »	2 50
	— brûlé	» »	6 90	» »	2 50
	** — de garance	» »	6 90	» »	2 50
Sulfure de mercure	*Cinabre	» »	8 15	» »	3 »
	— vert clair et foncé	» »	4 65	» »	1 75
Chromate plomb, cyanure fer. (2)	* — vert jaune n°s 1, 2, 3	» »	4 65	» »	1 75
	Cristal	» »	2 50	» »	1 »
	*Indigo	» »	4 65	» »	1 75
Antimoniate de plomb	*Jaune d'antimoine	» »	6 »	» »	2 25
Carbonate et chrom. de plomb	* — brillant	6 60	2 80	» »	1 10
Sulfure de cadmium	** — de cadmium : citron, pâle, clair, moyen, foncé et orange	» »	7 40	» »	2 75
Chromate de plomb	*Jaune de chrome : clair, moyen, foncé, orange	6 60	2 80	» »	1 10
Chromate de zinc	*Jaune citron ou de zinc	» »	3 90	» »	1 50
Colorant hydrazinique alum.	** — indien simili	» »	4 65	» »	1 75
Euxanthate de magnésie	** — — vert	» »	3 90	» »	1 50
Oxyde de fer précipité	** — de Mars	» »	3 90	» »	1 50
	— minéral	» »	3 20	» »	1 25
Antimon. plomb, sulf. chaux	* — de Naples	7 60	3 20	» »	1 25
	* — — vert	7 60	3 20	» »	1 25
Antimoniate de plomb	* — Pinard n° 1 (clair)	» »	6 »	» »	2 25
— —	* — — n° 2 (moyen)	» »	6 »	» »	2 25
— —	* — — n° 3 (foncé)	» »	6 »	» »	2 25
Chromate et carb. de plomb	— de Rome	» »	2 80	» »	1 10

(1) N. B. A moins d'indications spéciales, nous livrons toujours le BLANC D'ARGENT à la consistance courante il faudra donc bien spécifier Fluide ou Épais chaque fois qu'on le désirera ainsi.

(2) Le cristal se mélange aux couleurs à l'huile pour en diminuer l'intensité ; spécialement recommandé pour les glacis.

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Le Blanc de Titane

Le Blanc d'Argent (carbonate de plomb) et le Blanc de Zinc (oxyde de zinc) sont les deux blancs employés actuellement dans la peinture à l'huile.

Le Blanc d'Argent est couvrant, mais susceptible de noircir.

Le Blanc de Zinc est peu couvrant, mais fixe.

Il était de la plus haute importance de trouver un Blanc réunissant les qualités de ces deux Blancs en éliminant leurs défauts.

Le BLANC DE TITANE est destiné à remplacer le Blanc de Zinc et le Blanc d'Argent. Il est plus couvrant que le Blanc d'Argent et sèche un peu plus lentement, sans, toutefois, que la durée de sa siccativité excède celle du Blanc de Zinc.

Le BLANC DE TITANE est l'oxyde d'un métal considéré, jusqu'ici, comme une curiosité de laboratoire, sans applications industrielles. On l'extrait de l'ilménite, minéral noirâtre, et on obtient une combinaison physique sous forme d'association intra-moléculaire, de l'oxyde de titane, avec des sels de baryum et de calcium.

Cette combinaison est effectuée non par mélange mécanique de substances, mais par voie humide et recristallisation ; elle donne naissance à un nouveau corps micro-cristallin, absolument différent de ses composants dans ses propriétés et par son aspect.

Le BLANC DE TITANE, traité par une succession d'opérations appropriées, donne à ce produit des qualités d'opacité, de division, de stabilité, d'innocuité et d'inertie recherchées dans les pigments destinés à la peinture artistique.

L'opacité est obtenue par la combinaison dont il a été question plus haut. L'oxyde de titane pur ne la possèderait pas et le corps nouveau qui en dérive est formé de molécules d'une dimension inférieure à un millième de millimètre.

La stabilité est absolue ; le BLANC DE TITANE conserve intégralement sa blancheur.

Des expériences ont prouvé que le BLANC DE TITANE n'est pas vénéneux. Il présente, pour ceux qui l'emploient, une innocuité absolue.

La propriété d'inertie consiste, pour une couleur, à ne pas changer de nuance, soit seule, soit mélangée à d'autres pigments. Le BLANC DE TITANE est complètement inerte et n'exerce aucune action sur les huiles, les essences et les vernis. Il est insensible aux vapeurs sulfureuses et acides.

D'après cet exposé, on conçoit aisément l'avenir d'une telle couleur et les services qu'elle rendra.

N. B. — Le BLANC DE TITANE est moins cher que le Blanc d'Argent. Il est vendu broyé, pour le tableau, pour la décoration artistique et pour la gouache.

BLANC DE TITANE	POUR LE TABLEAU		
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	» »	» »	» »
	POUR LA DÉCORATION ARTISTIQUE		
	1/2 Tube	Tube	Le Kilo
	» »	» »	» »
	GOUACHE.		» »

DES ÉCHANTILLONS DE TUBES A L'HUILE SONT ENVOYÉS SUR DEMANDE

R. C. Seine 194.649

Fig. 1. Front page and excerpts from the 1924 Lefranc catalogue [8] describing the synthesis method and qualities of titanium white pigment

There is no information about whether the artists followed these recommendations, thus reliable data on the chronology and frequency of the use of titanium white in paintings can only be obtained by examining authentic and dated works. In 2018 *B.A. van Driel et al*. [7] conducted a study of 189 paintings by Dutch artists created in period from 1920 to 2000 using a portable X-ray fluorescence (pXRF) and traced the chronology of titanium white application. However, only a few micro-samples of paints containing titanium dioxide have been studied in more detail.

This paper presents the results of a research project devoted to identification and characterization of titanium dioxide whites in paintings of Russian and foreign artists from museum and private collections. The first stage of the project was the study of the paintings created in the period from 1920 to the early 1990s using pXRF for the express identification of titanium in the paint layers. The next step was to examine the micro-samples of paints containing titanium dioxide by the complex of analytical techniques and to reveal differences in chemical composition of white paints used in various periods of 20th century.

Titanium whites can be found as pure titanium dioxide (TiO_2) or containing various additives and fillers, such as zinc white (ZnO), barium sulfate ($BaSO_4$), calcium sulfate ($CaSO_4$), calcite ($CaCO_3$), etc. In the first half of the 20th century, titanium white was produced as a composite pigment, a product of TiO_2 precipitation on a matrix consisting of $BaSO_4$ or $CaSO_4$, and the properties of such paints differ from those of paints made by mechanically mixing TiO_2 with fillers. Until the end of the 1930s, titanium dioxide was obtained only in the form of anatase. Later, to improve the quality of the pigment the new method was developed and since the beginning of 1940s titanium dioxide was also produced in the rutile crystal modification [1].

Thus, the following key characteristics should be determined when studying TiO_2-based paints:

- Chemical composition;
- Particle morphology (composite/non-composite pigments);
- The crystal structure of titanium dioxide (anatase/rutile).

In the second half of the 20th century new types of binders like modified oils, acrylates, alkyds and polyvinyl acetate started to be commonly used in manufacturing of TiO_2-based artistic paints, thus the binding medium should be identified as well.

Experimental part

Dataset

A total of 184 paintings created between 1920 and 1990 were analyzed by pXRF. Titanium was detected only in sixteen works, which were then studied in more detail. The micro-samples of both white and colored paints were taken and analyzed by means of complex of phisicochemical and optical methods.

With the exception of some paintings, all works are signed and dated and belong to museum and private collections. For the present study, the artworks created in oil technique were primarily selected.

Methods

The first stage of the experimental work was to detect titanium white in the 20th century works of art. For this purpose, pXRF analyzer was used and both white and chromatic paint layers were examined (usually 5-6 points in the painting).

The next step was the investigation of micro-samples of the paint layers in which titanium was detected by pXRF. The samples were taken under a binocular stereoscopic microscope (MBS-9, 25× magnification) and then analyzed by complex of optical and physicochemical methods. Initially, the samples were examined under transmitted polarized light (PLM) to identify inorganic pigments and fillers in their composition. In addition, PLM along with scanning electron microscopy (SEM) proved to be an effective tool for differentiating composite and non-composite titanium whites. To determine the elemental composition and obtain element distribution maps, energy dispersive X-ray fluorescence spectrometer (EDS) was used. The crystal structure of titanium dioxide was defined by Raman spectroscopy. The binder of the primer and paint layers, as well as a number of pigments and fillers were identified by Fourier transform infrared spectroscopy (FTIR). Some samples were also analyzed by gas chromatography-mass spectrometry (GC/MS) to determine precise chemical composition of binder.

XRF

Measurements were performed using a Hitachi X-MET 8000 Expert GEO pXRF. The analyzer has Rh target X-ray tube (4W; 50kV max., 200μA max.). Analytical range is from Mg to U. Measurement spot size is 10.7mm x 9.4mm. Signal accumulation time was set to 20s.

PLM

For the examination of the micro-samples using PLM a POLAM L213-M (LOMO) microscope was employed. The specimens were examined under 720× magnification.

SEM-EDS

Microscopical analyses were performed on a TM4000 (Hitachi Co.) scanning electron microscope coupled with a Quantax 75 energy dispersive X-ray fluorescence spectrometer (Bruker Nano GmbH). Images and elemental analyses were obtained at 15kV.

Raman

Measurements were carried out using a Renishaw InVia Qontor Raman microscope equipped with linearly polarized laser 785±0.5nm, 1200 lines/mm diffraction grating and 50× objective (N.A.=0.8). Raman spectra were recorded with 80mW incident power, spot size of ~ 1.2μm. Parameters of recording: measurement range 100-3200cm^{-1}, integration time 10s at each point, 3 spectra accumulations.

FTIR

Infrared spectra were collected on a LUMOS microscope (Bruker) in the attenuated total reflection (ATR) mode with a Ge ATR crystal, from 4000 to 600cm^{-1} and for 64 scans with a resolution of 4cm^{-1}. Vibrational spectra, FTIR and Raman, were compared with IRUG (Infrared and Raman Users Group) database.

GC/MS

The instrument used was an Interlab GCMS equipped with Mega 5MS column 5% phenyl polysilphenylene-siloxane (30m × 0.25μm × 0.25mm). The molecules were ionized in an Electron Impact ion source at 70eV electron energy and at ion source temperature of 230°C, GC-MS interface at 280°C. The GC oven temperature was 60 °C (held for 3.0min.) with a 7 °C min^{-1} rate to 200 °C (5min) and then with a 7 °Cmin^{-1} rate to final temperature of 290 °C (30min).

Based on analytical task, different modes of operation of the quadrupole mass filter were used: a standard ion scan in the specified mass range (SCAN) (50-350Da) and a mixed (cyclic) scanning mode (SCAN/SIM) making the mass filter to alternate scanning ions in user specified mass range. Spectra were compared to NIST library standards.

Sample preparation, extraction and derivatization of samples were performed according to the procedure described in [9].

Methodology for qualitative and quantitative composition determination in titanium dioxide-based paints using SEM-EDS

As it was mentioned earlier, titanium white may contain various components, such as ZnO, $BaSO_4$, $CaSO_4$, $CaCO_3$ and others, taken in a certain weight ratio. They could be added both at the stage of production of industrial pigment and during manufacturing of artistic paints. In order to establish the technological features of titanium white and link them with the time of pigment production, the identification of these additives and the determination of their quantity is an important task.

In developing the methodology, we considered a number of factors, including the fact that artists could use several types of whites. In this regard, while examining a white paint in which titanium and zinc are detected, it is necessary to determine whether this paint is, for example, a mixture of titanium and zinc whites that the artist mixed on a palette, or whether it is titanium-zinc white that was produced as a commercial paint with a certain ratio of zinc and titanium oxides.

As part of the research work, a methodology for quantitative and qualitative composition determination in TiO_2-based paints was developed. It consists in calculation of the quantitative ratios of various elements (Ti, Zn, Pb, Ba, Ca, etc.) in the sample by EDS technique. The key point is to measure the whole area of the paint sample and register the total X-ray spectrum. This makes it possible to reduce the errors caused by the geometry of the sample, its uneven surface, as well as the inhomogeneity of the paint layer. As a result, the quantitative ratios of elements in the paint specimens, which are two- or three-component systems with a specified composition, are reproduced with higher accuracy for all micro-samples taken from the painting.

Table 1 presents the results of the study of the micro-samples of the paint layer from two paintings by Russian artists: *The Spill on Kerzhenets* (1977) by N.M. Romadin and *On the Carpet* (1980) by P.N. Krylov. In the first case, Ti and Zn were registered in five samples of the paint layer with the constant Ti/Zn ratio of about 35/65 in wt.%. In one sample only Zn was detected. Thus, we can conclude that the artist used titanium-zinc white paint, as well as zinc white.

Table 1. The results of calculation of Ti/Zn, Ti/Pb, Ti/Ba and Zn/Pb ratios by EDS technique in the micro-samples of the paint layer of two paintings by Russian artists

Painting	Color of paint sample	Elemental ratio (wt.%)*				
		Ti/Zn	Ti/Pb	Ti/Ba	Zn/Pb	Zn
N.M. Romadin. *The Spill on Kerzhenets*. 1977. Oil on cardboard, 87×109. Samara Regional Art Museum	white	34.8/65.2	-	-	-	-
	blue	-	-	-	-	100.0
	pink	34.0/66.0	-	-	-	-
	light blue	34.6/65.4	-	-	-	-
	yellow	32.1/67.9	-	-	-	-
P.N. Krylov. *On the carpet.* 1980. Oil (?) on cardboard, 37.5×51.7. Private collection	white	85.9/14.1	-	88.6/11.4	-	-
	blue	5.8/94.2	-	-	-	-
	green	17.1/82.9	72.8/27.2	86.1/13.9	88.6/11.4	-
	yellow	-	-	-	25.2/74.8	-
	burgundy	-	-	-	-	100.0

*For all paint samples, ratios were determined only for the specified elements, wt. % of which were recalculated to 100%. Other identified elements were excluded from the calculation.

In the work *on the carpet* the elemental analysis of the samples showed the presence of three elements Ti, Zn and Pb, which are usually referred to titanium, zinc and lead whites, respectively. There was no correlation between three elements: the ratios Ti/Zn, Ti/Pb and Zn/Pb varied between samples, and in some of them only Zn was detected. Also, in the samples with high Ti content (white and green paint samples), barium sulphate was identified, and the Ti/Ba ratio turned out to be similar. This led us to the conclusion that there are three types of whites present in the painting: titanium white with barite, zinc white and lead white.

For a correct interpretation of the data, it is necessary to examine at least five micro-samples taken from different areas of the paint layer, both white and colored. Also, the methodology can only be used for the samples in which the elements Ti, Zn, Pb, Ca and Ba refer to TiO_2, ZnO, $(PbCO_3)_2{\cdot}Pb(OH)_2$, $CaSO_4$ or $CaCO_3$ and $BaSO_4$ compounds[2], respectively.

To estimate the accuracy of the calculation of the quantitative composition, reference paints were examined using the proposed methodology. The reference samples were prepared by mixing of TiO_2 and ZnO taken in specified proportions 50/50, 20/80, 70/30 and then painted on the canvas board (Fig. 2). The results of the EDS measurements are presented in Table 2.

[2] For example, presence such pigments as lead yellow, zinc yellow, barium yellow in the studied sample will affect calculation of the ratios.

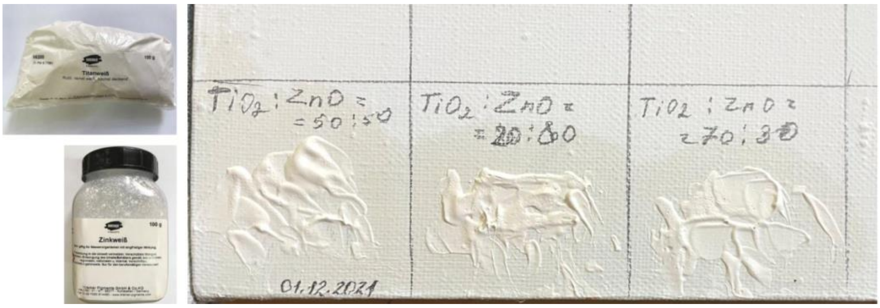

Fig. 2. Titanium-zinc white reference paints out with different TiO_2/ZnO ratio (in wt.%)

Table 2. The results of calculation of oxides ratios TiO_2/ZnO by EDS in three micro-samples of reference paints out

TiO_2/ZnO ratio (wt.%) in the reference paints out	
Specified composition	**EDS results**
20/80	24.8/75.2
	25.1/74.9
	25.2/74.8
50/50	51.2/48.8
	53.1/46.9
	52.1/47.9
70/30	70.5/29.5
	68.7/31.3
	69.6/30.4

Results and discussion

Occurrences of titanium dioxide whites

All 184 examined paintings were divided into three groups.

The first group includes eight works from the collection of American painting of The State Museum of Oriental Art (Moscow). Among them, titanium white was identified in three undated works by C.F. Ryder, M.P. Bewley and F.D. Waugh. According to the museum documentation, as well as the results of technological research, it was revealed that all paintings were created in the second quarter of the 20th century. Only for the painting *Mountain pass* by C.F. Ryder the time of its creation has been establish more precisely. The presence of blue and green phthalocyanine pigments in the paint layer indicates that the painting was created no earlier than 1939 [10], and it could not have been painted after 1949, when the artist died.

The second group includes two works by Alexey Korovin who lived and worked in Paris from 1923 to 1950, as well as the paintings by Nikolay and Svyatoslav Roerich, who traveled extensively and lived in India and the United States. The paintings by A.K. Korovin are dated 1940 and, unlike all other examined works, were made in water-soluble technique. Titanium white was identified in both of the paintings. Out of the six works by S.N. Roerich painted at different periods of his career and dated 1926, 1928, 1936, 1954 and 1974, and one work by N.K. Roerich dated 1940, titanium white was found only in *Karma Dorje* (1974) by Svyatoslav Roerich.

The third and most representative group consists of the paintings by Soviet artists. Here, out of 167 examined works, titanium white was identified only in ten of them. Figure 3 shows the total number of examined paintings and the works in which titanium white was found over the decades[3].

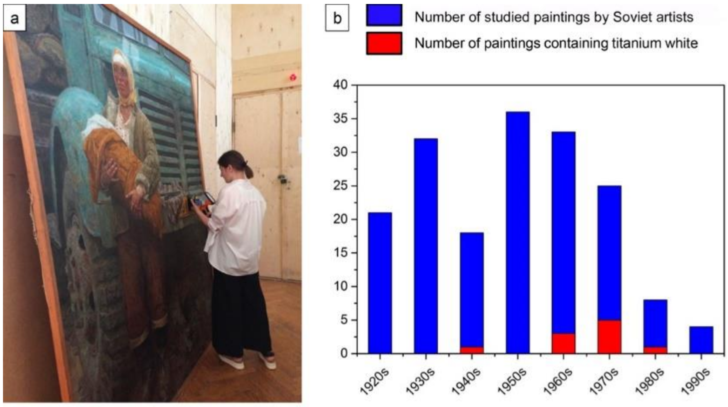

Fig. 3. (a) A study of Soviet artists' paintings of the 1920-90s using a pXRF. Samara Regional Art Museum, (b) Total number of studied paintings and paintings containing titanium white, plotted by decade

The earliest case refers to the painting *Spring* by N.M. Romadin created in 1948 (Table 4, # 1). In the other works by the artist painted in 1948, 1954, 1956, 1964, 1970 and 1977 titanium white was detected only in the last one, *The Spill on Kerzhenets* (Table 4, # 8). Interestingly, no titanium white was found among 36 paintings executed in the 1950s (Fig. 3). This may be due to the fact that the *"Iron Curtain"* practically deprived Soviet artists of the opportunity to use European artistic paints, which they had actively used before.

Figure 3 shows the convincing introduction of titanium white in Soviet artists' palette in the 1970s (5 works out of 20) which may be related to the fact that Leningrad Factory of Artistic Paints had already arranged the production of oil paints based on titanium dioxide [3].

Interestingly, the obtained results on the chronology of the Soviet artists' use of titanium white are similar to the results presented in B.A. van Driel et al. research [7]. According to their data, titanium dioxide was first found in several paintings in the 1950s. The active use of the new paint by Dutch artists also occurred in the 1970s while the pigment was already in production by company Royal Talens since the early 1930s [2].

Thus, the experimental data obtained by studying the works of both European and American and Soviet artists show that the use of titanium white in the first half of the 20th century was extremely rare and that it appears in the palette of artists closer to the 1940s, that is actually 20 years after the introduction of paint on the market.

Chemical composition of titanium dioxide-based paints

Composite pigments

An advertisement for artistic paint *Blanc de Titane* presented in Lefranc catalogue (1924) (Fig. 1) describes the method of its production and its chemical composition in the following way: "a composite is obtained as an intramolecular association of titanium oxide with barium or calcium salts. Such a composition is prepared not by mechanical mixing of the substances, but by wet synthesis and recrystallization. As a result, a new microcrystalline compound is produced which properties and morphology are completely different from the individual components that make up the compound. And the new compound consists of particles less than one micron in size" [8, translated from French]. In the later catalogues of 1927 and 1930 we found the same advertisement, with the only supplement that "numerous experiments have shown that the

[3] At present, the statistical selection of paintings from the 1980-90s is not large enough (only 11), so we cannot draw any conclusions about the use of titanium white in this period.

addition of a small amount of zinc oxide slightly reduces the excess opacity and density of titanium white, without affecting their other qualities in any way" [11, 12].

The study of titanium white in the American paintings showed that their characteristics correspond to the aforementioned descriptions of composite pigments. When examining the paint samples using PLM, as well as SEM (Fig. 4b, c) we observed homogeneous mixtures in which it was impossible to distinguish individual particles of the components.

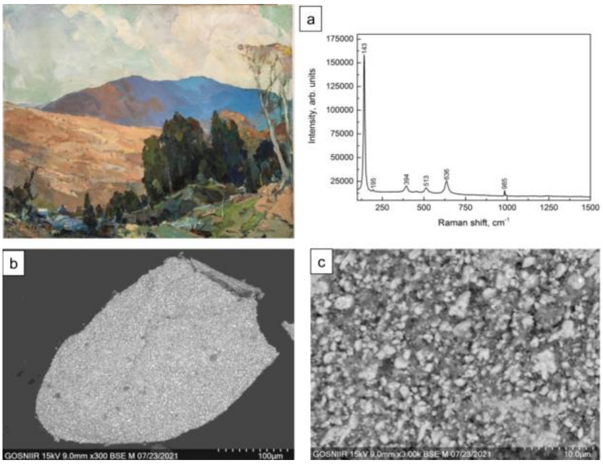

Fig. 4. C.F. Ryder. *Mountain pass*. 1940s. Oil on canvas, 63×75. ©The State Museum of Oriental Art, Moscow; (a) Raman spectrum of anatase TiO_2 in white paint sample; (b)-(c) SEM images of white TiO_2-based paint sample.

The size of most of the particles was about a few micrometers or less. Elemental analysis of the micro-samples also demonstrated a uniform distribution of Ti, Ba[4] and Zn (Fig. 5). The crystal structure of TiO_2 was identified as anatase (Fig. 4a). The calculation of the quantitative ratios of main elements performed according to the methodology described in Experimental section, showed the following average values: $TiO_2/BaSO_4$ = ~35/65wt.% and $TiO_2/BaSO_4/ZnO$ = ~30/50/20wt.% (see obtained results for each sample in Table 3). The obtained ratios are similar to the ones of some industrial composite titanium whites produced in the 1920-40s in Europe and the USA [1].

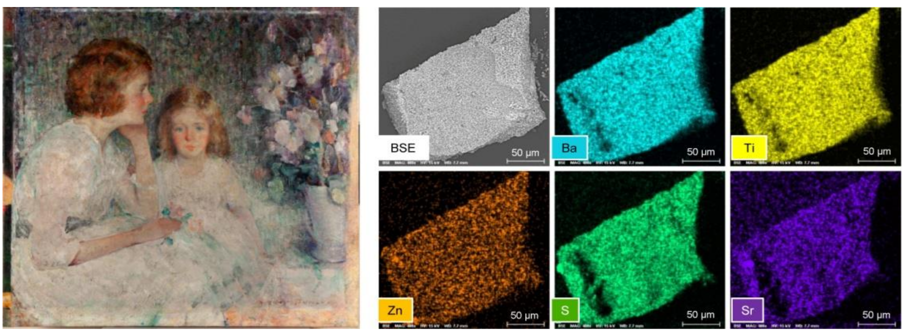

Fig. 5. M.P. Bewley. *Happy age*. 1920-40s. Oil on canvas, 79×75. ©The State Museum of Oriental Art, Moscow. Element distribution maps in white TiO_2-based paint sample

[4] To obtain composite $TiO_2/BaSO_4$ pigments, *blanc fixe* (barium sulfate) as well as ground baryte could be used as a matrix [13]. At the same time, baryte was generally the starting material for the production of the synthetic analogue [14, p. 40]. This can explain the presence of strontium in the studied samples (see Fig. 5), which is a natural impurity in baryte [15].

For comparison, Figure 6 demonstrates the distribution of the same elements in non-composite titanium white that was identified in the painting *Still Life with a Guitar* which was prescribed to French artist Georges Braque.

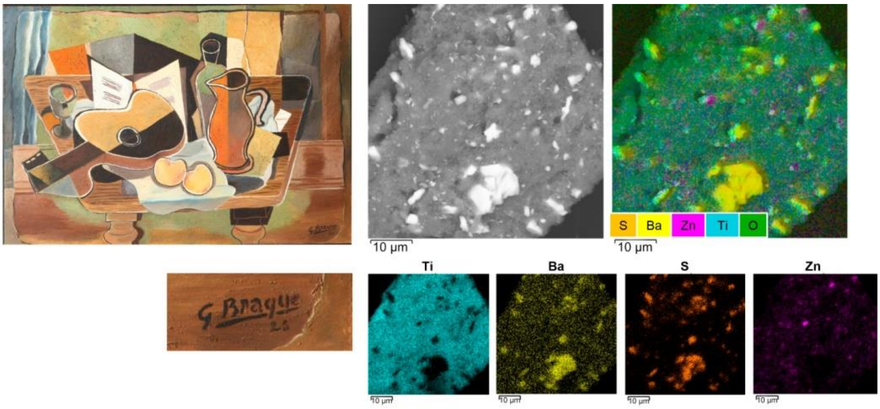

Fig. 6. Unknown artist. *Still Life with a Guitar*. Second half of the 20th century. Oil on plywood, 45×65. ©The State Rostov-Yaroslavl Architectural and Artistic Museum-Reserve. Element distribution maps in white TiO_2-based paint sample

Coarse crystalline particles (some of them exceeds 10μm), which consist of Ba and S and are attributed to barium sulfate, are clearly visible in the SEM image of the sample (Fig. 6), as well as in a transmitted polarized light. The distribution of Ti and Zn in the sample is relatively uniform. Thus, it is definitely a mechanical mixture of titanium and zinc whites with the addition of barium sulfate as an inert filler.

Table 3. The results of calculation of Ti/Ba/Zn, Ti/Ba, Ti/Zn and $TiO_2/BaSO_4/ZnO$, $TiO_2/BaSO_4$ and TiO_2/ZnO ratios by EDS technique in the micro-samples of the paint layer of three paintings by American artists

Painting	Color of paint sample	Elemental ratio (wt.%)			Compounds ratio (wt.%) (average)		
		Ti/Ba/Zn	Ti/Ba	Ti/Zn	TiO_2/ $BaSO_4$/ ZnO	TiO_2/ $BaSO_4$	TiO_2/ ZnO
M.P. Bewley. *Happy age*. 1920-40s. Oil on canvas, 79×75. The State Museum of Oriental Art, Moscow	white	30.5/45.9/23.6	40.1/59.9	68.8/31.2	~30/50/20	~35/65	~70/30
	green	25.0/50.9/24.1	33.3/66.7	65.8/34.2			
	red	26.7/47.9/25.4	36.0/64.0	64.3/35.7			
	white	-	-	0/100			
	white	27.6/40.6/31.8	40.7/59.3	59.2/40.8			
F.D. Waugh. *Sunny day*. 1920-40s. Oil on canvas, 60×75. The State Museum of Oriental Art, Moscow	purple	28.0/48.1/23.9	36.9/63.1	68.3/31.7	~30/50/20	~35/65	~70/30
	green	28.2/42.7/29.0	40.0/60.0	63.4/36.6			
	white	27.8/47.8/24.5	36.8/63.2	63.4/36.6			
	white	27.9/50.8/21.3	35.6/64.4	70.7/29.3			
	blue	25.2/40.3/34.5	38.9/61.1	51.8.48.2			
C.F. Ryder. *Mountain pass*. 1940s. Oil on canvas, 63×75. The State Museum of Oriental Art, Moscow	yellow	-	-	0/100	~30/50/20	~35/65	~70-75/30-25
	light green	24.0/52.3/23.7	31.5/68.5	65.0/35.0			
	white	28.9/48.7/22.4	37.3/62.7	68.9/31.1			
	white	28.8/49.1/22.1	37.1/62.9	70.2/29.8			
	purple	29.0/48.9/22.0	37.4/62.6	69.5/30.5			

Composite titanium white pigment based on barium sulfate was also identified in two works by A.K. Korovin painted in gouache and dated 1940. According to the results of calculations, $TiO_2/BaSO_4$ ratio was about 35/65 wt.% which is similar to the ratio of these compounds obtained for composite titanium white in American works (see Table 3). However, in the paintings by Alexey Korovin there was no ZnO in the composition of white paints. In addition to titanium white, in both paintings the artist used lithopone which is also a composite pigment. Thus, composite titanium white was also used in water-soluble paints which is in agreement with the literature [1].

Titanium dioxide whites in the works of Soviet artists

The key characteristics of titanium white identified in the paintings of Soviet artists are presented in Table 4.

Table 4. The composition of the primer and white paint layers in the paintings by Soviet artists containing titanium dioxide whites (in parentheses the weight ratio is given calculated by EDS)

№	Painting	Year	Primer composition	White pigments	TiO_2 crystal structure	TiO_2 based paints binder
1	N.M. Romadin. *Spring*. Oil on paper, cardboard, 47.5×70.5. Samara Regional Art Museum	1948	None	Lead white, Zinc white, Titanium white	Anatase	Oil
2	I.V. Shevandronova. *Girl with a bow*. Oil on cardboard, 40×27. Samara Regional Art Museum	1960	Zinc white	Zinc white, Titanium-zinc white (TiO_2/ZnO=~65/35)	Rutile	Oil
3	L.D. Gudiashvili. *Bride and Bridegroom.* Oil on canvas, 55.6×42. Private collection	1964	Primed by artist. Chalk with orange ochre, and kaolinite	Lead white with admixture of titanium white, Zinc white	Rutile	Oil
4	V.I. Ivanov. *Nicanor Agafonovich Turkin.* Oil on hardboard, 64×51. Samara Regional Art Museum	1969	None	Titanium-zinc white (TiO_2/ZnO=~50/50)	Rutile	Oil
5	V.V. Vatenin. *Red Still Life*. Oil on cardboard, 64×52. Samara Regional Art Museum	1971	Chalk, zinc white	Lead white, Zinc white, Titanium white	Anatase	Polyvinyl acetate
6	A.G. Tyshler. *Galatea*. Oil on canvas, 74×59. The Museum-panorama *Borodinskaia Bitva* (The Battle under Borodino)	1974	Commercially-prepared primer – zinc white	Titanium-zinc white (TiO_2/ZnO=~80/20)	Rutile + Anatase	Oil(?)
7	A.A. Mylnikov. *Early Spring.*Oil on canvas, 70×88. Private collection	1976	Commercially-prepared primer – titanium white with chalk	Zinc white, Titanium white (TiO_2/$CaCO_3$= ~70/30)	Rutile (both in primer and paint layer)	The primer binder is emulsion Paint layer binder - acrylate
8	N.M. Romadin. *The Spill on Kerzhenets*. Oil on cardboard, 87×109. Samara Regional Art Museum	1977	None	Titanium-zinc white (TiO_2/ZnO=~40/60), Zinc white	Anatase	Pentaerythritol esters of fatty acids
9	Y. Tsei. *The Bad Dreams.* Oil on canvas, 55.5×63.5. Krasnodar Region Art Museum	1979	Primed by artist. Titanium white with calcite (TiO_2/$CaCO_3$= ~55/45) and zinc white	Zinc white	Rutile	The primer binder is polyvinyl acetate
10	P.N. Krylov. *On the carpet*. Oil (?) on cardboard, 37.5×51.7. Private collection	1980	Commercially-prepared primer – titanium-zinc white (TiO_2/ZnO= ~95/5) with barite	Zinc white, Titanium white with barite (TiO_2/$BaSO_4$= ~85/15), Lead white	Ritile (in primer); Rutile + Anatase (in paint layer)	The primer and paint layer binder is oil(?)

The production of artists' oil paints based on titanium dioxide in the Soviet Union started in 1972 [3]. Thus, TiO_2-based paints identified in the paintings created before this date, must be of foreign origin. The exception is the work *Red Still Life* by V.V. Vatenin (1971) (Table 4, #5) in which polyvinyl acetate was used as a binder of paint containing TiO_2. This work could be created with paints of Soviet production, because the artistic paints on polyvinyl acetate tempera were introduced in the USSR in 1961 (Table 5). The works created after 1972 could have been painted using both foreign and Soviet-made paints.

Among the studied works, the painting *Bride and Groom* (1964) by Lado Gudiashvili (Table 4, #3) attracts particular attention, in which the main component of white paint was lead white with an admixture of titanium dioxide in the form of rutile. To date, this is the only case of identification of such whites in our practice. There is no reliable information about the time of introduction of this paint and a role of such a small addition of titanium dioxide (~2wt. %).

The artistic paint *Titanium white* introduced in the USSR since 1972 was a mixture of titanium and zinc whites and according to the technical specifications, pentaerythrol fatty acid ester of sunflower or cotton oil was used as binder (Table 5). Out of five works created after 1972, only in the painting *The Spill on Kerzhenets* by N.M. Romadin (1977) (Table 4, #8) titanium-zinc white on oil fatty acid pentaerythrites was identified which indicates its domestic production (Figs. 7 and 8).

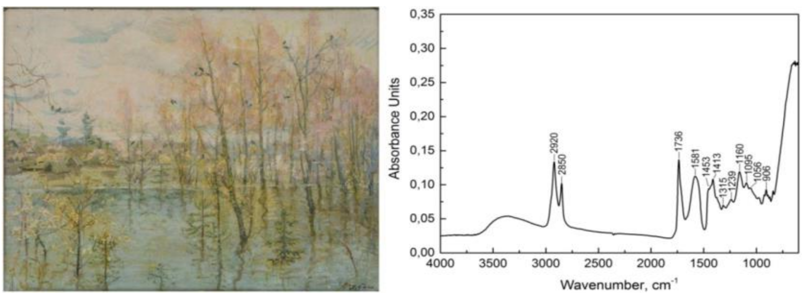

Fig. 7. N.M. Romadin. *The Spill on Kerzhenets*. 1977. Oil on cardboard, 87×109. ©Samara Regional Art Museum. FTIR spectrum of white TiO_2-based paint sample: a number of low intensity absorbance bands in 1060-1018cm^{-1} range (C-O-H vibrations) indicates the possible presence of pentaerythritol fatty acid ester [3]

Interestingly, despite the fact that industrial TiO_2 pigment both in anatase and rutile structures was produced in the USSR, only anatase pigments were used for production of artistic paints [3]. Thus, rutile structure of TiO_2 in the paint layer indicates that the artist used the paint of foreign origin. For example, in *Early Spring* by A.A. Mylnikov (1976) (Table 4, #7), both in ground and paint layer, titanium dioxide in rutile modification was defined. Meanwhile, acrylate was identified as the binder of TiO_2-based paint which was not used in the USSR in the manufacture of titanium white paints[5].

Table 5. The time of introduction on the Soviet market of TiO_2-based artistic paints in various binders [3]. For each case the presence of ZnO (including TiO_2/ZnO ratio) and inert fillers is specified

Year	Binding medium	ZnO	Inert fillers
1961	Polyvinyl acetate tempera (PVA)	none	none
1968	Gum-arabic (gouache)	none	none
1972	Pentaerythrol fatty acid ester of sunflower or cotton oil	TiO_2/ZnO = 80/20 (wt.%)	none
1977	Alkyd	TiO_2/ZnO = 50/50 (wt.%)	Bentonite
1988	Dehydrated castor oil	TiO_2/ZnO = 80/20 (wt.%)	Aerosil A-300

[5] According to the technical specifications and logbooks from the archive of Leningrad Factory of Artistic Paints.

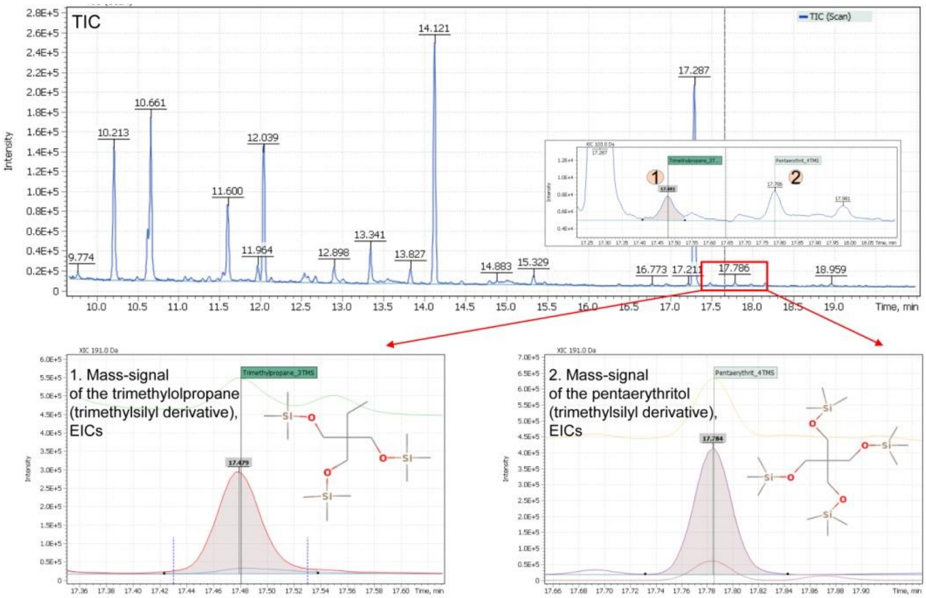

Fig. 8. Total ion chromatogram (TIC) of the binder extract of TiO_2-based paint from the painting *The Spill on Kerzhenets* by N.M. Romadin. Additionally, the elution areas on the chromatogram of the target components are shown, characterizing the presence of pentaerythritol in the binder composition

Various additives and inert fillers can also serve as attributing markers of domestic paints. For example, in the work *on the carpet* by P.N. Krylov (1980) (Table 4, #10) titanium white in mixture with barium sulfate were identified in the primer and the paint layer. In contrast to paint formulas of foreign companies [1, 2], barium sulfate was not applied as a filler in production of titanium white in the USSR[5].

According to the results, until 1970s titanium white was not detected as a component of a primer in the works of the Soviet artists. The first commercially prepared primer consisting of a mixture of titanium white with chalk was discovered in *Early Spring* by A. A. Mylnikov (1976) (Table 4, #7). A mixture of titanium white with calcite was revealed in the composition of the author's ground in the painting *Bad Dreams* by Y. Tsei (Table 4, #9).

Conclusions

The technological study of authentic and dated paintings from the period 1920-90s, which included works by both foreign and Soviet artists, allowed us to make the following conclusions about the chronology and frequency of the use of titanium white:

1. Among more than 180 examined paintings titanium white was found only in sixteen, which indicates that the artists preferred the traditional zinc and lead whites in their work;

2. The earliest occurrences of titanium white in examined works date back to the 1940s, i.e., twenty years after the appearance of the artistic paint on the market. Thus, there is no evidence to consider 1924 [8] as the date of the beginning of the commonly use of titanium white in paintings;

3. According to the results of the studies of paintings by Soviet artists (167 works) the active use of titanium white began in the 1970s. Interestingly, the results correlate to the ones presented in the research of 189 works of Dutch artists [7] in which titanium dioxide was first

detected in several paintings from the 1950s, and convincing use of the pigment also occurs in the 1970s.

In the course of the research work the methodology for determination of the qualitative and quantitative composition of titanium dioxide-based paints was proposed, and the paints of different production method can be distinguished. The criteria for identification of composite titanium white produced in the first half of the 20th century were revealed.

By comparing literature on the technology of manufacture of the paints with the experimentally obtained data, we identified several technological features that facilitate differentiation of the paints of Soviet and foreign production.

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