

The influence of mould fungus on pigments used in wall and ceiling décor on the example of the wooden church of Saint George in Ostropa

ADRIANNA LIPIEC¹, BOGUSŁAW ANDRES²

¹Department of Wood Science and Wood Preservation, Faculty of Wood Technology, Warsaw University of Life Science – SGGW

²Department of Wood Science and Wood Preservation, Institute of Wood Sciences and Furniture, Warsaw University of Life Science – SGGW

Abstract: *The influence of mould fungus on pigments used in wall and ceiling décor on the example of the wooden church of Saint George in Ostropa.* This research aimed to establish the change in colour of selected pigments used in polychrome due to the effects of *Aspergillus niger*. The research was conducted on the following pigments: cremnitz white, zinc white, vermilion, colcothar, chrome green, artificial ultramarine, burnt umber, carbon black, smalt, minium, azurite, Prussian blue and chalk. Measurements were taken using a colorimeter in the CIELAB colour space. The biggest change in colour was exhibited by artificial ultramarine, while the most stable in colour turned out to be minium. The smallest change in colour of dried samples was shown by burnt umber, while the biggest change was noted again for artificial ultramarine.

Keywords: polychrome, pigments, CIELAB, mould, *Aspergillus niger*

INTRODUCTION

Wooden architecture is a characteristic feature of the Polish landscape. Once identified most commonly with a village, today it is part of the national heritage. Polish wooden architecture is very diverse due to the country's location at the crossroads of East and West. Historic religious buildings, which we can still admire today, deserve special attention. Interiors seem to be more beautiful than structural carpentry solutions and plastic shapes (Szymański 1970). Wall polychromes are designed and made for a specific architectural object. They exhibit a close relationship with the wall, building, area, and sometimes the country in which they came to be (Roznerska, Mikołajczyk 1995).

Regardless of what technique they were made in, paintings are subject to aging. Various types of factors, biotic and abiotic, adversely affect paintings, both their surfaces and protective layers – varnish. On surface, organic pigments are particularly susceptible to colour changes. Microorganisms have a significant share in the destruction of wall paintings (Ślesiński 1989). In religious buildings, there is often high humidity and a lower temperature, which are conducive to the development of microorganisms. Despite the diverse symptoms of fungus and bacteria development, which weaken individual layers of paintings, they result in discoloration, stains, peeling, and chipping of paints. Wall painting in such places is particularly exposed to harmful factors, so it is very important to properly protect them. Quite often, the destruction of wall paintings is the result of improper conservation (Ślesiński 1989). Damage of this type is often irreversible (Roznerska, Mikołajczyk 1995).

MATERIALS AND METHODS

Test samples were prepared in the same way as the polychromes in the former parish church. St. George in Ostropa. Information on the technique of making polychrome in the above-mentioned object was taken from the studies of Krynicka-Szroeder 2011, Kurkiewicz and Rogóż 2011, Cupa and Szroeder 2011 as well as Gorzelik et al. 2019.

The tests were carried out on 42 samples of oak (*Quercus* L.) with dimensions of 50 × 50 × 5 mm. The samples were covered with a layer of whitewash made of hydrated lime (CaO

+ MgO \geq 90% by weight) and distilled water. After thorough drying, the whitewash was smoothed with sandpaper. The paints used for the tests were made by combining pigments with a binder. Yolk tempera was used as the binder. Two variants of the binder with different density and viscosity were made. In the end, the binder used had the following proportions: one-part chicken yolk, one-part linseed oil from Szmal Art, and one-part distilled water. The mixture was ground to obtain uniform consistency.

The pigment-to-binder proportions were determined separately for each paint. The right proportions were very important for the paint to last. Too little pigment caused insufficient coverage and too low colour intensity. On the other hand, too much pigment caused not all dye particles to combine with the binder, and hence after drying, the pigment flaked off of the sample. After numerous tests, the optimal amount of pigment and binder was obtained, achieving durable paint with adequate coverage. Pigments from Kremer Pigmente GmbH from the “historical pigments” product line were used in the research.

The paint was applied to each sample covered with whitewash in 3 to 6 layers, depending on the degree of coverage of the pigment. Smalt (catalogue number 10000) – 3 layers; zinc white (cat. No. 46300), chrome green (cat. No. 44210), carbon black (cat. No. 47010), azurite (cat. No. 10200) and Prussian blue (cat. No. 45202) – 4 layers; cream white (cat. 46000), vermilion (cat. 10620), colcothar (cat. 488600), burnt umber (cat. No.40710) and chalk (cat. No. 588005) – 5 layers; artificial ultramarine (catalogue number 45010) and minium (catalogue number 422500) – 6 layers. Some samples were left covered only in whitewash. A comparative analysis of the chemical composition of the pigments used for the study with the pigments used in the polychrome in the church. St. George in Ostropa was not carried out.

Before infection, each sample was measured with an NR200 spherical spectrophotometer using the CIELAB colour system. Four measurements were taken from each sample, one per each of the four corners of the samples.

Aspergillus niger van Tieghem mould fungus was used for the study. The tests were carried out in accordance with test procedure No. 355/98. The tests were carried out in glass Petri dishes with a maltose-agar medium. Glass trays were placed on the medium, samples were placed on them, and then sprayed with *A. niger* spore suspension. The remaining 14 control samples were placed in the dishes and were not infected. All the dishes with the infected and uninfected test specimens were placed in a laboratory incubator for one week-long incubation at 27°C and 90% humidity.

After the incubation period, the samples were visually assessed for the extent of mould growth on the paint layer. Then, they were cleaned of hyphae mushrooms, using a soft brush so as not to damage the paint layer. As before infection, all values L^* , a^* , b^* in samples were re-measured using a spectrophotometer, determining the colour change and calculating the parameters: ΔE^* , ΔL^* , ΔC^* and ΔH^* . Another measurement was taken after drying the samples to compare colour changes.

The absolute colour difference ΔE^* , was calculated using the equation:

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

where:

$$\Delta L^* = L_2^* - L_1^*$$

$$\Delta a^* = a_2^* - a_1^*$$

$$\Delta b^* = b_2^* - b_1^*$$

ΔE^* – the colour difference between the measurement taken on the infected sample and the control sample;

ΔL^* – the absolute difference in chromatic coordinate values between measurements on a sample infected with fungus and a control sample;

Δa^* , Δb^* – the difference in achromatic coordinate values between the sample infected with the fungus and control sample.

The difference in brightness ΔL^* , was calculated from the following equation:

$$\Delta L^* = L_2^* - L_1^*$$

The difference in chroma ΔC^* , was calculated from the equation:

$$\Delta C^* = \Delta C_2^* - \Delta C_1^*$$

where:

$$\Delta C_1^* \text{ was calculated using } \Delta C_1^* = [(a_1^*)^2 + (b_1^*)^2]^{1/2}$$

$$\Delta C_2^* \text{ was calculated using } \Delta C_2^* = [(a_2^*)^2 + (b_2^*)^2]^{1/2}$$

The difference in shadow ΔH^* , was established from the equation:

$$\Delta H^* = kH[(\Delta E^*)^2 - (\Delta L^*)^2 - (\Delta C^*)^2]^{1/2}$$

where:

$$kH = 1, \text{ while } (a_2^* \times b_1^* - a_1^* \times b_2^*) \geq 0$$

$$kH = -1, \text{ while } (a_2^* \times b_1^* - a_1^* \times b_2^*) < 0$$

It was assumed, that an average observer would notice the difference in colour in the following manner:

$0 < \Delta E < 1$ – unnoticeable difference

$1 < \Delta E < 2$ – difference noticed by an experienced observer,

$2 < \Delta E < 3.5$ – difference noticed by an inexperienced observer,

$3.5 < \Delta E < 5$ – noticeable difference,

$5 < \Delta E$ – impression of changed colour.

RESULTS

The difference in colour was measured using a spectrophotometer. Results are shown in tables 1 and 2.

For cremnitz white, the difference in colour change is greater when comparing dry samples than damp samples. The colour difference values are greater than 3, so they are visible to humans. Changes caused by mould fungus occurred toward yellow and red colours. The chroma increased to a higher degree on dry samples, and the fungus also caused the samples to darken.

The results of zinc white measurements show slight changes in the shade of the samples. Moisture did not significantly affect the results of dry and wet samples. Mould fungus acting on zinc white samples caused changes in the direction of yellow and red. The samples darkened, the chroma increased slightly, and the colour change is visible to the human eye.

The measurement results for vermilion are very noticeable. They exhibited a difference in colour, chrome, brightness, and shade changes. They changed towards green and blue. These changes are visible to most people. The change in the shade was caused by the infection of mould fungus; moisture did not have a significant effect.

Mould fungus affecting samples painted with colcothar caused a slight difference in the colour change. The change was made towards green and blue. Chroma has decreased. Wet samples were slightly lighter than dry samples.

Chrome green colour changes occurred towards red and blue. The mould caused a reduction in chroma; the change was greater on dry samples. Dry samples darkened and damp ones brightened. The humidity of the samples had little effect on the change in the colour tone.

The results of the colour difference for artificial ultramarine indicate colour changes very visible to humans. The changes occurred in the brightness, darkening of the sample, and the significant decrease in chroma. The colour transformed into green and yellow. Ultramarine is particularly susceptible to moisture which may have caused the resulting changes.

Table 1. A comparison of spectrophotometer measurements for pigments on dry samples prior to infecting with fungus and dry samples after infecting with fungus.

Pigments	Dry sample – prior to infecting with fungus			Dry sample infected with fungus			ΔE	ΔL	ΔC	ΔH
	L_1^*	a_1^*	b_1^*	L_2^*	a_2^*	b_2^*				
Cremnitz white	94.32	0.19	10.99	75.14	3.20	21.19	21.93	-19.18	10.44	2.01
Zinc white	95.72	0.65	9.98	75.30	3.65	13.69	20.97	-20.42	4.17	2.32
Vermilion	51.35	47.88	33.00	46.33	15.77	12.87	28.23	-5.02	-37.85	-1.93
Colcothar	40.07	18.76	14.05	39.55	7.69	9.38	12.03	-0.52	-11.31	-4.07
Chrome green	60.41	-16.86	23.32	53.10	-8.49	13.34	14.94	-7.31	-12.96	-1.34
Artificial ultramarine	52.51	5.59	-40.39	45.59	2.89	5.17	46.16	-6.92	-34.85	-29.47
Burnt umber	53.60	5.41	9.17	42.21	3.47	6.95	3.26	-11.39	-2.88	-
Carbon black	29.81	-0.18	-1.19	47.13	1.55	4.98	18.47	17.32	4.01	-5.01
Smalt	73.24	-2.10	-7.31	57.92	-0.19	2.15	18.11	-15.32	-5.45	7.97
Minium	71.47	37.40	43.11	61.13	38.40	46.01	10.79	-10.34	2.86	-1.15
Azurite	76.42	-6.48	-7.52	48.16	-2.25	16.06	37.05	-28.26	6.29	-23.12
Prussian blue	45.28	-11.26	-27.62	38.64	-0.42	-1.57	28.99	-6.64	-28.20	-1.04
Chalk	93.49	0.22	11.31	64.27	4.32	14.19	29.65	-29.22	3.52	3.59
Whitewash	98.37	0.09	-0.21	94.53	0.73	5.42	6.84	-3.84	5.24	-2.14

The mould used for the tests caused changes on the burnt umber. The sample darkened; however, the humidity of the samples was not caused by this phenomenon, the chroma decreased, the colour changes occurred towards green and blue. The humidity of the samples affected the difference in the colour change.

The results of the colour difference for carbon black showed visible colour changes caused by mould, and noticeable to humans. The samples brightened because of the mould fungus, changes occurred towards the red and yellow colour. Chroma increased slightly. The fungus affected the brightness and chroma of smalt. These changes are noticeable to humans. The changes occurred towards yellow and red. The humidity of the samples had an impact on the difference in chroma values and the brightness of the samples.

Microorganisms affected the total results in the minium sample. Changes in the dry samples occurred in the direction of red and yellow, and in the wet samples in the direction of blue and green. Chroma has significantly decreased due to the mould. The moisture content of the samples affected this pigment.

The experimental fungus acting on the azurite coated samples caused a significant change in the brightness of the paint layer. Changes occurred towards red and yellow. The mould fungus also caused chroma to increase.

The results for Prussian blue treated with mould show a change in the brightness of the paint layer and clear colour changes to red and yellow. Chroma under the influence of microorganisms has decreased dramatically.

For chalk samples, the mould fungus caused the samples to darken, as well as to change the colour in the red and blue directions. The humidity of the samples did not affect the results. The difference in colour change is clearly visible to humans.

Table 2. A comparison of spectrophotometer measurements for pigments on damp samples prior to infecting with fungus and damp samples infected with fungus.

Pigments	Damp control sample			Damp infected sample			ΔE	ΔL	ΔC	ΔH
	L_1^*	a_1^*	b_1^*	L_2^*	a_2^*	b_2^*				
Cremnitz white	91.88	0.34	15.42	75.42	3.16	21.18	17.67	-16.46	5.99	2.33
Zinc white	94.57	0.10	9.73	74.88	3.71	13.67	20.40	-19.69	4.43	2.97
Vermilion	49.60	46.18	32.23	46.09	15.28	12.75	36.70	-3.51	-36.41	-2.98
Colcothar	35.94	17.60	12.04	39.67	7.77	9.42	10.84	3.73	-9.11	-4.54
Chrome green	46.41	-14.74	19.14	53.06	-8.66	13.38	10.69	6.65	-8.22	1.58
Artificial ultramarine	39.62	15.38	-47.78	45.64	2.84	5.09	54.67	6.02	-44.37	-31.37
Burnt umber	32.98	5.02	6.40	42.12	3.38	6.79	9.29	9.14	-0.55	-1.57
Carbon black	24.61	-0.24	-0.64	47.48	1.84	4.79	23.60	22.87	4.36	-3.86
Smalt	56.42	-3.40	-7.44	58.44	-0.09	1.86	10.08	2.02	-6.32	7.59
Minium	66.17	47.29	59.34	61.86	39.66	48.32	14.08	-4.31	-13.37	0.96
Azurite	64.88	-6.93	6.76	47.86	-2.50	16.49	20.10	-17.02	7.00	8.08
Prussian blue	25.17	-1.62	-12.63	38.95	-0.90	-1.79	17.55	13.78	-10.73	1.73
Chalk	90.33	0.69	19.85	64.32	4.38	13.91	26.93	-26.01	-5.28	4.56
Whitewash	86.22	-0.29	1.81	95.27	0.84	4.51	9.46	9.05	2.75	0.16

The yolk used to make the tempera is an organic material, which means that it is an ideal breeding ground for mushrooms and can cause changes on each of the pigments. The cause may also lie in adding too much binder to the pigments. Organic pigments are significantly more vulnerable to the mould because of their composition. Mould needs the following elements to grow: phosphorus, potassium, magnesium, lime, sulphur, copper, manganese, sodium, and zinc, which is why the pigments containing the abovementioned elements in the composition, are more susceptible to fungal interference (Gutarowska, 2010). Artificial ultramarine, which contains sodium and sulphur, has proved to be the most susceptible to the influence of the mould fungus. Pigments such as vermilion and azurite, even though they contain substances toxic for fungus, such as copper or mercury, have undergone significant changes, which translates into their ultimate values. The reason behind this phenomenon occurring in vermilion may be the amount of nutritious binder, which causes the mercury in this dilution to be no longer toxic to the mould, and therefore leads to such changes. In contrast, azurite darkens strongly under the influence of hydrogen sulphide from the atmosphere (Hopliński, 1990), which could contribute to these changes. It is also worth mentioning the effect of moisture – hydrogen peroxide is formed from water vapour and oxygen from the air, under the influence of light and heat, which not only attack organic binders but can also oxidize and bleach organic pigments (Doerner, 2017).

CONCLUSIONS

The interference of the mould fungus on polychrome depends to a large extent on the pigment used. Based on the results of the research, it can be stated that microorganisms cause various colour changes of all pigments tested. Burnt umber turned out to be the most resistant to colour changes. A largest colour change was found on samples coated with artificial ultramarine. Vermilion, azurite, Prussian blue, and carbon black pigments also showed a visible change in colour. Each of the changes occurring on the samples is visible to humans.

Mould fungus and moisture significantly affect the brightness of the pigment colour, which can be seen especially on samples of carbon black, which brightened, and on samples of cremnitz white, white lead, chalk, and azurite, which significantly darkened.

The largest change of chroma was noted on vermilion and artificial ultramarine, while the smallest was found on carbon black and burnt umber.

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Streszczenie: *Wpływ grzybów pleśniowych na pigmenty stosowane w dekoracjach ścian i stropów na przykładzie drewnianego kościoła pw. Św. Jerzego w Ostropie.* Przedmiotem badań było ustalenie zmiany barwy wybranych pigmentów stosowanych w polichromii, pod wpływem działania *Aspergillus niger*. Badania przeprowadzono na następujących pigmentach: biel kremowa, biel cynkowa, cynober, czerwień żelazowa, zieleń chromowa, ultramarina sztuczna, umbra palona, czerń węglowa, smalta, minia, azuryt, błękit pruski oraz kreda. Pomiary wykonano przy użyciu kolorymetru w przestrzeni barw CIELAB. Największą zmianę barwy próbek poddanych działaniu grzyba testowego wykazała ultramarina sztuczna, natomiast najbardziej stabilną barwą charakteryzowała się minia. Najmniejszą zmianę barwy próbek wysuszonych po działaniu grzyba pleśniowego cechowała się umbra palona, natomiast największą odnotowano również w przypadku sztucznej ultramariny.

Corresponding author:

Bogusław Andres,
Institute of Wood Sciences and Furniture
Warsaw University of Life Sciences – SGGW
166 Nowoursynowska St.02-776 Warsaw, Poland
email: boguslaw.andres@sggw.edu.pl;
phone: +48 22 59 38 657