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MUD FROM THE SITARJEVEC MINE AS A PIGMENT FOR TEXTILE PRINTING

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SUMMARY: The Sitarjevec mine, located near the town of Litija (Central Slovenia), is recognized by the strong yellow colour of its dripstone structures and mine mud deposits. The mine mud, composed predominantly of goethite, accumulates on the ground of the mine shafts as the result of the interaction between percolating underground water, iron ore minerals and microorganisms. Since the accumulation of limonite mine mud is an ongoing process, larger quantities of mud have been deposited in the mine shafts since its closure. These deposits present a real threat of unleashing a mine mud spill on the town of Litija. Such a scenario has already previously occurred. In order to find new potential routes for recycling larger quantities of this mine mud, the present research work was performed to assess the use of mine mud as a pigment in the dye industry. In the first stage, the chemical (XRF) and microstructural (SEM) characteristics of the mine mud were defined together with the identification of its phase composition (XRD), particle size distribution and specific surface area (BET). Furthermore, the pigment was used to colour textile printing paste on a laboratory scale. To define the most appropriate quality of textile prints the rheological response of the various textile printing paste samples was investigated in terms of their plastic viscosity, indicating their suitability for use in textile printing. Test prints were conducted, and the properties of leaching and fastness in the prints were assessed.

Keywords: mine mud, recycling, pigment, printing paste, textile, rheology

1 INTRODUCTION

The Sitarjevec mine, located in the town of Litija, Slovenia, was first mentioned in the 16th Century. It is presumed, however, that mining in this area was present as early as 4000 years B.C. Until 1965, when the mine was closed, it represented one of the largest and richest ore deposits in Slovenia. The main ores were lead, mercury, zinc, copper, iron and barite [1]. About two decades ago, monitoring of the formation of speleothems – stalactites, stalagmites, drapery and straws – which formed in the shafts following the closure of the mine, began. They are recognized as one of the fastest-growing dripstone speleothems worldwide [2].

The mine is also recognized because of the strong yellow colour of the deposits. The mine mud – deposits of Fe-rich residue, composed predominantly of goethite – gathers in the mine shafts due to the interaction between percolating underground water, iron ore minerals, and microorganisms. This mud has been recognized as a source of ochre pigment [3].

The large quantities of mine mud and underground water present a real threat to the old historical centre of Litija. As drainage of the acid mine water from the shafts of the abandoned mine has gradually been limited, it is estimated that more than 6000 cubic meters of acid mine water has accumulated in the mine over the last few decades. Accidents related to outbursts of mine mud occurred in Litija in 1895 and 1932 [4]. As stated by Kirby et al. [5], the utilization of material that is currently considered to be an environmental contaminant could present a financial benefit in the remediation of mine drainage, as well as help avoid additional environmental disturbances due to the mining of Fe-bearing minerals.

Furthermore, for the purposes of adventure tourism, the mine mud must be cleaned from the shafts, making it a waste material. At the end of the year 2017, the Municipality of Litija opened 100 m of the export shaft to the public. Since then they have renovated a further 300 m of mining shafts for museum exhibitions and guided tours. Sitarjevec mine evidently has potential as a natural science and outdoor history classroom to become the main tourist attraction in the town of Litija. Additionally, opportunities for further potential applications to exploit the substantial quantities of mud from the mine are being investigated, such as its use as a sustainable, natural colouring agent – a pigment for textile printing. Accordingly, the physical properties and chemical and mineralogical composition of the pigment found in the mine have been analysed

and are presented in this work.

New products for tourists at the Sitarjevec mine, such as protective clothing for visitors and tourist guides, have been designed. Designs include patterns printed on textiles using pigment from the mine. During the printing process pigment needs to be mixed into an adequate medium – printing paste – to be transferred and fastened to textiles.To achieve textile prints of an appropriate quality, the rheological response of the various samples of printing paste was investigated in order to find the composition of printing paste most suitable in terms of its visco-elastic properties – apparent viscosity, yield stress, shear modulus, and structural recovery – to be satisfactorily printed on textile. The fastness properties of the prints were also investigated.

The ochre pigment from the mine is assumed to be primarily composed of the mineral goethite (α-FeOOH), which is a major component of many ores, sediments, and soils, and one of the most thermodynamically stable iron oxides [6]. Goethite can be found in both humid and semiarid regions and also appears as the weathering product of various iron-containing rocks. Naturally occurring goethite collected from mines or other iron ore deposits has been characterized in terms of its chemical and mineralogical composition and temperature dependent transformations in order to assess potential applications for its use in various industrial processes, for technological purposes [7], as a colouring agent in art [8,9,5], for glazed ceramics [10], and for purposes of conservation and restoration [11].

To the best of the authors' knowledge, iron ore deposits such as mine mud from the Sitarjevec mine have been scarcely researched in terms of their potential application in textile printing. Onar Camlibel et al. [12] were successful in showing the antibacterial, UV protection, flame retardancy and colouration properties of iron ores as additives in the coating of textile surfaces.

The objective of this study was to characterize the ochre pigment from the Sitarjevec mine, assess its suitability in the field of textile printing, and present possibilities regarding the use of natural material from the mine, recognized for its visible characteristic i.e. colour, as a pigment for printing on textile souvenirs.

2 MATERIALS AND METHODS

2.1 Material collection and preparation

Mine mud was collected from the main shaft at the Sitarjevec mine. It was filtered through a sieve with holes of 0.63 mm to remove any larger pieces, dried, annealed for two hours at nine different temperature (150, 200, 250, 300, 550, 800, 900, 1000, 1100 °C), ground, and then passed through a sieve with openings of 0.063 mm. Annealing temperatures were chosen on the basis of the variation of the colours obtained due to exposure of the pigment to different temperatures. A change in colour is apparent at ambient temperatures up to 300 °C. Above this temperature, the colour of the annealed samples remains similar up to a temperature of 800 °C. After exceeding this temperature, differences in colour become visible once again.

For the purposes of textile printing, the particle size distribution of the pigment particles should be in the range between 0.2 μm and 1 μm [13]. To achieve particles with an appropriate particle size distribution, the natural pigment was micronized at Cinkarna Celje, using a pilot 8'' jet mill/ micronizer equipment.

2.2 Mixture design

The mix design of the printing pastes was adjusted based on preliminary test prints performed with the ground pigment and various commercially available textile printing pastes. Six mixes were shortlisted, incorporating micronized ocher pigment, demineralized water, and two commercially available textile printing pastes, Printperfekt Lac 110 Neu (Bezema, Switzerland) and Elastil Coprente FG (Minerva, Italy), with high covering properties. The series including Printperfekt Lac 110 Neu and Elastil Coprente FG printing paste were denominated PP and EC, respectively. The composition of each of the mixtures is presented in Table 1.

The selection of the most suitable mixture from the set of printing paste samples investigated was based on several criteria, namely: (1) the ability of the printing paste to maintain stable rheological properties similar to the reference printing paste after the addition of the dry micronized pigment and, in some cases, water (2) the environmental acceptability of the material, (3) the ease of printing and properties of fastness, and (4) the similarity of the print colour to the colour sensation in the main shaft of the Sitarjevec mine.

Table 1: Mixture composition of the printing paste samples investigated

Sample ID		Mixture composition			
		PP (%)	EC (%)	Micronized pigment (%)	Water (%)
PP series	PP	100	-	-	-
	PP5bV	95	-	5	-
	PP5V5	90	-	5	5
	PP5V10	85	-	5	10
EC series	EC	-	100	-	-
	EC20bV	-	80	20	-
	EC20V5	-	75	20	5
	EC20V30	-	50	20	30

Furthermore, a water- and oil-repellent finishing agent (Dynasilan F8815) was used on the samples in the finishing process before carrying out the leaching and fastness tests.

2.3 Methods

The ochre pigment was characterized in terms of its physical properties, and its chemical and mineralogical composition.

The morphological features of the pigment particles were examined using a scanning electron microscope JSM-5500LV (JEOL, Tokyo, Japan).

The particle size distribution of the ground and micronized pigment sample was determined using an SYNC laser diffractometer (Microtrack MRB, Verder Scientific GmbH & Co. KG, Germany). The material was dispersed in isopropyl alcohol in a container on the FLOWSYNC unit for wet measurements.

The mineralogical composition of the pigment was analyzed by X-ray powder diffraction (XRD) on both the natural and the annealed samples. Powder diffraction data were collected using CuKα radiation on an Empyrean diffractometer (PANalytical, Almelo, The Netherlands) operated at 45 kV and 40 mA. The measurements were made in flat-plate Bragg–Brentano θ–2θ geometry over an angular range of 8 to 70 °2θ using a step size of 0.02 °2θ and an accumulated time per step of 100 s. The resulting diffraction pattern was analyzed using HighScore Plus (PANalytical, Almelo, The Netherlands) powder diffraction analysis software.

The specific surface area of the natural and annealed pigment samples was determined by nitrogen gas sorption using ASAP 2020 equipment (Micromeritics, Norcross, Georgia). The samples were evacuated at a temperature of 105 °C and an evacuation rate of 0.67 kPa/s until a final vacuum of 2 Pa was achieved. The specific surface area was determined following the method proposed by Brunauer, Emmet, and Teller (SSA_{BET}).

For chemical analysis, the samples were prepared in triplicate as fused beads with a diameter of 40 mm and height of 3.6 mm. The chemical composition of the pigment was measured with a Perform'X ARL (Thermo Fischer, Madison, WI, USA) wavelength dispersive X-ray fluorescence spectrometer (WD XRF). UniQuant™ software was used to determine the major and minor oxides present in the sample.

Loss on ignition of the pigment was determined according to SIST EN 15169 (2007). The dried sample was placed in an oxidizing muffle furnace for 2 hours at 1000 °C and cooled to room temperature in a desiccator before being weighed. The change of mass after this step was recorded as LOI (Loss On Ignition).

Investigation methods were carefully selected in order to find a printing paste/ pigment mixture with technical characteristics (printing characteristics and fastness) similar to the reference printing paste and proof of its environmental inertness.

Measurements of the rheological behaviour of the printing paste mixtures were performed on an MCR 302 (Anton Paar GmbH, Austria). Tests including the amplitude sweep test, the creep test, the flow behaviour test and the ORO test were performed in order to derive the structural recovery of the samples being investigated. RheoCompass™ V1.20.493 (Anton Paar GmbH, Austria) software was used for data processing. Homogenization of components within the printing paste samples was executed with an ULTRA-TURRAX® homogenizer (IKA®-Werke GmbH & Co. KG, Germany) for 3 min at 600 rpm.

Analysis of the environmental impact of the pigment mixed into the printing paste was performed based on the results of the leaching test. In the textile printing process, pigment particles, which potentially contain toxic elements, were mixed into the printing paste, and pigment mixtures were printed on cotton fabric in a rectangular pattern. The leaching test was performed according to SIST EN 1744-3 (2002), using demineralized water as a leaching solution. The ratio of the dry mass of printed samples to the volume of leaching solution was 1:10. Samples were prepared in three different ways: (1) the textile was printed with printing paste (PrP), (2) the textile was printed with printing paste and pigment (PrP&P), (3) the textile was printed with printing paste and pigment, then after the fixation process it was subjected to the water- and oil-

repellent finishing process (PrP&P&F). The application of the water- and oil-repellent finishing was considered necessary to minimise moisture uptake and soiling of the protective clothing. Chemical analysis of the leachate was performed according to SIST EN ISO 17294-2 (2017). The total content of elements, including As, Ba, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, and Zn, was determined by inductively coupled plasma mass spectrometry (ICP-MS). The Cl^- and SO_4^{2-} content in the leachates was determined by UV/Vis spectrophotometry according to ISO 15923-1:2013. The content of F^- in the leachates was determined according to the SPADNS method (Macherey Nagel, cat. no. 918 142).

Colour fastness to artificial light, to washing (40 °C) and to dry and wet rubbing were tested in order to assess the compatibility of the pigment with the printing paste and to determine the suitability of the pigment for the purpose of printing. Tests were conducted according to ISO 105-B02, SIST EN ISO 20105-C01 and SIST EN ISO 105-X12, respectively. Fastness properties were tested on the PrintPerfekt Lac 110 Neu printing paste with the addition of 5 wt.% of pigment (PP5bV).

3 RESULTS AND DISCUSSION

3.1 Material characterization

Scanning electron microscope images of the ground pigment particles revealed that the particle size distribution (PSD) was in the range of nano- and micro-sizes, and some aggregates were also found. The PSD showed that all particles were smaller than 35 µm. The median particle sizes D_{90}, D_{50} and D_{10}, based on a volume distribution, were determined to be 12.49 µm, 1.48 µm and 0.34 µm, respectively. The PSD range of the investigated pigment was thus more than 30 µm, which, according to the criteria that determine the color of the pigment, is a wide distribution given the impact it has on the colour intensity of the pigment and all subsequent applications. According to Jones [14], decreasing the PSD range increases the purity of the colour and its brilliance.

Figure 1 shows XRD patterns obtained at the various annealing temperatures. It confirms that the natural pigment is of high purity under standard conditions, and that it is composed of the mineral goethite. The XRD patterns in Figure 1 show that goethite is stable up to approximately 200 °C. By increasing the temperature beyond 250°C peaks representative of hematite started to become distinguishable from the background, confirming the thermally-induced phase transformation [15].

The BET specific surface area (SSA_{BET}) results are consistent with the XRD results, showing an increase in the SSA_{BET} from 119,2 m^2/g to the maximum of 151,6 m^2/g when the temperature increased to 250 °C, which is ascribed to the formation of slit-shaped micropores as a result of the dehydroxylation of goethite and the formation of hematite. A substantial decrease to 47,7 m^2/g is then evident at 550 °C, followed by a continuous reduction in the specific surface area as annealing temperature increased, as internal and interparticle sintering occurred [16,17].

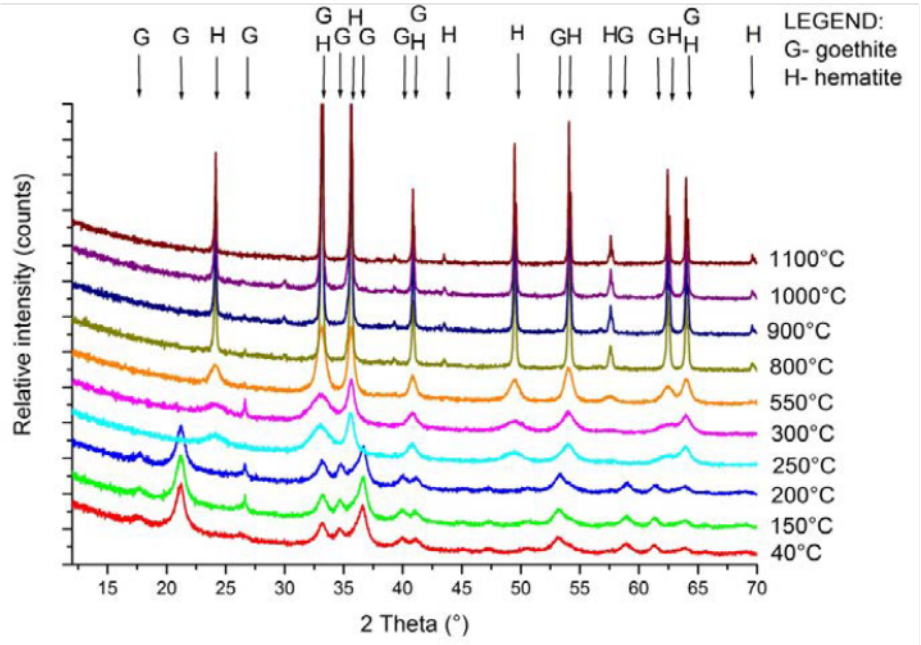

Figure 1: XRD patterns of an investigated sample of pigment annealed at different temperatures

The chemical composition of the pigment sample is presented in Table 2. The contents of Fe_2O_3, SiO_2 and Al_2O_3 were 72.32 %, 2.27 % and 1.20 %, respectively. The presence of oxides other than Fe_2O_3 shows the presence of impurities coming from the surrounding base rock. The loss on ignition (LOI_{1000}) was 22.47 %, indicating the thermal decomposition of phases present in the sample. The LOI_{1000} results mostly from dehydration, i.e., the loss of water adsorbed on the outer and inner surfaces of minerals, and dehydroxylation, i.e., the loss of chemically bound water [16]. The XRD data confirms that the dehydroxylation of goethite occurred efficiently at temperatures higher than 550 °C, as shown in Figure 1.

Table 2: Chemical composition of the natural pigment

Parameter	*Content (wt.%)*	*Std. Dev. (wt.%)*
Na_2O	0.59	0.036
MgO	0.27	0.017
Al_2O_3	1.20	0.060
SiO_2	2.27	0.080
K_2O	0.14	0.008
CaO	0.09	0.006
MnO	0.10	0.006
Fe_2O_3	72.32	0.150
ZnO	0.29	0.019
Other oxides*	0.27	0
LOI	22.47	0.022

*total content of other oxides in traces

3.2 Textile printing pastes

The results of particle size analysis of the micronized natural pigment sample showed a PSD range of between 0.0860 µm and 7.78 µm. The median particle sizes D_{90}, D_{50} and D_{10}, based on a volume distribution, were determined to be 1.74 µm, 0.5 µm and 0.19 µm, respectively. The PSD range of the pigment particles following micronization is appropriate for textile printing [13].

As there is a lack of comprehensive work about screen printing [18], further research is needed to define the appropriate mix of printing paste, pigment, and potentially water to achieve a printing paste with acceptable printability, as determined from its rheological response. The rheological properties measured, including loss (G') and storage (G'') modulus, the loss factor ($\tan\delta$), the limit of the viscoelastic region (γ_L), flow point (τ_f), static (τ_{sy}) and dynamic (τ_{dy}) yield stress and apparent viscosity (η), are presented in Table 3. In the PP-based printing paste samples all four materials behave as a viscoelastic solid, as G' > G'', within the limit of the viscoelastic (LVE) region. The loss factor was $\tan\delta < 1$, of the order $2x10^{-1}$, for all the samples examined, meaning that their structure resembled that of a gel in the LVE region. The flow point was similar for samples PP and PP5bV, at approximately 60 Pa, while it decreased by a factor of three in the PP5V10 sample. The addition of water substantially decreased the flow point (Table 3) and the structural strength of samples PP5V5 and PP5V10 in comparison to the reference sample PP, which can be seen from the decreasing values of G' and G''. The data in Table 3 also show that the viscous behaviour of the PP and PP5bV samples is similar, with only a slight reduction in values of dynamic yield stress and apparent viscosity at shear rates of 1, 10 and 50 s^{-1}. This reveals that, up to 5 wt.%, the addition of pigment does not significantly influence the flowability properties in comparison to the reference sample PP. In contrast, when water is added, as in the PP-based printing paste samples PP5V5 and PP5V10, the dynamic yield stress and apparent viscosity are substantially altered.

Table 3: Rheological parameters of the PP-based printing paste series

Sample ID	Storage modulus within the LVE, G' (Pa)	Loss modulus within the LVE, G'' (Pa)	Loss factor, tanδ (-)	Limit of the viscoelastic region, γ_L (%)	Flow point, τ_f (Pa)	Static yield stress, τ_{sy} (Pa)	Dynamic yield stress, τ_{dy} (Pa)	Apparent viscosity, η, at shear rate 1 s^{-1} (Pa.s)	Apparent viscosity, η, at shear rate 10 s^{-1} (Pa.s)	Apparent viscosity, η, at shear rate 50 s^{-1} (Pa.s)
PP	2318	444	0.192	0.002	62	21.45	38.72	73.4	14.70	5.72
PP5bV	2350	561	0.239	0.002	60	19.21	41.77	78.5	15.30	4.53
PP5V5	1380	343	0.249	0.002	43	13.78	27.78	51.87	10.09	3.80
PP5V10	523	136	0.260	0.003	17	5.89	12.04	23.38	4.78	1.88

Additionally, tests of structural recovery showed that the structure of the PP-based printing paste samples recovers quickly in all four samples under investigation, after approximately 12 to 18 s. Samples with the addition of water, i.e. PP5V5 and PP5V10, tended to recover faster than the reference printing paste PP or the printing paste with only the addition of pigment, PP5bV, but the 6 s difference is supposed to be insignificant in real applications.

Results for the EC series of printing paste samples showed that a more substantial amount of pigment is needed in order to achieve the colour required, as the EC printing paste covers the pigment colour more effectively than the PP printing paste (Figure 2). Furthermore, significant dilution of the EC printing paste was needed for a comparable rheological response to be achieved in samples incorporating the pigment, which was shown to compromise the properties of the EC printing paste. The PP printing paste performed better, both in terms of colour and rheological behaviour, especially in the case where only 5 wt.% of pigment was added (sample PP5bV).

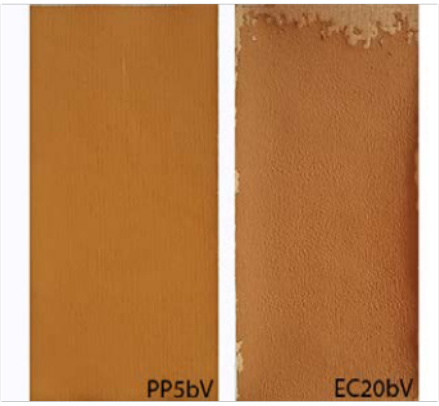

Figure 2: Photograph of samples, printed with printing paste Printperfekt Lac 110 Neu (5 wt.% of pigment) – PP5bV, and Elastil Coprente FG (20 wt.% of pigment) – EC20bV, showing the differences in colour and quality of the print

Printed textiles are known for their potentially hazardous effects during both production and use. A study of a total of 52 samples of textiles found the toxicity of printed cotton and cotton/linen textiles to be significantly higher than those that were unprinted [19]. The results of the leaching test show that the values of most of the heavy metals were lower in the PrP&P sample compared to the PrP sample. The only two parameters where values of the leachate were higher from the PrP&P sample compared to the PrP sample were Ba and sulphate. With the finishing process, most of the values of the PrP&P leachate decreased, the exceptions being Ni, Zn and sulphate.

Taking into consideration the legislation regarding the discharge of waste water into waters with a drainage area smaller than 10 km^2 [20], the most critical parameters in the leachate of all three samples were the concentrations of As, Co, fluoride and sulphate. As exceeded the limit value in the PrP leachate; Co exceeded the limit value in both the PrP and PrP&P leachate, but the value decreased to a satisfactory concentration (i.e. below the limit) when the finishing process was applied; fluoride exceeded the limit value in all three samples; and sulphate is at the legislation limit in the PP&P leachate and exceeds the limit in the PrP&P&F leachate. For situations where the drainage area is larger than 10 km^2, concentrations of all the elements fall far below their respective limit values.

Table 4: Colour fastness properties of the samples printed with PP printing paste, with and without water- and oil-repellent finishing

Analysis	Visual assessment			
	Grey scale fastness grade of the printed sample (no finishing)		Grey scale fastness grade of the printed sample with finishing	
Colour fastness to artificial light	5		5	
Colour fastness to washing	5		5	
Colour fastness to rubbing	dry	wet	dry	wet
	4	1	4	4

Colour fastness to artificial light and washing was excellent in both samples, with or without the water- and oil-repellent finishing (Table 4). Colour fastness to dry rubbing was good in both samples, but in the case of the untreated samples (without finishing) the colour fastness to wet rubbing is poor. A possible reason for the inadequate wet rubbing properties is the concentration of pigment added as dry matter. Adding pigment to the printing paste in a concentration of 5 % could be exceeding the ability of the binder in the printing paste to crosslink on the textile. According to other authors [21,22], this property is most compromised when subjected to wet rubbing. The process of finishing significantly improved the colour fastness of the samples to rubbing under wet conditions.

4 CONCLUSIONS

The potential for mine mud from the Sitarjevec mine to be used as a pigment for textile printing was proven. After the characterization of mine mud, both natural and annealed, the research focused on the natural pigment. It was shown that a small quantity of pigment (5 % / printing paste), creating a print similar in colour to the colour sensation of the mine mud in its original whereabouts, mixed into the appropriate printing paste has an insignificant effect on the rheological properties of the mix. The printing paste sample PP5bV, which was composed of PP and 5wt.% pigment, without the addition of water, behaves similarly to the reference printing binder PP in terms of the rheological parameters measured. Based on the rheological examinations performed soon after mixing, this mixture composition should, therefore, achieve satisfactory results during the printing process.

The leaching results show that elements in the pigment, crosslinked in the printing paste, do not present any additional environmental hazard. Not only are the pigment and printing paste well crosslinked, in most cases the concentrations of elements in the leachate from the PrP&P sample are even lower than in the leachate from the PrP sample. .

The fastness properties of the printed samples are good, especially in those that had been treated with the water- and oil-repellent finishing.

The results of this study represent a basis for further research into the possibilities of printing using pigment from the Sitarjevec mine. More detailed research regarding the rheological behaviour is expected, including the addition of some auxiliaries, with additional fastness tests.

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