

ACHROMATIC CERAMIC PIGMENTS

ZDENĚK ŠOLC, LIBOR ŠOLC*, LUBOMÍR FAJFR*

*Institute of Chemical Technology, Department of Inorganic Technology, 532 10 Pardubice***Department of Silicate Chemistry, Research Institute Monokrystaly, 511 19 Turnov*

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Fluorides and chlorides, particularly the combinations $\text{BaF}_2 + \text{CaF}_2$ or $\text{LiF} + \text{NaCl}$, appear to be the most efficient mineralizing additions for the preparation of grey zircon pigments of the $\text{ZrSi}-\text{AlNiCo}$ or $\text{ZrSi}-\text{NiCoCrFe}$ types with respect to their optical properties. At a mean 30 % spectral reflectance, the difference between the highest and the lowest value amounts to 5 %.

A black pigment of the rutile type (TiSbV) was prepared under various conditions of reaction mixture composition and firing. In view of the optical properties (optimum flatness of the spectral reflectance curve) and of the amount of eluable vanadium, the following composition and firing conditions were found to be the most suitable ones: the $\text{Sb} : \text{V}$ molar ratio = 1.4 : 0.6, 20 wt. % admixtures in the form of Sb_2O_3 and NH_4VO_3 , firing at 1,150 to 1,200 °C for 2 hours. The pigment is made from TiO_2 of Czechoslovak manufacture, Pretiox AV 01, has a flat spectral reflectance curve and a vanadium eluability of 0.02 % of the calcinate weight.

INTRODUCTION

The term achromatic is used for grey, black and white pigments. Apart from the general requirements put on ceramic pigments, such as thermal stability, hiding power, non-toxicity and others, with achromatic pigments there is the additional demand for a uniform spectral reflectance all over the visible light spectrum. The development of such a pigment at the Monokrystaly Turnov institute yielded three basic compositions with a relatively low cobalt content (a raw material imported for hard currency), schematically designated $\text{ZrSi}-\text{AlNiCo}$ (further on composition A) and $\text{ZrSi}-\text{NiCoCrFe}$ (further on compositions B) and C), [2]. The optimum mineralizer and the firing conditions for the three compositions were sought with the aim of attaining the flattest possible spectral reflectance curve. The other pigment of rutile type, $\text{Ti}-\text{SbV}$, was prepared from locally manufactured white pigment Pretiox AV 01 (similarly to the rutile yellow [1]); provided the optimum firing conditions and the reaction mixture composition are strictly observed, the course of the spectral reflectance curve is very favourable.

EXPERIMENTAL

The following raw materials were used in the preparation of the grey zircon pigment: ZrO_2 (Type 7, Goldschmidt, FRG), SiO_2 (local ground quartz SUK), cobalt oxide (RKO, imported from Belgium), NiO (Lachema Kaznějov), Cr_2O_3 (type GX, Bayer, FRG), Fe_2O_3 (local red pigment Fepren TD 202). The other type of the TiSbV pigment was prepared from local TiO_2 (Pretiox AV 01), Sb_2O_3 (Žiar nad Hronom), NH_4VO_3 (Lachema, imported). The particle size distribution curves for the basic oxides, ZrO_2 and TiO_2 , determined by electron microscopy, show that for ZrO_2 , particles up to 8 μm take up 10 %, those of up to 14.5 μm 50 %, and up to 27 μm 90 %. In the case of TiO_2 , there are 10 %, 50 % and 90 %

of particles smaller than 0.27 μm , 0.47 μm and 0.8 μm respectively. The reaction mixtures were wet ground in a porcelain ball mill (grey zircon pigment) or ground dry (rutile black). The firing was carried out in the L 212.11 muffle kiln made by Elektrobád Frankenhausen (GDR) in air atmosphere. Following the firing, the material was leached twice in boiling water (elution of soluble mineralizers and particularly of unretained vanadium). Analyses of the aqueous eluates from TiSbV for the amount of unretained vanadium were effected by titration with a solution of Fe^{2+} salt using diphenylamine as indicator.

All of the pigments prepared in this way were applied in the current types of glazes (transparent 6474 or opaque PW 141) in amounts of 10 wt. % with a firing temperature of 1000 °C. The colority of the pigments was always evaluated only in the glaze by measuring the spectral reflectance over the 400 to 700 nm range using the DATACOLOR instrument and evaluating the L^* , a^* and b^* coordinates of the space of equal colour differences according to the CIE $L^*a^*b^*$ 1976 system. The L^* coordinate corresponds to the brightness, a^* and b^* to pure colours (+ a red, - a green, + b yellow and - b blue) [3, 4]. The purity of grey or black can thus be assessed either according to the distance from the centre of coordinates a^* , b^* , or according to the flatness of the spectral reflectance curve. This can be defined by the ratio of the difference between the maximum and minimum value of reflectance ΔR and by the mean value of reflectance $\bar{R}$ in the wavelength region measured, i.e. flatness $P = \Delta R/\bar{R}$.

EXPERIMENTAL RESULTS

1. The results of experiments with preparing a grey pigment of zircon type

The type ZrSi—NiCoAl or ZrSi—NiCoCrFe pigments practically exhibit the X-ray diffraction pattern of ZrSiO_4 . The peaks of the spinel phase are very weak, almost indiscernible. The admixture elements therefore pass into the structure and form solid solutions; the occurrence of inclusions is very limited. The charged substitution defects can be compensated by oxygen vacancies.

The present study was above all concerned with determining the effect of the type and composition of the mineralizer and the firing temperature.

Pigments of the zircon type make mostly use of type NaF + NaCl mineralizers acting as a flux. The presence of the fluoride is additionally justified by that, over a certain temperature range, it assists in the transfer of the silicic components by the gaseous phase. The mineralizers employed therefore mostly contained fluoride and formed mixtures melting over the interval of 750 to 1000 °C [4]. All of the pigment samples were employed as additives to opaque glaze PW 141 after firing and elution. The quality of the colour was assessed by measuring the spectral reflectance curve over the wavelength range of 400—700 nm and evaluating the colour differences in the CIE $L^*a^*b^*$ 1976 system. Flatness of the spectral reflectance curve has proved to be the most suitable criterion.

Only selected experiments which led to the lowest values of ratio P are listed in the Tables. The experimental series *A* is characterized above all by the rising end of the reflectance curve (in the region above 650 nm). This phenomenon has been strongly suppressed with series *B*, whose reflectance curve is flatter, slightly rising towards the higher wavelengths. With samples of series *C*, similarly to those of series *A*, the reflectance increases in the region above 650 nm, the experiments listed in Table III being the only exception.

Table I

Reflectance curve characteristics of pigment formulations A (ZrSiNiCoAl) in glaze PW 141. Reaction mixture fired at 920 or 980 °C with a time of holding of 3 hours.

Sample No.	Mineralizer conc. (in wt. %)	Firing temperature °C	CIE coordinates $L^*a^*b^*$ 1976			$P = \frac{\Delta R}{R}$	$\Delta R \%$
			L^*	a^*	b^*		
10	LiF (1.5)	920	72.76	—5.73	5.59	0.28	12
12	LiF (3.0)	920	71.67	—5.51	5.01	0.29	12.4
13	LiF (3.0)	980	71.26	—5.11	5.01	0.24	10.3
14	Na ₃ AlF ₆ (1.5)	920	72.62	—5.04	5.42	0.22	9.5
17	Na ₃ AlF ₆ (3.0)	980	71.33	—6.02	3.46	0.29	12.4
20	BaF ₂ (3.0)	920	69.70	—6.22	2.80	0.28	12.0
21	BaF ₂ (3.0)	980	70.45	—5.69	3.11	0.29	12.4
22	NaCl (1.5)	920	69.16	—5.89	3.71	0.28	12.0
32	CaF ₂ (3.0)	920	69.68	—6.09	3.39	0.27	11.6
43	NaF + BaF ₂ (3.0)	980	70.83	—5.98	4.33	0.28	12.0
45	NaF + CaF ₂ (3.0)	980	69.27	—5.80	5.15	0.24	10.3
47	LiF + Na ₃ AlF ₆ (3.0)	980	72.61	—5.64	5.16	0.23	9.9
48	LiF + BaF ₂ (3.0)	980	73.17	—5.02	5.32	0.21	9.0
61	KCl + CaF ₂ (3.0)	980	71.36	—5.61	5.57	0.29	12.5
	Reimbold-Strick K2286		57.38	—5.16	4.19	0.38	16.0
The mean reflectance amounted to about 0.46 (46 %)							

Table II

Reflectance curve characteristics of selected pigment formulations B (ZrSiNiCoCrFe) in glaze PW 141. Reaction mixtures fired at 980 °C with a time of holding of 3 hours. Mineralizer concentration 3 wt. %.

Sample No.	Mineralizer	CIE coordinates $L^*a^*b^*$ 1976			$P = \frac{\Delta R}{R}$	$\Delta R \%$
		L^*	a^*	b^*		
5	NaCl	61.55	—2.74	6.09	0.23	6.9
6	KCl	62.49	—3.85	6.03	0.20	6.0
9	CaF ₂ + BaF ₂	48.10	—0.07	2.75	0.18	5.4
21	CaF ₂ + LiF	48.78	—1.65	4.87	0.28	5.5
27	KCl + NaCl	64.39	—2.67	6.33	0.23	7.6
30	LiF + NaCl	55.14	—2.59	4.80	0.20	4.6
33	LiF + KCl	59.35	—2.86	5.66	0.24	6.7
35	LiF + NaF	47.61	—3.25	0.13	0.24	4.3
36	LiF + Na ₃ AlF ₆	50.42	—1.84	3.49	0.24	4.5
3	BaF ₂ + Na ₃ AlF ₆ + CaF ₂	58.46	—4.11	2.19	0.21	6.0

From this aspect, the composition of series B is the best, and at the same time the Co content in the form of RKO oxide (commercial designation of Co₂O₃) is only 2.97 wt. %. Table I indicates that the best results are provided by the LiF and Na₃AlF₆ mineralizers and by the combinations NaF + CaF₂, LiF + Na₃AlF₆,

Table III

Reflectance curve characteristics of selected samples of pigment formulations C (Zr Si Ni Co Cr Fe) in glaze PW 141. Reaction mixtures fired at 980 °C with a time of holding of 3 hours. Mineralizer concentration 3 wt. %.

Sample No.	Mineralizer	CIE coordinates $L^*a^*b^*$ 1976			$P = \frac{\Delta R}{\bar{R}}$	$\Delta R \%$
		L^*	a^*	b^*		
8	LiF	60.08	—3.99	2.76	0.28	8.1
13	NaF + BaF ₂	55.99	—3.28	3.13	0.29	7.3
16	Na ₂ SiF ₆ + CaF ₂	52.89	—3.81	2.93	0.22	4.8
30	LiF + NaCl	63.18	—3.64	3.99	0.28	8.9
33	LiF + KCl	64.71	—4.51	3.36	0.28	9.2
35	LiF + NaF	62.39	—3.99	3.74	0.21	6.5

and particularly LiF + BaF₂ (weight ratio 1 : 1). Over the given range, neither the firing temperature nor the concentration of the mineralizer affect the P factor to any significant degree. This is why the concentration of 3 % and the temperature of 980 °C were used in the subsequent experiments. In series B (Table II), the best results were obtained with fluorides and chlorides: CaF₂ + BaF₂ (1 : 1), LiF + NaCl, KCl, or BaF₂ + Na₃AlF₆ + CaF₂. Sample No. 9, with a reflectance curve flatness of 18 % ($P = 0.18$), exhibits almost complete elimination of the raised ends of the reflectance curve (an example of a typical relationships is shown in Fig. 1). This sample was also prepared in larger amounts (250 g) and the flatness of the reflectance curve was less than 0.20. Similarly, in series C, differing only

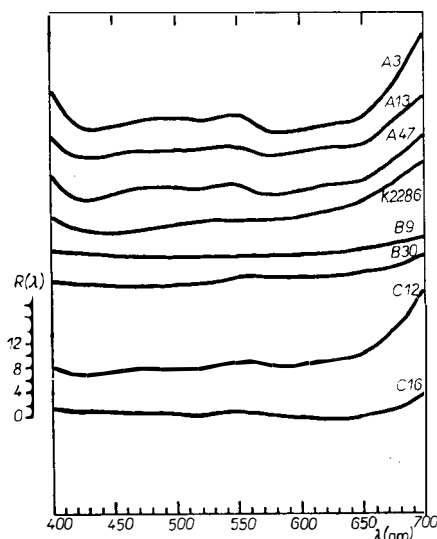


Fig. 1. Examples of spectral reflectance curves of grey pigment formulations A, B and C after application in the PW 141 glaze. The mean reflectance value is about 28—30 %.

in percent contents of Ni, Co, Cr and Fe oxides, the most efficient mineralizer was fluoride in the combination $\text{LiF} + \text{NaF}$, or $\text{CaF}_2 + \text{Na}_2\text{SiF}_6$. The 'colority' of the three groups of compositions (A, B, C), in coordinates of identical colour differences to CIE $L^*a^*b^*$ 1976, is plotted in Fig. 2.

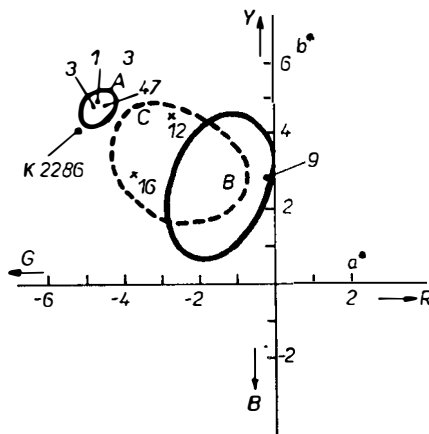


Fig. 2. Grey pigment of formulations A, B and C applied in glaze PW 141, colority region of coordinates a^* , b^* in the CIE $L^*a^*b^*$ 1976 system.

2. The results of experimental preparation of a black pigment with a rutile structure

According to the patents by F. Hund [5], a black pigment can be obtained substituting titanium in the rutile structure with Sb and V ions. The results a solid solution of Sb and V oxides in the rutile structure and the substitution charged defects show mutually compensating charges. In view of the ionic radii of Sb^{3+} , Sb^{5+} , V^{3+} and V^{5+} (0.090, 0.062, 0.067 and 0.040 nm respectively), and the ionic radius of Ti^{4+} (0.064 nm), Sb obviously occurs as Sb^{5+} and vanadium as V^{3+} and possibly V^{5+} .

X-ray analysis and calculation of lattice parameters of the tetragonal rutile-type structure with $D_{4h}^{14} - P 4/m$ showed that dissolution of vanadium oxide alone in rutile does not affect the lattice parameters at all up to a vanadium content of 50 wt % of elementary V; $a = b = 4.60 \pm 0.002$, $c = 2.96 \pm 0.003$ Å. Antimony oxide, up to 50 wt. % of the element, raises just a little the lattice parameters: $a = b = 4.60$ to 4.61 ± 0.003 Å. The changes in lattice parameters due to the combination of the two elements are listed in Table IV.

At high concentrations of Sb and V oxides both separately and in combination (roughly above 20 wt. % of the elements) most of the characteristic diffraction peaks show a decrease of intensity and even disappearance of reflectance of some densely occupied atomic planes in the rutile structure. However, as such high concentrations are not used in the preparation of the pigment, the behaviour of the system Ti—Sb—V was not studied in greater detail.

The results shown in Table IV indicate an only slight decrease of a and c parameters with increasing vanadium content at a constant Sb content and a constant V content. The former phenomenon is probably associated with the small radius

Table IV

Lattice parameters of the rutile structure a , c (Å) on substitution of titanium by vanadium and antimony

Sample No.	Content (wt. %)		Lattice parameters		Eluable V	
	Sb	V	a	c	% V in pigment	% V of initial V
47	2	2	4.593 ± 0.002	2.963 ± 0.003	0.032	1.61
48	2	4	4.597 ± 0.003	2.967 ± 0.005	0.034	0.84
49	2	8	4.597 ± 0.001	2.956 ± 0.002	0.038	0.47
50	2	16			0.042	0.26
97	20	20	4.588 ± 0.004	2.972 ± 0.003	0.11	0.54
98	20	30	4.581 ± 0.010	2.976 ± 0.011	0.21	0.70
99	20	40	4.561 ± 0.009	2.959 ± 0.009	0.25	0.62
100	20	50	4.561 ± 0.005	2.967 ± 0.005	0.27	0.54
47	2	2	4.593 ± 0.002	2.963 ± 0.003	0.032	1.61
51	4	2	4.600 ± 0.002	2.968 ± 0.004	0.027	1.33
52	8	2	4.595 ± 0.003	2.964 ± 0.005	0.024	1.19
53	16	2	4.601 ± 0.003	2.969 ± 0.002	0.021	1.05
97	20	20	4.588 ± 0.004	2.972 ± 0.003	0.11	0.54
101	30	20	4.598 ± 0.007	3.001 ± 0.009	0.25	0.75
102	40	20	4.602 ± 0.003	3.027 ± 0.004	0.14	0.71
103	50	20	4.603 ± 0.004	3.059 ± 0.008	0.10	0.50

of the V^{5+} ion and thus with the formation of mutually compensated defects Sb_{Ti}° , V_{Ti}° , V_{Ti}° : on the other hand, the latter is related with the necessary occurrence of the Sb_{Ti}° defect with a large ionic radius of Sb^{3+} . The Table also specifies the amount of unretained and thus eluable vanadium, in terms of the amount of fired product and in that of the amount of vanadium in the reaction mixture before firing at 1150 °C for two hours. The vanadium was eluted in two stages in boiling water. Although in experiments 47–50 and 97–100 the initial vanadium content was increased, its eluable amount increased just very little; it decreased mildly with rising content of Sb.

The conditions for the preparation of the black pigments were sought with regard to the minimum possible content of eluable vanadium and the flattest possible shape of the spectral reflectance curve over the range $\lambda = 400$ to 700 nm.

a) The effect of mineralizer type

The reaction mixture contained 20 wt. % of Sb_2O_3 and NH_4VO_3 admixtures; the ratio Sb : V was 1 : 1 or 0.8 : 1.2. The reaction mixture was fired at 1150 °C for 2 hours. The following substances were used as mineralizers in amounts of 3 wt. %: H_3BO_3 , $NaF + NaCl$ (1 : 1), Na_2SiF_6 , $K_2CO_3 + 2 H_3BO_3$, $CaCO_3 + 2 H_3BO_3$, Na_3AlF_6 , $NaF + \gamma-Al_2O_3$, LiF and Bi_2O_3 . A black colour of the pigment (always assessed after addition to the 6474 transparent glaze) was achieved only with samples free of mineralizer or with the use of Bi_2O_3 and H_3BO_3 . The other mineralizers led to brown-black or grey pigments. With respect to the content of eluable vanadium, the best results were obtained with the samples free of mineralizers (0.07 % V in pigment), with H_3BO_3 (0.09 %) and with Bi_2O_3 (0.10 %). In the other cases, the content of eluable vanadium was higher up to 20 times.

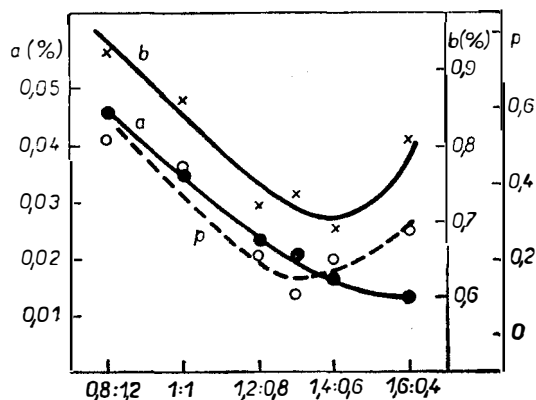


Fig. 3. Vanadium eluable from the fired product in terms of the Sb : V ratio (0.8 : 1.2 to 1.6 : 0.4); a — % V per 1 g of fired product, b — % V in terms of V introduced, p — reflectance curve flatness $p = R/R$, $R = 5-6\%$.

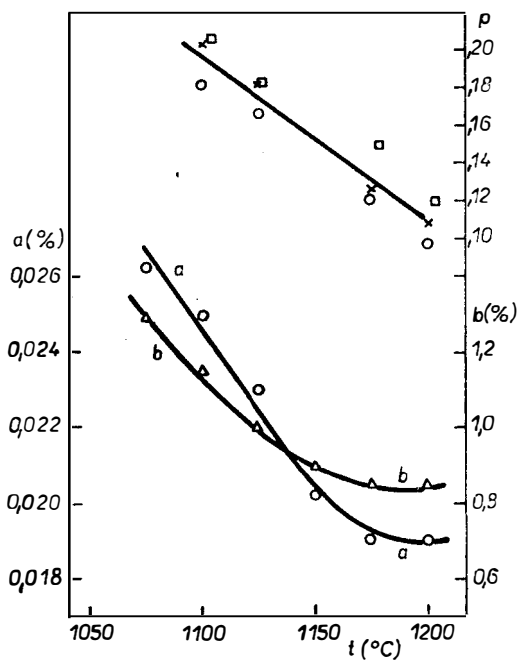


Fig. 4. Temperature of firing the reaction mixture vs. the amount of eluable vanadium and the quality of the pigment. Rapid heating rate, holding time 2 hours at the maximum temperature, the Sb : V ratio in the reaction mixture 1.4 : 0.6, 20 wt. % of $Sb_2O_3 + NH_4VO_3$ in the reaction mixture. The temperature of firing the 6474 glaze (pigment content 10 wt. %) was 950 °C (x), 1000 °C (O) and 1050 °C (□); a — percent of vanadium eluated from 1 g of fired product, b — percent of eluated vanadium in terms of vanadium introduced, p — flatness of the reflectance curve, $R = 5-6\%$.

b) The effect of molar ratio of the admixtures

The ratio Sb : V was varied over the range from 0.8 : 1.2 to 1.6 : 0.4; no mineralizer was used; the samples were fired at 1150 °C for 2 hours. Fig. 3 shows the result of four executions of each experiment (relative error $\pm 15\%$). It appears that from both points of view (the lowest amount of eluable vanadium and the lowest value of P , i.e. the flattest shape of the spectral reflectance of the pigment in the 6474 glaze), a higher Sb : V ratio is most suitable. However, decreasing the V content beyond the Sb : V ratio of 1.6 : 0.4 no longer yields a visually black pigment, but a merely black-brown one. At a mean reflectance of 5 to 6 %, the value of $P = 0.2$ indicates a difference of only 1 % between the minimum and the maximum reflectance over the λ range of 400 to 700 nm. The lower V content is also advantageous in terms of costs (imported material).

c) The effect of temperature used in firing the reaction mixture and the glaze

At a ratio of substitution admixtures Sb : V = 1.4 : 0.6 and at their content (as Sb₂O₃ and NH₄VO₃) of 20 wt. %, the effect of the firing conditions was investigated without the use of mineralizers. The results are summarized in Fig. 4. With respect to eluable vanadium and flatness of the reflectance curve, the best results are obtained from the highest temperatures, i.e. 1175–1200 °C (at still higher temperatures, the material tends to fuse into lumps that are difficult to process). Glaze firing at 1050 °C already leads to a mild deterioration of optical properties. The same results were obtained with experiments at the ratio Sb : V = 1.6 : 0.4. A decrease of the heating rate down to 5 °C/min had no distinct effect.

Experiments with varied contents of the Sb₂O₃ + NH₄VO₃ over the range from 5 to 30 wt. % of admixtures have borne out an earlier finding [6] in that the optimum amount is 20 wt. %. The higher contents do not improve the results; moreover, raising the amount of eluable vanadium; lower contents (e.g. already 15 %) yield grey to brown colour shades.

CONCLUSION

According to X-ray analysis, grey pigments of the zircon type, exhibit practically solely the structure of ZrSiO₄. The transient elements thus enter the zircon structure by substitution. For three formulations of reaction mixtures, developed at the Monokrystalý Turnov Research Institute (designated A, B, C), the most efficient mineralizer for the preparation of an optically adequate grey pigment was sought. The results were evaluated according to the criterion of the course and flatness of the optical reflectance curve, measured on pigments utilized in the PW 141 glaze and by comparison with the foreign pigment K 2286 made by Reimbold-Strick.

With respect to the evaluation of optical properties, the best results were obtained with formulation B (ZrSiNiCoCrFe) having a relatively low content of Co oxide (2.9 %). Among ten types of single-component mineralizers and their two- and three-component combinations, the combined fluoride-containing types, particularly BaF₂ + CaF₂, LiF + NaCl and others, were found to be most efficient ones. The flatness of their reflectance curve amounted to 0.18, i.e. at a mean value of the spectral reflectance coefficient of 30 % the difference between the highest and the lowest reflectance amounted to 5 %. For example, with sample No. 9 the reflectance uniformity over the visible light region is much more favourable than that of the foreign sample (Figs. 1 and 2).

The black rutile pigment (TiSbV) was prepared from various reaction mixture formulations at various firing conditions. In view of the lowest possible content of eluable vanadium and the desirable flatness of the reflectance curve, the following formulation rules appear suitable:

- TiO_2 in the form of anatase Pretiox AV 01, 20 wt. % of $\text{Sb}_2\text{O}_3 + \text{NH}_4\text{VO}_3$ admixtures;
- the Sb : V molar ratio should be 1.4 : 0.6;
- the reaction mixture should contain no mineralizer;
- firing: heating rate 5°C min^{-1} , maximum temperature 1150 — 1200 $^\circ\text{C}$, time of holding 2 hours.

On application in the 6474 transparent glaze (firing temperature 950—1000 $^\circ\text{C}$), the pigment exhibits a flat spectral reflectance curve (flatness 0.20, difference 1.09 % between the maximum and the minimum reflectance value, mean reflectance 5.28 %). About 0.02 % V is eluted from the calcined reaction mixture (i.e. several tenths of a gram from 1 kg of calcinate).

In view of the very satisfactory optical properties (flatness of the reflectance curve, a high refraction index and thus a high hiding power) and of a suitable thermal stability in the glaze, at least up to 1050 $^\circ\text{C}$ (cf. Fig. 3, the top curve), the pigment is also suitable for glazing applications. Its high content (80 wt. %) of the local raw material TiO_2 Pretiox is another advantage.

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NEPESTRÉ KERAMICKÉ PIGMENTY

Zdeněk Šolc, Libor Šolc*, Lubomír Fajfr*

Katedra anorganické technologie, VŠCHT, 532 10 Pardubice

**Výzkumný ústav Monokrystaly, 511 19 Turnov*

Jsou popsány dva typy nepestrých keramických pigmentů — zirkonový šedý a rutilový černý. Šedý zirkonový pigment typu $\text{ZrSi}-\text{AlNiCo}$, resp. $\text{ZrSi}-\text{NiCoCrFe}$ vykazuje rentgenograficky prakticky jen strukturu ZrSiO_4 . Zbarvení proto dodávají další oxidy přechodných prvků, které substituují ionty Zr v ZrSiO_4 . Byla použita tři složení reakční směsi (označená jako A, B, C) vyvinutá autory [2]; pro ně pak byl hledán optimální mineralizátor (10 látek a jejich dvoj-, resp. trojkombinace). Kritériem vhodnosti mineralizátoru byla co nejvyšší plochost remisní křivky $P = \Delta R/R$; ΔR — rozdíl nejvyšší a nejnižší hodnoty remise, R — průměrná hodnota remise v oboru 400—700 nm v %. Remise byla měřena vždy až po aplikaci pigmentu v krycí glazuře PW 141. Mineralizátory, resp. jejich kombinace, jejichž použití vedlo k pigmentům s větší plochostí remisní křivky (nižší P) než zahraniční vzorek K 2286, jsou uvedeny v tabulce I. až III. Nejlepších výsledků bylo dosaženo s fluoridy Li, Mg a Ba, a to u složení reakční směsi B (obr. 1 a 2). Např. u vzorku B 9 činil při průměrné remisi $R = 30\%$ rozdíl mezi nejvyšší a nejnižší hodnotou ΔR pouze 5%; výrazně bylo potlačeno obvyklé zvýšení remise v okrajových oblastech viditelného spektra.

V případě černého rutilového pigmentu (typ TiSbV podle patentů Hunda [5]) byly zjišťovány optimální podmínky jeho přípravy s ohledem na maximální plochost remisní křivky a minimální obsah nezachyceného (vyloužitelného) vanadu. Při použití tuzemského TiO_2 (anatas Pretiox AV 01) jako hlavní složky reakční směsi (80 hmotn. %), je optimální poměr Sb : V v reakční směsi 1,4 : 0,6. Podmínky výpalu: ohřev 5 K. min⁻¹, max. teplota 1150 až 1200 °C s 2h výdrží. Není třeba přidávat mineralizátor. Dosažené výsledky ukazují obr. 3 a 4; plochost remisní křivky $P = 0,20$ při $\Delta R = 1\%$, obsah vyloužitelného vanadu 0,02 hmotn. % V z výpalku. Aplikace pigmentu je vhodná i při teplotách glazování 950—1050 °C.

Rentgenometrické studie ukazují na velmi malé změny mířkových parametrů struktury rutilového typu i při vysokém obsahu vanadu nebo antimonu (tabulka IV.).

Obr. 1. Příklad remisních křivek šedých pigmentů složení A, B, C po aplikaci v glazuře PW 141. Průměrná hodnota remise je cca 28—30%.

Obr. 2. Šedý pigment složení A, B, C aplikovaný v glazuře PW 141, oblast barevnosti souřadnic a^* , b^* systému CIE $L^*a^*b^*$ 1976.

Obr. 3. Vanad vyluhovatelný z výpalku v závislosti na poměru Sb : V (0,8 : 1,2 až 1,6 : 0,4); a — % V na 1 g výpalku, b — % V vztahené na vložený vanad, p — plochost remisní křivky $p = \Delta R/R$, $R = 5$ —6%.

Obr. 4. Vliv teploty výpalku reakční směsi na obsah vyloužitelného vanadu a na kvalitu pigmentu. Náběh teploty rychlý, výdrž při max. teplotě 2h, poměr Sb : V v reakční směsi 1,4 : 0,6, 20 hmotn. % $\text{Sb}_2\text{O}_3 + \text{NH}_4\text{VO}_3$ v reakční směsi. Výpal glazur 6474 (obsah pigmentu 10%) na teploty 950 °C (×), 1000 °C (○), 1050 °C (□); a — % vyloužení vanadu v 1 g výpalku, b — % vyloužení. V vztahené na vložený vanad, p — plochost remisní křivky, $R = 5$ —6%.

АХРОМАТИЧЕСКИЕ КЕРАМИЧЕСКИЕ ПИГМЕНТЫ

Зденек Шольц, Лябор Шольц*, Лубомир Файфр*

Химико-технологический институт, кафедра неорганической технологии,
532 10 Пардубице

*Научно-исследовательский институт Монокристаллы, 511 19 Турнов

В приводимой работе описываются два бесцветных керамических пигмента: циркониевый серый и рутиловый черный.

У циркониевого серого пигмента типа ZrSi—AlNiCo , или ZrSi—NiCoCrFe практически доказана структура ZrSiO_4 только рентгенографически. Поэтому окраска вызывается лишь дальнейшими оксидами переходных элементов, которые замещают ионы Zr в ZrSiO_4 . Были использованы три состава реакционной смеси (обозначение через A, B, C), разработанные авторами [2], для них был также найден оптимальный минерализатор (10 веществ и их двой- или трехкомбинации). Критерием пригодности минерализатора оказывается наибольшая плоскостность кривой степени отражения $P = \Delta R/R$, ΔR — разность наиболее высокой и наиболее низкой величины коэффициента яркости, R — средняя величина коэффициента яркости в пределах 400—700 nm в %. Коэффициент яркости всегда измеряли только после применения пигмента в непрозрачной глазури PW 141. Минерализаторы или их комбинации, использование которых послужило для получения пигментов с большей плоскостностью кривой степени отражения (более низкой P) по сравнению с импортным образцом K 2286, приводятся в табл. I—III. Наилучшие результаты были получены с фторидами Li, Mg и Ba, а именно у состава реакционной смеси B (рис. 1 и 2). Например, у образца B 7 при среднем коэффициенте яркости $R = 30\%$ разность между наиболее высокой и наиболее низкой величиной ΔR составляет только 5 %, резко понижается обыкновенное повышение коэффициента яркости в краевых областях видимого спектра.

В случае черного рутилового пигмента (тип TiSbV согласно патенту Хунда [5]) устанавливались оптимальные условия его получения с учетом максимальной плоскостности кривой степени отражения и максимального содержания неуставливаемого (выпелачиваемого) ванадия. При применении отечественного TiO_2 (анатас Pretiox AV 01) в качестве основного компонента реакционной смеси (80 % по весу) оптимальное отношение Sb : V в реакционной смеси — 1,4 : 0,6. Условия обжига: нагрев 5 K. мин⁻¹,

максимальная температура 1150—1200 °C с 2 ч. выдержки. Добавка минерализатора уже не нужна. Полученные результаты приводятся на рис. 3 и 4; плоскостность кривой степени отражения $R = 0,20$ при $\Delta R = 1\%$, содержание выщелачиваемого ванадия 0,02 % по весу V из огарка. Использование пигмента пригодно даже при температурах глазурирования 950—1050 °C.

Рентгенографическим исследованием показываются весьма небольшие изменения параметров решетки рутила даже при высоком содержании ванадия или сурьмы (табл. IV).

Рис. 1. Пример кривых степени отражения серых пигментов составом А, В, С после применения в глазури PW 141. Средняя величина коэффициента отражения приблизительно 28—30 %.

Рис. 2. Серый пигмент составом А, В, С, применяемый в глазури PW 141, область цветностей координат a^* , b^* системы CIE $L^*a^*b^*$ 1976.

Рис. 3. Ванадий, выщелачиваемый из огарка в зависимости от отношения Sb : V (0,8 : 1,2 до 1,6 : 0,4); а — % V на 1 г огарка, б — % V при пересчете на примененный ванадий, p — плоскостность кривой степени отражения $p = \Delta R/R$, $R = 5$ до 6 %.

Рис. 4. Влияние температуры обжига реакционной смеси на содержание выщелачиваемого ванадия и на качество пигмента. Рост температуры оказывается быстрым, выдержка при максимальной температуре 2 часа, отношение Sb : V в реакционной смеси 1,4 : 0,6, 20 % по весу $Sb_2O_3 + NH_4VO_3$ в реакционной смеси. Обжиг глазури 6474 (содержание пигмента 10 %) до температур 950 °C (о), (х), 1000 °C 1050 °C (□); а — % выщелачиваемого ванадия в 1 г огарка, б — % выщелачиваемого ванадия при пересчете на применяемый ванадий, p — плоскостность кривой степени отражения, $R = 5$ —6 %.