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Study of ceramic pigments based on $Er_2Ce_{2-x}Mo_xO_7$

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Bretsznajder Special Chapter

Abstract This contribution is focused on the synthesis, characterization and optical properties of new inorganic pigments which are environment friendly and can substitute some toxic metals in interesting colour compounds. Pyrochlores belong to the group of high-temperature pigments, and are a variety of actual and potential applications for several materials. Examples include catalysts, thermal barrier coatings, solid electrolytes, nuclear waste forms and host materials for luminescence centers. The pigments were prepared by the solid state reaction and also by method of suspension mixing of materials in the series with increasing content of molybdenum. The pigments were applied into organic matrix and ceramic glaze. The colour properties of these applications were investigated depending on content of Mo, method of preparation and temperature of calcination (1350–1550 °C after step 50 °C). The optimum conditions for their synthesis were determined. The pigments were evaluated from standpoint of their structure, colour and particle sizes. Characterization of $Er_2Ce_{2-x}Mo_xO_7$ pigments ($x = 0.1$, 0.3, 0.5 and 0.7) suggests that they have a potential to be alternative yellow or orange colourants for paints, plastics, ceramics and building materials.

Keywords Inorganic pigments · Pyrochlore compounds · Non-toxic pigments · Solid state reaction · Colour properties

Introduction

Inorganic natural and synthetic pigments produced and marketed as fine powders are an integral part of many decorative and protective coatings. They are used for mass colouration of materials such as plastics, glaze, ceramics and porcelain enamels. In these applications, pigments disperse in the media forming a heterogeneous mixture. The powder used to colour ceramics are more important in that they must possess thermal and chemical stability at high temperature and must be inert to the action of molten glaze [1]. The characteristics required for commercial uses of ceramic pigments are: colour-tone and saturation, colour covering, tinting-strength, brightening and brilliance ability, non-reactivity, insolubility, chalking resistance, dispersibility, etc. [2].

However, most of conventional inorganic pigments contain the toxic metal such as Cd, Co, Cr, Hg, Pb and Sb that can adversely attack the environment and human health. Therefore, development of safe inorganic pigments has been required to replace toxic inorganic pigments by environment friendly pigments or less toxic substances [3].

In recent years, complex oxides with general formula $A_2B_2O_7$ have been of great interest to many researchers. These compounds exhibit a defect fluorite-type structure or an ordered pyrochlore-type structure, which is mainly governed by the ionic radius ratio of A^{3+} and B^{4+} [4]. The stability of the pyrochlore structure depends strongly on this ratio of the A- and B- site cations, r_A/r_B [5].

The pyrochlore structure exhibits a remarkable range of compositions with over 500 different combinations of A- and B- site cations having been synthesized. The A-site cation is generally occupied by larger tri- and tetravalent actinides and lanthanides, and B-site is typically Ti, Zr, Hf or Sn [4, 6]. The symmetry is cubic belonging to the Fd3m

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(No. 227) space group and the unit cell comprises eight formula units. The structure is composed of a 2 × 2 × 2 arrangement of sub-cells each of which is similar to a single fluorite unit cell. If we write the general formula as $A_2B_2O_6O'$and choose to fix the origin on the B site, the ions occupy four crystallographically non-equivalent positions: A at 16d, B at 16c, O at 48f and O′ at 8b. There is an interstitial site that is at 8a [7].

The pyrochlore compounds have a wide variety of interesting physical and chemical properties such as high-melting point, high-thermal expansion coefficient, low-thermal conductivity, high-thermal stability, unique luminescence, high-radiation stability and ability to accommodate defects [8].

The basic representative of pyrochlores is the Naples yellow $Pb_2Sb_2O_7$ but it contains problematical Pb and Sb. So, the aim is to prepare ecological inorganic pigment of mixed oxides based on the Ce–Er–Mo with yellow or orange colour. The pigments were synthesized by classical ceramic method, i.e. solid state reaction, and also by method of suspension mixing of materials. The final colour hue of pigment depends on the individual components content, temperature of calcination and on the way of application, too.

Experimental

The pigments $Er_2Ce_{2-x}Mo_xO_7$ ($x = 0.1$, 0.3, 0.5 and 0.7) were synthesized by two different methods, i.e. solid state reaction (SSR) and suspension mixing of materials (SMM). As the initial compounds for preparation of the sample by ceramic method were used CeO_2 (ML-Chemica, Troubsko, CZ), MoO_3 (Lachema, a.s., Brno, CZ) and Er_2O_3, which was obtained from Rare Earth Products Ltd., India. These compounds are ranked amongst technical as regards purity.

The precursors employed for the traditional ceramic way of preparation were homogenized in the porcelain mortar with pestle. The mixtures were then calcinated in corundum crucibles in an electric resistance furnace with the heating rate of 10 °C $\min^{-1}$. The calcination temperatures in interval from 1350 to 1550 °C after step 50 °C were maintained for 2 h. The second way of preparation of the pigments, suspension mixing of materials, presented as two-step process has one different starting compound, i.e. CeO_2 was replaced by $Ce(SO_4)_2{\cdot}4H_2O$. In the first step, the starting compounds are homogenized by wet in the porcelain mortar, final mixture is subsequently assigned to the preheated steel plate (approx. 400 °C) and then thermally elaborated for a few minutes. The second step constitutes the calcination at demanded temperatures of gained powder semiproduct in the electric furnace for the same conditions like by ceramic method.

All prepared pigments were applied into organic matrix (Parketol, Balakom a.s. CZ) in mass tone and evaluated for colour change by measuring of spectral reflectance in the visible region of light (400–700 nm) using a ColorQuest XE (HunterLab, USA). Some of them (in 10% w/w) were applied into a middle-temperature borate-silicate (transparent leadless) glaze G 05091 (Glazura, s.r.o., Roudnice nad Labem, CZ) and temperature of glazing was 1000 °C during the time of 15 min. The measurement conditions for colour change were following: an illuminant *D65*, 10° complementary observer and measuring geometry *d/8°*. The colour properties are described in terms of CIE $L^*a^*b^*$ system (1976). The value a^* (the red–green axis) and b^* (the yellow–blue axis) indicate the colour hue. The value L^* represents the lightness or darkness of the colour in relation to scale extending from white ($L^* = 100$) to black ($L^* = 0$). The value C (chroma) represents saturation of the colour and is calculated according to the formula: $C = (a^{*2} + b^{*2})^{1/2}$. The colour of pigment is also expressed by the hue angle $H°$ defined by an angular position in the cylindrical colour space (for the orange $H° = 35-70°$ and for the yellow $H° = 70-105°$).

The distribution of particle sizes of the calcinated powders was obtained by laser scattering using Mastersizer 2000 MU (Malvern Instruments, Ltd. GB). It is a highly integrated laser measuring system (He-Ne laser, $\lambda = 633$ nm) for the analysis of particle size distribution. The structure of the prepared pigments was also investigated. The synthetized pigments were studied by X-ray diffraction analysis. The X-ray diffractograms of the samples were obtained using the equipment Diffractometer D8 Advance (Bruker, GB), CuK_λ radiation with scintillation detector. The formation of pigments was followed by thermal analysis using the STA 449C Jupiter (NETZSCH, Germany) which allows evalution of data and simultaneous registration of the thermoanalytical curves TG and DTA [9]. The SEM-EDX, using JOEL JSM-5500 LV apparatus equipped with analyser IXRF Systems and detector Gresham Sirius 10, was employed to study two selected samples of pigments [10]. The bandgap values are calculated using Kubelka–Munk function which is given by $K–M = (1-R)^2/2R$, where R is the reflectance value. The values of K–M coefficients were obtained from measuring with the help of ColourQuest XE and the value of the wavelength is substituted in the formula E (eV) = 1236/wavelength (nm) [11].

Results and discussion

The aim of the research was to find the best conditions for the preparation of the pigments and also to determine the influence of growing content of molybdenum, the

Table 1 The effect of Mo content on the colour properties of $Er_2Ce_{2-x}Mo_xO_7$ samples (calcinated at 1350 °C)

x	Organic matrix					Ceramic glaze				
	*L**	*a**	*b**	*C*	*H°*	*L**	*a**	*b**	*C*	*H°*
0.1	86.44	8.54	21.63	23.25	68.45	85.64	7.20	13.45	10.02	61.84
0.3	85.51	8.29	33.00	34.03	75.90	85.38	6.44	17.40	10.24	69.69
0.5	83.49	10.06	41.68	42.88	76.43	83.03	5.42	20.53	10.31	75.21
0.7	79.12	5.58	30.58	31.08	79.66	80.32	4.17	11.97	9.66	70.79

calcination temperatures and also method of preparation on their colour properties after application into organic matrix and in some cases into a ceramic glaze.

The colour hue of pigments applied into organic matrix is visible dependent on the content of Mo (Table 1). The values of brightness *L** are become lower with the growing amount of Mo. Opposite to them are the values of colour coordinates *a**, *b** and so chroma *C* is escalating. The final colour shade is shifting from light orange through marked orange to dark orange (fulvous) hue with increasing Mo content. The colour of pigments applied into ceramic glaze is in all cases light orange. These applications are characterized by low values of colour coordinates *a**, high grant of brightness *L** and very narrow interval of chroma *C* (9.66–10.31). The influence of Mo concentration is evidently only by application into organic matrix and the best colour results achieve the pigments with content of Mo $x = 0.5$. The colour difference between ceramic glaze and organic matrix application is very well obvious from Fig. 1.

The influence of calcination temperature on colour properties was also investigated. From Table 2 it follows that increasing calcination temperature decreases values of *L** and *H°* up to 1500 °C. On the other hand values of colour coordinates are growing. The highest saturation *C* was obtained by temperature 1450 °C. Growing temperature causes also decline of bandgap energy values Eg (eV) that verified our presumption. This fact confirmed with the change of the colour from orange to dark orange.

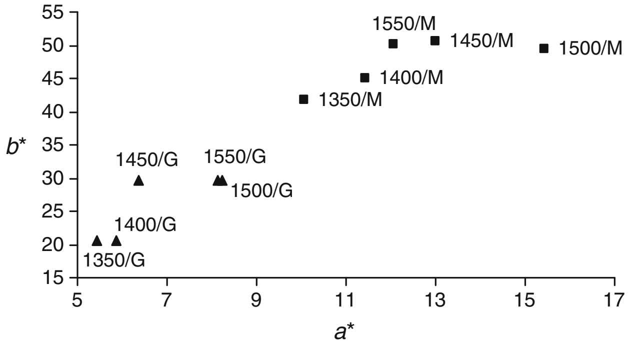


Fig. 1 The influence of calcination temperature on the colour coordinates *a** and *b** of the $Er_2Ce_{1.5}Mo_{0.5}O_7$ pigment applied into organic matrix (*M*) and ceramic glaze (*G*)

The particle size distribution can markedly affect the colour properties of inorganic pigments. Therefore, the synthesized samples were measured from this point of view. The mean particle sizes (d_{50}) of pigments used for colouring of ceramic glazes or bodies lie in the region from 5 to 15 μm. The test was carried out with unmilled pigments [12]. From the values presented in the Table 2 it is obviously that the mean values (d_{50}) of the particle size are varied in interval from approx. 8.5 to 11.5 μm. The influence of calcination temperature on the particle size distribution is demonstrated in Fig. 2.

Results from pigments prepared by suspension mixing of materials (SMM) are noticed in Table 3. The influence of calcination temperature is not as expressive as in the case of solid state reaction (SSR) but it is seen the same tendency as by SSR with increasing calcination temperature. The samples prepared by SMM have higher values of brightness *L** and markedly lower chroma *C*. The lighter coloration relate to wider band gap energies and by organic matrix as form of application the colouring of the samples is light orange.

From the values presented in the Table 3 it is visible that the mean particle size is rising with ascending temperature of calcination. The average particle size of $Er_2Ce_{1.5}Mo_{0.5}O_7$ pigment after calcination obtained at 50% cumulative mass is from 0.70 to 6.16 μm.

The pigment $Er_2Ce_{1.5}Mo_{0.5}O_7$ was also studied by powder X-ray diffraction analysis. It has been verified, that compounds prepared at the lower temperatures (1350, 1400 °C) are two-phased, where the cubic phase of the pyrochlore $Er_{0.5}Ce_{0.5}O_7$ was identified besides free CeO_2. The fluorite-type of CeO_2 structure of the samples with cubic symmetry with lattice parameter $a = 0.5404$ nm was determined. From temperature 1450 °C samples were homogenous and exhibited diffraction line that could be assigned only to pyrochlore compound (Fig. 3).

In comparing of the both method of preparation only one temperature of calcination, i.e. 1350 °C was chosen. From X-ray diffraction analysis standpoint of view method of

Table 2 The effect of calcination temperature on the colour properties and value Eg of $Er_2Ce_{1.5}Mo_{0.5}O_7$ samples (prepared by SSR, organic matrix)

T/°C	*L**	*a**	*b**	*C*	*H*°	Eg/eV	Particle size range/µm	Mean particle size d_{50}/µm
1350	83.49	10.06	41.68	42.88	76.43	2.84	2.68–20.06	8.78
1400	81.23	11.44	45.00	46.43	75.74	2.82	3.93–25.62	11.63
1450	80.76	12.99	50.55	52.19	75.59	2.79	2.87–19.04	9.05
1500	78.68	15.44	49.34	51.70	72.62	2.78	2.85–23.56	10.77
1550	80.63	12.07	50.01	51.45	76.43	2.76	1.87–25.16	11.03

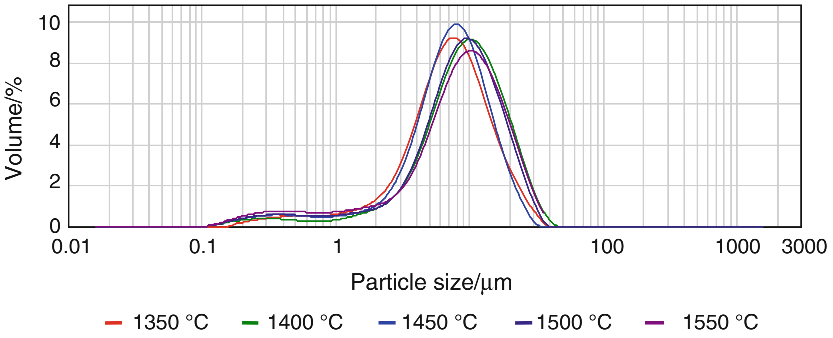


Fig. 2 Particle size distribution of the samples $Er_2Ce_{1.5}Mo_{0.5}O_7$ prepared by solid state reaction

Table 3 The effect of calcination temperature on the colour properties and value Eg of $Er_2Ce_{1.5}Mo_{0.5}O_7$ samples (prepared by SMM, organic matrix)

T/°C	*L**	*a**	*b**	*C*	*H*°	Eg/eV	Particle size range/µm	Mean particle size d_{50}/µm
1150	87.46	4.59	25.35	25.76	79.74	2.93	0.26–5.40	0.70
1250	84.72	6.17	28.81	29.46	77.91	2.92	0.76–13.83	3.11
1350	84.90	6.30	28.74	29.42	77.64	2.91	1.91–20.17	6.16

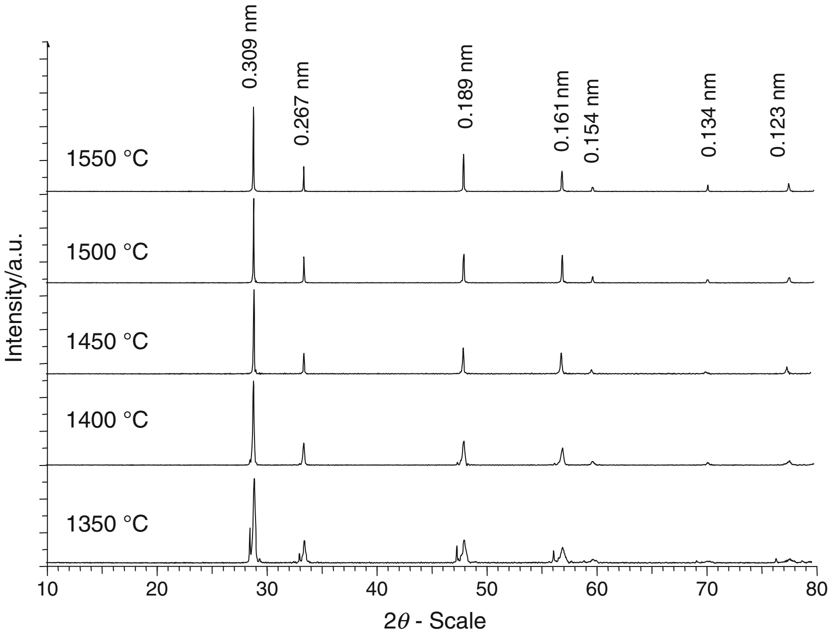
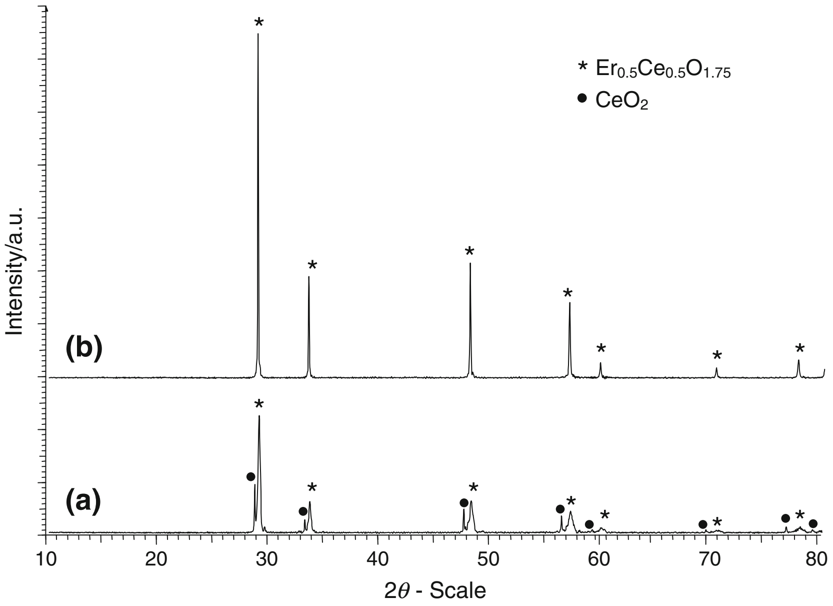


Fig. 3 Diffractograms of the $Er_2Ce_{1.5}Mo_{0.5}O_7$ pigments prepared by solid state reaction

suspension mixing of materials is preferable. It was appeared only single-phased of pyrochlore with very high intensity of peaks (three times higher than by method of solid state reaction). The pyrochlore compound is cubic with detected lattice parameter $a = 0.5356$ nm. It crystallizes in space group of symmetry Fd3m (No. 227).

Fig. 4 Diffractograms of the $Er_2Ce_{1.5}Mo_{0.5}O_7$ pigments at temperature of calcination 1350 °C: (*a*) SSR, (*b*) SMM



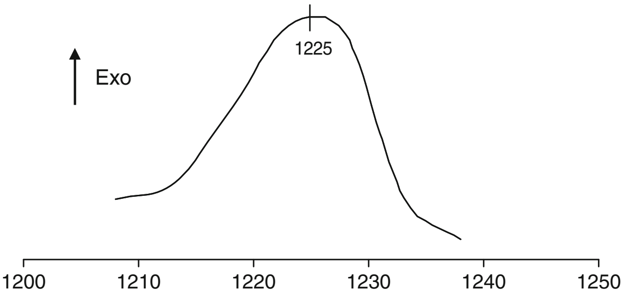


Fig. 5 The part of DTA curve of the $Er_2Ce_{1.5}Mo_{0.5}O_7$ pigment prepared by SSR and calcinated at 1350 °C

The pigment prepared by solid state reaction and calcinated at 1350 °C was heterogeneous because free CeO_2 was identificated in a small amount beside pyrochlore compound (Fig. 4).

The reaction mixture for pigment $Er_2Ce_{1.5}Mo_{0.5}O_7$ prepared by ceramic method was also followed by TG–DTA. The formation of the pigment was detected using method of thermal analysis and examined in the temperature range of 50 to 1300 °C. The starting reactants for the synthesis $Er_2Ce_{1.5}Mo_{0.5}O_7$ compound by solid state reaction were mixed oxide Er_2O_3, CeO_2 and MoO_3 in an adequate molar ratio.

The behaviour of host oxide CeO_2 during the thermal analysis is already known. In the case of this oxide partial oxygen loss was detected by TG–DTA measuring which corresponds with one endothermic effect at the temperature 1449 °C [13]. By TG curve the mass lost at the temperature range from approx. 50 to 600 °C (it was about 0.22%) there was detected in our starting mixture. The part of DTA curve of reaction mixture (before thermal treatment) is shown in Fig. 5. There was registered a small exothermal peak with maximum at 1225 °C. This effect is associated to the formation of the solid solution of $Er_2Ce_{1.5}Mo_{0.5}O_7$ and corresponds with results of X-ray analysis.

SEM images of $Er_2Ce_{1.5}Mo_{0.5}O_7$ (Fig. 6) show the crystal structure of the pigments. From the pictures, it is obviously that method of SSR (Fig. 6a) produces larger agglomerates than suspension mixing of materials (Fig. 6b). By the SSM method, particles are smaller which is also confirmed by particle size distribution.

Fig. 6 The SEM images of the $Er_2Ce_{1.5}Mo_{0.5}O_7$ pigment calcinated at 1350 °C **a** solid state reaction, **b** suspension mixing of materials

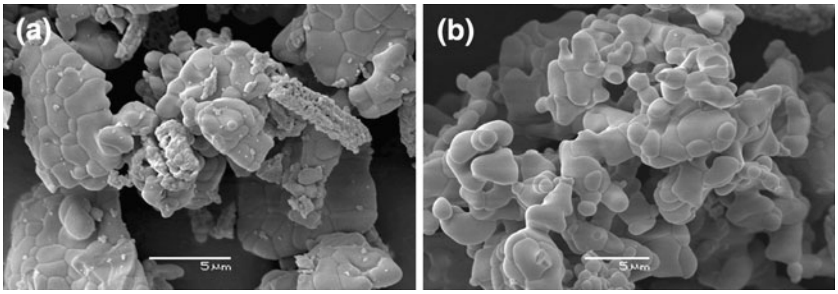


Table 4 The effect of method of preparation on the colour properties and characteristic of $Er_2Ce_{1.5}Mo_{0.5}O_7$ samples (temperature of calcination 1350 °C)

Characteristic of pigments	Method of preparation	
	Solid state reaction (SSR)	Suspension mixing of materials (SMM)
*L**	83.49	84.90
*a**	10.06	6.30
*b**	41.68	28.74
C	42.88	29.42
H°	76.43	77.64
Eg/eV	2.84	2.91
Particle size range/µm	2.68–20.06	1.91–20.17
Mean particle size d_{50}/µm	8.78	6.16
Detected phases	$Er_{0.5}Ce_{0.5}O_{1.75}$ CeO_2	$Er_{0.5}Ce_{0.5}O_{1.75}$

Conclusions

The main aim of this study was verified the different methods of preparation of $Er_2Ce_{2-x}Mo_xO_7$ pigments and compared obtained results from the point of view of their influence on the colour properties of the pigments. For synthesis of the samples traditional ceramic method, i.e. SSR and method of SMM was used.

At first the pigments were prepared by the SSR. The best content of molybdenum $x = 0.5$ was provided. Pigment with the excellent colour properties was obtained at higher temperature of calcination, i.e. 1450 °C and after application into organic matrix (dark orange hue). The method of suspension mixing of materials was also used for the preparation of the $Er_2Ce_{1.5}Mo_{0.5}O_7$ compound for the reason of decrease of the final temperature of calcination. And it managed—the best results were obtained at 1250 °C. The DTA analysis indicates the formation of pyrochlores around of temperature 1230 °C, but for pigmentary application, it is better to synthesize the product at higher temperature, at least 1450 °C (by SSR) and it corresponds with results of the X-ray analysis. Only one temperature of calcination, i.e. 1350 °C (Table 4) is chosen for the better comparing.

Method of SSR produces pigments with higher saturation and also colour coordinates *a** and *b**. The hue of applications is orange and these pigments are suitable to application into ceramic glaze (mean particle size is up to 15 µm). On the other hand these samples are two-phased and their particles are larger than particles prepared by SMM. So, we can choose method of preparation of pyrochlore compounds based on subsequent use of pigments. But very interesting discovery of this study is a fact that the pyrochlore compound was prepared which is also environmentally friendly and could contribute to the basic assortment of yellow or orange inorganic pigments.

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