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Ceramic pigments with chromium content from leather wastes

R.I. Lazău *, Cornelia Păcurariu, D. Becherescu, R. Ianoş

"Politehnica" University of Timişoara, Faculty of Industrial Chemistry and Environmental Engineering, Department of Science and Engineering of Oxide Materials, P-ta Victoriei No. 2, Timişoara 300006, Romania

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Abstract

Some thermoresistant pigments having spinel and tin sphene structure were synthesized using as chromophore (Cr^{3+}) source leather wastes with 6.5% Cr_2O_3 content. This particular chromium source brings a series of advantages, as: burning of the organic components supplies in situ a part of the necessary energy of the synthesis and the chromophore is well dispersed in the reaction mixture. The complete burning of the wastes without the emission of polluting compounds requires the reaction mixture to be introduced in the oven at temperatures above 800 °C.

Keywords: Color; Perovskites; Spinels; Ceramic pigments

1. Introduction

Approximately 600,000 tonnes solid leather wastes are being generated each year worldwide[1] by the leather industry. Their Cr_2O_3 content is at least 3.5%. The negative impact of the tanned leather wastes upon the environment is due to the chromium compounds toxicity, especially Cr^{6+} compounds. In literature there are indicated some solutions to reduce the polluting effect of these wastes, the most used being the incineration of the leather wastes with the view to obtain the green chromium oxide (Cr_2O_3).[1]

The present paper proposes a solution to use the leather wastes directly in the raw materials mixture designed to obtain the thermoresistant pigments with chromium content. This solution presents at least two advantages:

- the heat resulted from the burning of the organic component contained in the waste is being used in the energetic balance of the synthesis process of the pigments and
- the ash formed after burning the leather wastes, mainly consisting of Cr_2O_3, reacts with the partners in the mixture as an active reactant supplying the necessary chromophore (Cr^{3+}).

2. Experimental procedure

The favorable influence of the reducing atmosphere generated within the reaction mixture whilst the leather waste burns enhances the chromium binding as Cr^{3+}. The chosen solution requires making some raw materials mixtures to contain both classical raw materials for the thermoresistant pigment's industry ($CaCO_3$, ZnO, Al_2O_3 or $Al(OH)_3$, SiO_2, SnO_2, etc.) and the tanned leather waste—as Cr(III) source. In the reference samples, it has been used $(NH_4)_2Cr_2O_7$ as chromium source. The purpose of the experimental determinations was to use the tanned leather wastes in order to obtain some thermoresistant pigments with Cr(III) content, which belong to the most important crystallographic classes[2,3] and also develop a high practical interest: pigments with spinel structure and pigments with tin sphene structure.

In a first stage, it has been established the Cr_2O_3 content of the waste as being 6.5%. The designed compositions start from the stoichiometry of the crystalline phases representing the basis of each of the studied crystallographic classes:

(a) spinel structure
  - for pink color: $ZnO{\cdot}0.95Al_2O_3{\cdot}0.05Cr_2O_3$
  - for bluish-green color: $(1-x)ZnO{\cdot}xCoO{\cdot}(1-y)Al_2O_3{\cdot}yCr_2O_3$, where $x = 0.5$ and 0.25 and $y = 0.33$

(b) tin sphene structure (pink): $CaO{\cdot}SnO_2{\cdot}SiO_2$ (Cr^{3+})

* Corresponding author. Tel.: +40 256 403086; fax: +40 256 403060.
E-mail address: radulazau@gmail.com (R.I. Lazău).

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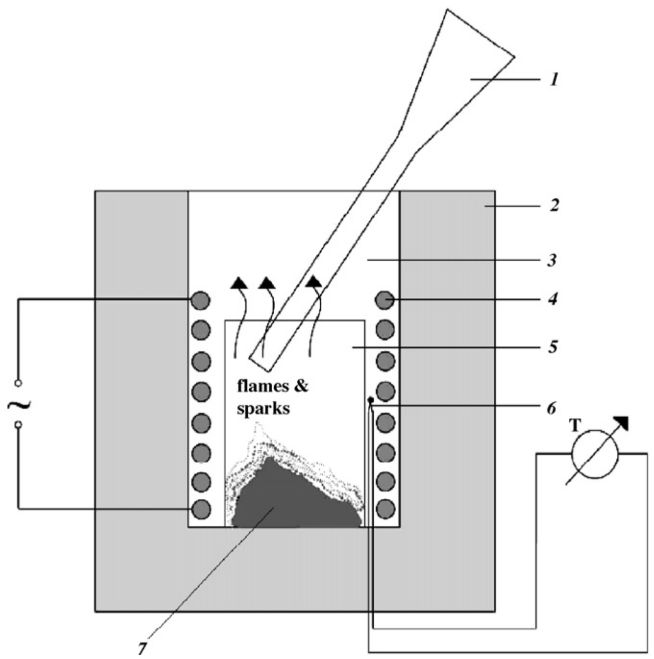

Fig. 1. The scheme of the device used to anneal the mixtures and obtain the pigments, where (1) feeding quartz tube with funnel, (2) refractory coat, (3) oven room, (4) heating elements, (5) refractory crucible, (6) thermocouple and (7) charge.

Cr_2O_3 has been introduced in all the samples as tanned leather wastes, except for the reference samples, where $(NH_4)_2Cr_2O_7$ was used. It has been used an increased water amount to ensure a good impregnation of the leather wastes with the insoluble oxides and the other soluble components. The resulted mixture has been heated up to boiling point stirring continually, than dried in the drying oven, at 150–180 °C. The dried samples show a good grinding ability resulting in pulverulent mixtures; these mixtures were calcined and it has been noticed that during the progressive heating polluting compounds form and evolve due to the gradual degradation of the organic components in the leather waste. In order to avoid this inconvenient, it has been referred to the waste incineration principles, meaning to introduce the wastes in the heated oven directly at temperatures over 800 °C. With this view, it has been used in the equipment in Fig. 1. Introducing the pulverulent mixture in the refractory crucible at 900 °C causes the composition to ignite almost instantly and burn quietly. After introducing the mixture, the oven was closed and heated up to the maintaining temperature (between 1000 and 1300 °C). After cooling down the samples were wet milled, washed (in order to separate the soluble components) and dried. The obtained pigments have been characterized by X-ray diffraction (using a DRON 3 diffractometer, Cu Kα radiation), diffuse reflectance spectrophotometry (using a SPEKOL 10 Karl-Zeiss Jena spectrophotometer) and they have also been tested in some ceramic glazes for faience tiles and kitchenware. The compositions of the studied mixtures are presented in Tables 1 and 2.

3. Results and discussion

3.1. Thermoresistant pigments with spinel structure

Based on the literature data and the previous results obtained by the authors[2,4–8] concerning the synthesis of the pink, respectively, bluish-green spinel structure pigments, the authors started from the zinc spinel stoichiometry ($ZnO{\cdot}Al_2O_3$), in which Al^{3+} was partly substituted by Cr^{3+}, as it may be seen from the recipes shown in Table 1. In order to obtain the bluish-green spinel pigments, a part of the Zn^{2+} ions has been also substituted by Co^{2+}. The minimum temperature, where the color of the samples becomes pure pink is 1200 °C, for 2 h. The color of the samples does not change between 1200 and 1300 °C. The increase of the Cr^{3+} content in the pigments (sample 3) does not lead to an intensification of the color but creates instead the possibility of Cr–O–Cr bonds appearance, thus the contamination of the pink color.

Samples 4 and 5 show a different color (bluish-green) after annealing at the same temperature – 1200 °C – due to the simultaneous presence of the chromophores Co^{2+} (tetrahedrally coordinated) and Cr^{3+} (octahedrally coordinated). The color tint depends on the ratio of the two chromophores. The presence of spinel phase, as $ZnAl_{0.95}Cr_{0.05}O_4$ solid solution (in the pink pigments), respectively, as $Zn_{1-x}Co_xAl_{2-y}Cr_yO_4$ solid solution (in the bluish-green pigments) is confirmed by the X-ray diffraction spectra of the pigments (Fig. 2). The identification of the spinel phase was made based on the JCPDS files 05–0669 for $ZnO{\cdot}Al_2O_3$, respectively, 44-0160 for $CoO{\cdot}Al_2O_3$. The diffuse reflectance spectra of samples 1–3 are those specific for the pink pigments with spinel structure[9–11] obtained by substituting Al^{3+} by Cr^{3+} (Figs. 3 and 4).

3.2. Thermoresistant pigments with tin sphene structure

The previous results of the authors[10–12] have shown that the best results may be obtained working with SnO_2 in excess

Table 1
The recipes of the spinel structure pigments

Sample no.	Oxides (molar ratio)				Chromium source	Synthesis temperature (°C)	Color after annealing
	ZnO	CoO	Al_2O_3	Cr_2O_3			
1	1	–	0.95	0.05	$(NH_4)_2Cr_2O_7$	1200	Ash-pink
2	1	–	0.95	0.05	Leather waste	1200	Pink
3	1	–	0.90	0.10	Leather waste	1200	Pink
4 (2.a)	0.5	0.5	0.66	0.33	Leather waste	1100	Bluish-green
5 (4.a)	0.75	0.25	0.66	0.33	Leather waste	1100	Bluish-green

Table 2
The recipes of the pigments with tin sphene structure

Sample no.	Oxides (molar ratio)			Cr^{3+} source ($5\%Cr_2O_3$)	Mineralizers		Raw materials	Color
	CaO	SnO_2	SiO_2		CaF_2 (%)	B_2O_3 (%)		
6 (P.60)	1	1.32	1.16	Leather waste	2	–	$CaCO_3$, SnO_2, SiO_2 (quartz), waste, CaF_2	Tawny red
7 (P.61)	1	1.32	1.16	Leather waste	2	2	$CaCO_3$, SnO_2, SiO_2, (quartz), waste, CaF_2, H_3BO_3	Chestnut red
8 (P.61.a)	1	1.32	1.16	Leather waste	2	1	$CaCO_3$, SnO_2, SiO_2 (quartz), waste, CaF_2, H_3BO_3	Chestnut red
9 (P.62)	1	1.52	1.16	Leather waste	2	2	$CaCO_3$, SnO_2, SiO_2 (quartz), waste, CaF_2, H_3BO_3	Tawny red
10 (P.101)	1	1.3	1	Leather waste	2	1	$CaCO_3$, SnO_2, SiO_2 (quartz), waste, CaF_2, H_3BO_3	Mauve-brown
11 (P.102)	1	1.3	3	Leather waste	2	1	$CaCO_3$, SnO_2, SiO_2 (quartz), waste, CaF_2, H_3BO_3	Reddish-brown
12 (P.103)	1	1.32	1	$(NH_4)_2Cr_2O_7$	2	1	$CaCO_3$, SnO_2, SiO_2 (quartz), $(NH_4)_2Cr_2O_7$, CaF_2, H_3BO_3	Liliaceous mauve
13 (P.104)	1	1.32	3	$(NH_4)_2Cr_2O_7$	2	1	$CaCO_3$, SnO_2, SiO_2 (quartz), $(NH_4)_2Cr_2O_7$, CaF_2, H_3BO_3	Brown-mauve
14 (P.105)	1	1.32	3	Leather waste	2	1	$Ca(NO_3)_2{\cdot}4H_2O$, SnO_2 SiO_2 (quartz), waste, CaF_2, H_3BO_3	Reddish-brown
15 (P.107)	1	1.32	2	Leather waste	2	1	$Ca(NO_3)_2{\cdot}4H_2O$, SnO_2 SiO_2 (quartz), waste, CaF_2, H_3BO_3	Reddish-brown

compared to the SiO_2 content and to the tin sphene stoichiometry; the mineralizers used were CaF_2 and B_2O_3. The studied compositions are shown in Table 2. The annealing temperatures were between 1150 and 1250 °C. The optimum annealing temperature in order to ensure a good resistance of the pigments related to the aggressiveness of the glass generating melts was found to be 1200 °C.

All the tested recipes lead to colors that vary between light liliaceous pink and chestnut red; the quality of the obtained pigments is assessed by color and the soluble chromium proportion (in the rising water) and it varies in a wide range. All the samples in which chromium has been introduced as leather waste are from this point of view better than the samples made with

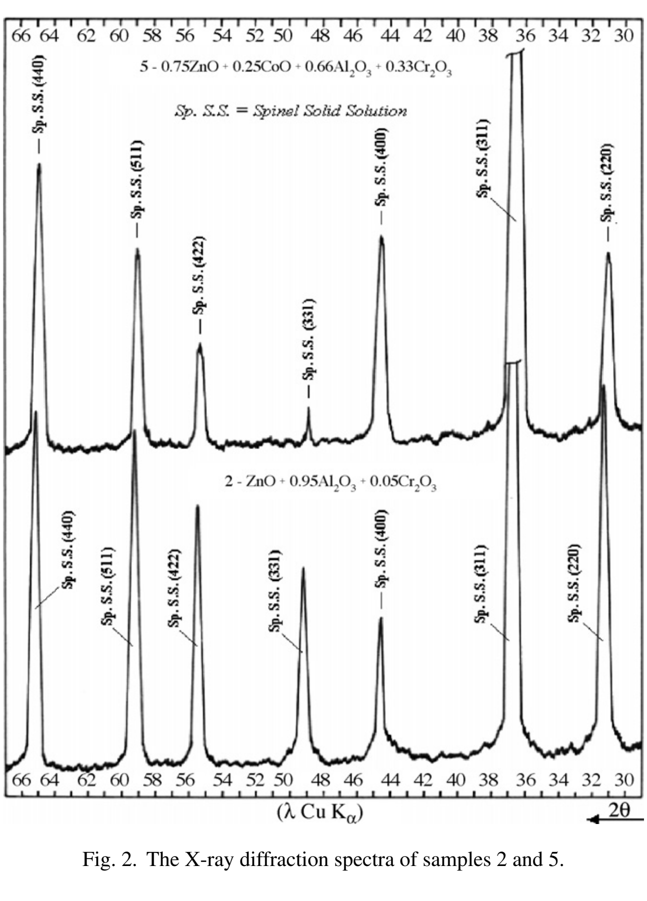

Fig. 2. The X-ray diffraction spectra of samples 2 and 5.

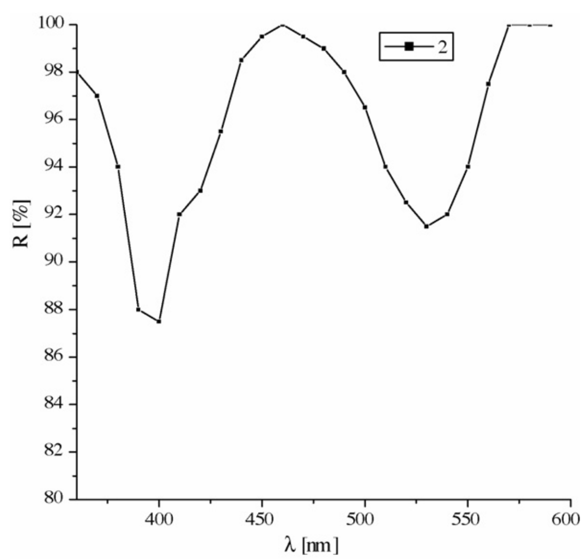

Fig. 3. The diffuse reflectance spectrum of pigment 2.

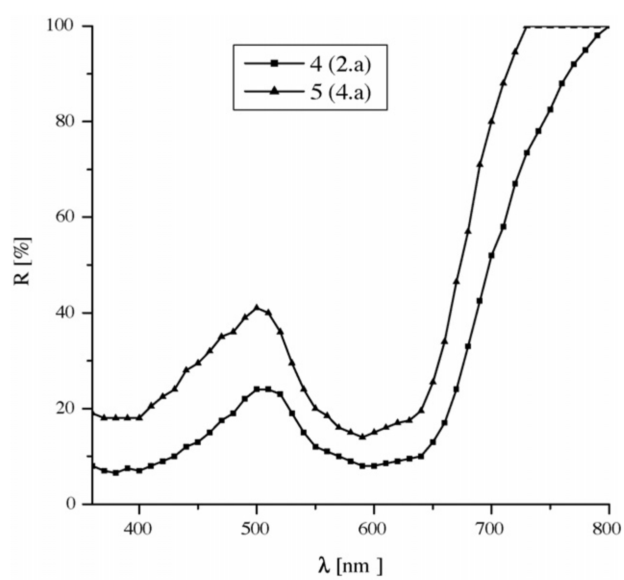

Fig. 4. The diffuse reflectance spectra of samples 4 (2.a) and 5 (4.a).

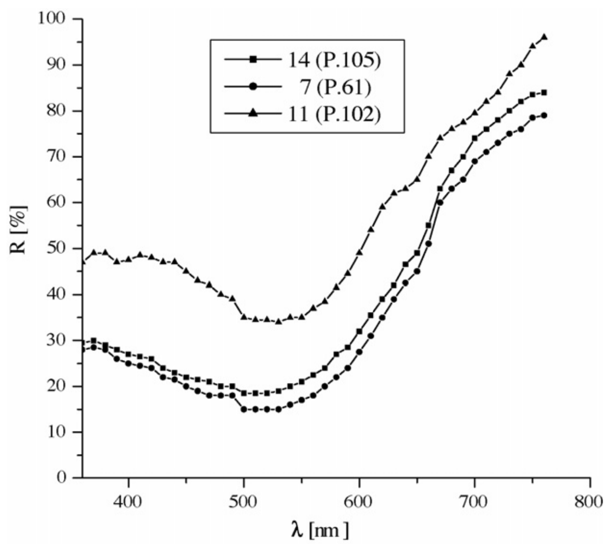

Fig. 5. The diffuse reflectance spectra of samples 7 (P.61), 11 (P.102) and 14 (P.105).

$(NH_4)_2Cr_2O_7$: more intense colored, with a marked red tint and the soluble chromium proportion in the rising water is almost negligible.

The color of the samples that differ by the way CaO has been introduced ($CaCO_3$, respectively, $Ca(NO_3)_2{\cdot}4H_2O$) is very similar. Still, the result is better in the case of using $Ca(NO_3)_2{\cdot}4H_2O$, especially in what concerns the behavior of the mixture during the annealing process. This may be explained by the additional oxygen content supplied by the nitrates decomposition, which contributes to the burning of the organic component of the waste. In these mixtures, the behavior of the waste is similar to that of the organic compounds (aminoacids, diamines, polyols, etc.) frequently used in the combustion method.[13,14]

The phase analysis by X-ray diffraction has shown that in all the studied samples the main phase is tin sphene (malayaite), together with cassiterite. In Fig. 5, there are shown the diffuse reflectance spectra of samples 7, 11 and 14.

3.3. Testing the pink pigments based on tin sphene, respectively, bluish-green spinel structures

The final criterion concerning the quality of the thermoresistant pigments is their behavior in coloring some vitreous coatings as ceramic glazes or enamels. Thus, some of the obtained pigments (which developed the most favorable colors) have been tested in coloring some faience glazes, this presenting a great practical interest. Concerning that the behavior of the thermoresistant pigment in the glassy matrix highly depends on the glass composition and the firing temperature, the pigments have been tested in different types of faience glazes from the current production of some tableware and tile faience factories in Romania. The pigments proportion in the glazes was 8%; the firing temperatures for the tested glazes were between 1150 and 1170 °C.

4. Conclusions

- The main contribution of the present paper relates to the possibility of reusing the leather wastes in obtaining some thermoresistant pigments of major interest for the ceramic industry. The proposed solution assures an improvement of the environment quality, as well as a decrease of the pigments cost—due to the specific of the used synthesis method.
- There have been approached two structural types of thermoresistant pigments (spinel and tin sphene), both having the same chromophore: Cr^{3+}. Chromium has been introduced by a classical source ($(NH_4)_2Cr_2O_7$), as well as by tanned leather wastes. The reaction mixtures have been subjected to thermal treatment at different temperatures (1000–1300 °C). It has been noticed that in both cases the formation of the designed phases (spinel and tin sphene) is enhanced by the use of the leather wastes as Cr^{3+} source.
- Testing the pigments obtained by using the leather wastes as chromium source in coloring some ceramic glazes has proved that they behave the same as the similar pigments obtained by classical methods; the pink pigments with tin sphene structure and the bluish-green pigments with spinel structure develop a major interest. Starting from transparent or opaque faience glazes, there have been obtained light-pink up to purple glazes and also bluish-green glazes, which comply with the quality requirements.
- The pink pigments with spinel structure do not resist the aggressiveness of the glass generating meltings, but they have been successfully tested in coloring some enamels. The same pigments obtained by the classical method show an identical behavior.

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