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ZIRCON CERAMIC PIGMENTS SYNTHESIZED FROM WASTE PRODUCT BY PETROLEUM INDUSTRY

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ABSTRACT

The proposed work shows a way to solve major environmental problems through the use of waste catalysts. In the present paper experiments were performed to recover waste catalysts from a catalytic cracking process by synthesizing blue-colored zircon ceramic pigments. Zircon ceramic pigments with basic zircon phase - $ZrSiO_4$ were synthesized by solid phase sintering at 800°C, 900°C, 1000°C, 1100°C and 1200°C. The optimal conditions for synthesis are determined. X-ray phase analysis, electron spin resonance spectroscopy, electron microscopy were used to determine the phase composition of pigments. The pigments obtained can be used in glazes for ceramic articles.

Keywords: *ceramic pigment, colour, zircon.*

INTRODUCTION

The most important requirement towards the ceramic pigments is that they must be stable at the high temperatures used in silicate industry [1]. Pigments should not react with their carriers (masses, engobes, glaziers and ceramic dyes) [2, 3].

Zircon pigments are comparatively new but they are already some of the most widely spread and perspective ceramic pigments [4]. Because of their resistance to dissolution in melted glaziers, zircon pigments are widely used and it assumed that today they are about 50 % of the total quantity of pigments used in the ceramic industry [5, 6]. The basis of the zircon pigments is the mineral zircon ($ZrSiO_4$) which plays the role of an acceptor, i.e. it accepts colouring ion. Pure zircon is colorless crystalline substance. Due to the alloys present in its crystal lattice, zircon has the ability to be colored in various colors [7, 8]. Many researchers have worked on the preparation of ceramic pigments, their use in glaziers and various ceramic products [9 - 12].

It petrol refining, catalysts are used in processes like catalytic cracking, catalytic reforming, hydro treatment (hydro-desulfurizaton), as well as in production of petroleum based chemical products related to the processes of dealkylation. An oil refinery processing about 7 000 000 t petroleum per year, uses from 50 to 100 t catalysts annually [13]. The data presented shows the relevance of the scientific issues in view of the huge amounts of waste catalyst which creates ecological problems.

EXPERIMENTAL

Raw materials

The basic materials for the synthesis of zircon pigments from waste catalysts were ZrO_2, $SiO_2.nH_2O$, MgO and the corresponding quantity of catalyst. The mineralizer used was Na_2SiF_6 with contents of 3.0 %, as its main role is to reduce the synthesis temperature. The quantity of mineralizer was taken from literary data [2]. A mineralizer with monovalent ion was selected since it forms melts with the lowest value of the surface tension and it is substantially more active compared to mineralizers with divalent alkali earth ion from the type MeX_2. The waste catalyst was taken from the installation

for hydrodesulfurization of heavy diesel fraction in LUKOIL Neftohim Burgas AD, and it had the following composition: γ-Al_2O_3 - 55 %, CoO - 25 %, MoO - 5 %, NiO - 15 %. Three pigment's compositions with 8 % and 15 % and 30 % waste were prepared.

Method of synthesis

The waste Ni-Co-Mo catalyst is composed from γ-Al_2O_3 as the main phase, CoO - as secondary phase and NiO and MoO_3 - as the accessor phase.

The pigments were synthesized by the technology of solid phase sintering. The most important operation on which the reliability of the technology and the stability of product quality depend is the preparation of the blend. With inadvertently prepared blend, the coloring effect in the sintered pigment may be reduced even when chemically pure materials and optimal compositions are used.

An important issue by the synthesis of pigments is the precise dosing of the different components and compliance with the recipe specified. The quantities of materials from the recipe for 100 g blend were weighed with precision of 0.1 g, then they were dry mixed and homogenized in a planetary mill PULVERIZETE - 6, product of the firm "FRITCH". The technological scheme for synthesis of pigments is shown in Fig. 1.

After breaking and grinding the waste catalysts to particle size of 1 - 3 μm, MgO was added to it in quantity necessary for formation of common spinel - $MgAl_2O_4$.

The sintering was carried out in a laboratory muffle furnace at heating rate of 300 - 400 °C/h in air, in closed porcelain crucibles with 2 h isothermal period at the final temperature. The pigments were sintered at 800°C, 900°C, 1000°C, 1100°C and 1200°C.

Method of analysis

Phase composition of the synthesized ceramic pigments was determined using X-ray diffraction (XRD) with a Bruker D8 diffractometer operating at 40 kV and 40 mA with CuK_α radiation. The EPR spectra were taken

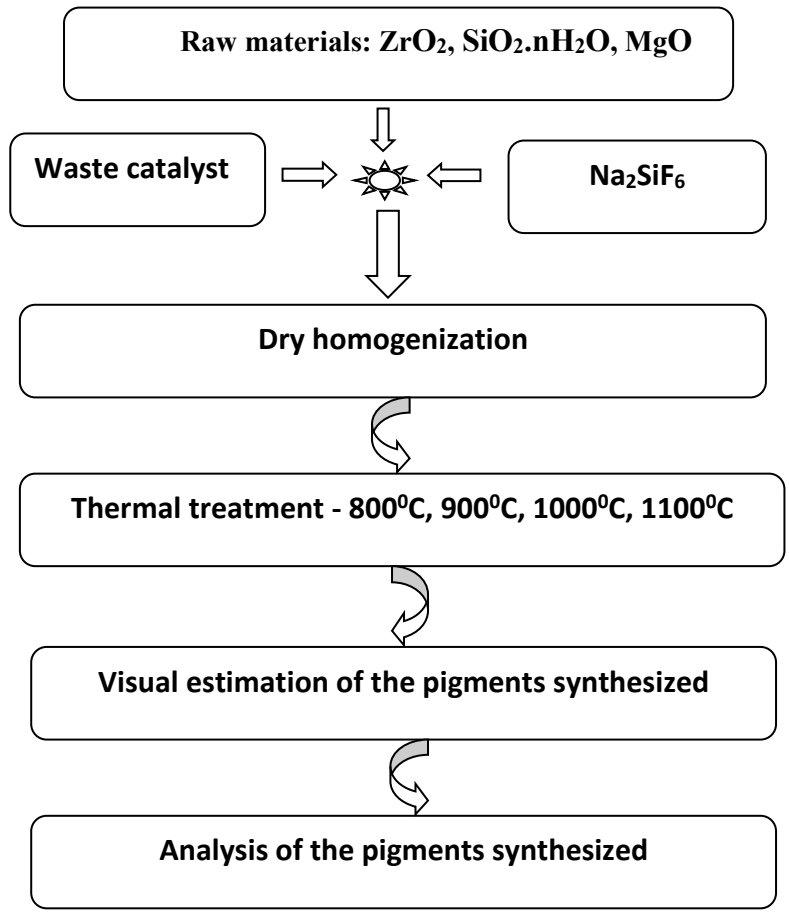

Fig. 1. Technological scheme for synthesis of the pigment.

with spectrophotometer B-ER-420 Bruker in the interval 120 K - 450 K. The electron microscope photographs were taken using scanning electron microscope "JEOL 6390" with INCA Oxford analyst. The color determination of the pigments is determined spectrally by a tintometer of Lovibond Tintometer RT 100 Color.

RESULTS AND DISCUSSIONS

X-ray analysis

X-ray phase analysis is a direct method for phase identification. The method is based on X-ray diffraction. The main task of the XRD analysis is identification of the different phases separately or in mixtures on the basis of the diffraction pattern recorded with the sample studied. Diffraction patterns of the synthesized ceramic pigments are presented in Fig. 2(A, B).

The waste catalyst most often is γ-Al_2O_3 on which the oxides of cobalt, nickel and molybdenum are deposited. It can be seen on the diffractograms of the isothermally treated blends that the whole quantity of MgO has been bonded in the spinel $MgAl_2O_4$ while the amount of γ-Al_2O_3 converted to corundum α-Al_2O_3 was insignificant.

These pigments obtained from waste catalysts by isothermal crystallization 1100°C for 2 h had stable and reproducible color. At this temperature, the CoO, NiO or both CoO and NiO contained in the blends are incorporated as isomorphic alloys in spinel composition

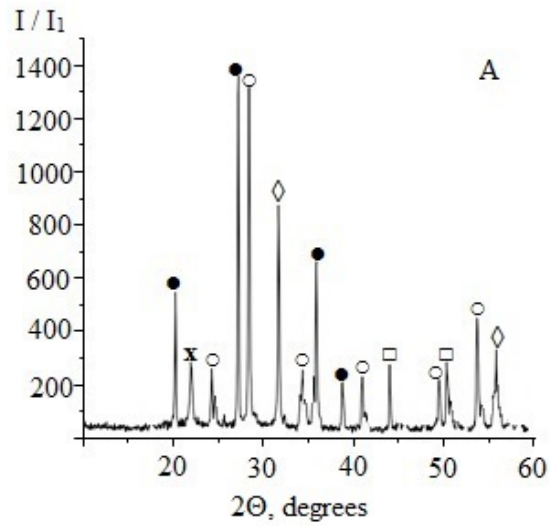

Fig. 2(A). X-ray pattern of zircon pigment containing 8 % waste catalyst synthesized at 1100ºC (● - $ZrSiO_4$, ○ - ZrO_2, x - α – cristobalite, ◊ - $MgAl_2O_4$, □ - Solid solution).

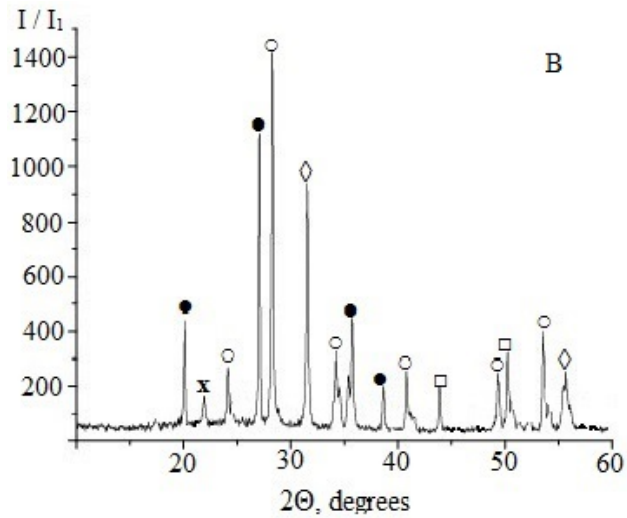

Fig. 2(B). X-ray pattern of zircon pigment containing 15 % waste catalyst synthesized at 1100ºC (● - $ZrSiO_4$, ○ - ZrO_2, x - α – cristobalite, ◊ - $MgAl_2O_4$, □ - Solid solution).

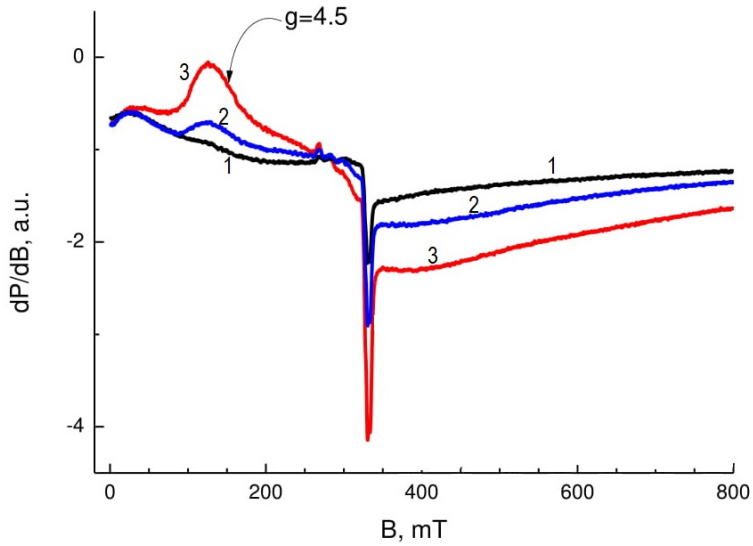

Fig. 3. ESR spectrum of the sample with 15 % waste sinthesized at 1100°C at 295 K (1 curve), 210 K (2 curve) and 120 K (3 curve).

$MgAl_2O_4$, thus forming solid solutions of the type $(Mg_{1-x}Co_x)Al_2O_4$, $(Mg_{1-x}Ni_x)Al_2O_4$ or $(Mg_{1-x}Co_{x/2}Ni_{x/2})Al_2O_4$. These solid solutions are responsible for the color of the pigments prepared from waste catalysts. An optimal amount of waste of 15 % has been selected.

Electron spin resonance spectroscopy (ESRS)

The electron paramagnetic resonance is based on the absorption of microwave energy by molecules, ions or atoms having electrons with unpaired spin which is done by the insertion of the sample in the magnetic field.

The ESR spectra of zircon pigments was performed on a spectrometer type B-ER-420 of Bruker-Physic, working in the X-range at a frequency of 9.8 GHz at room temperature, with precision of the determination of the spectral parameters ± 2G. The magnetic field was modulated with frequency of 100 kHz. The powdery samples were placed in quartz ampoules.

The ESR spectrum of the pigment with 15 % waste synthesized at 1100ºC was recorded in the temperature range 120 K - 295 K (Fig. 3).

At measurement temperatures below 200 K, a relatively wide line with g ≈ 4.5 is observed in the spectrum, the intensity of which increases with decreasing temperature. In the central part of the magnetic field (about 300 - 500 mT) a wide signal with the same temperature dependence as the signal with g ≈ 4.5 is established.

These two signals are associated with the existence of high spin Co^{2+} (d7, S = 3/2) ions in distorted tetrahedral symmetry [14]. The significant width of the described two lines does not allow resolving an ultrafine structure of 59Co (100 %, I = 7/2).

An ultrafine structure is established at values of the magnetic field 209 - 260 mT, and a superfine interaction constant of 6.6 mT was found.

Color measuring

Color is one of the most important indicators of pigment quality. Colored substances absorb and convert light rays of a certain wavelength into the visible portion of the spectrum, due to their atomic structure. The CIELab system defines colors not only of ceramic pigments but also of other materials, which indicates that this system is universal and widely used. The colour measurements were performed using the CIELab method. This method, which is the standard analysis in the ceramic industry, especially for the ceramic pigments allows to determine the whiteness and colour degree of tiles by measuring the three parameters: L^*, a^* and b^*, where:

- L^* (brightness), from absolute white $L^* = 100$ to absolute black $L^* = 0$
- a* - green color (-) / red color (+)
- b* - blue color (-) / yellow color (+)

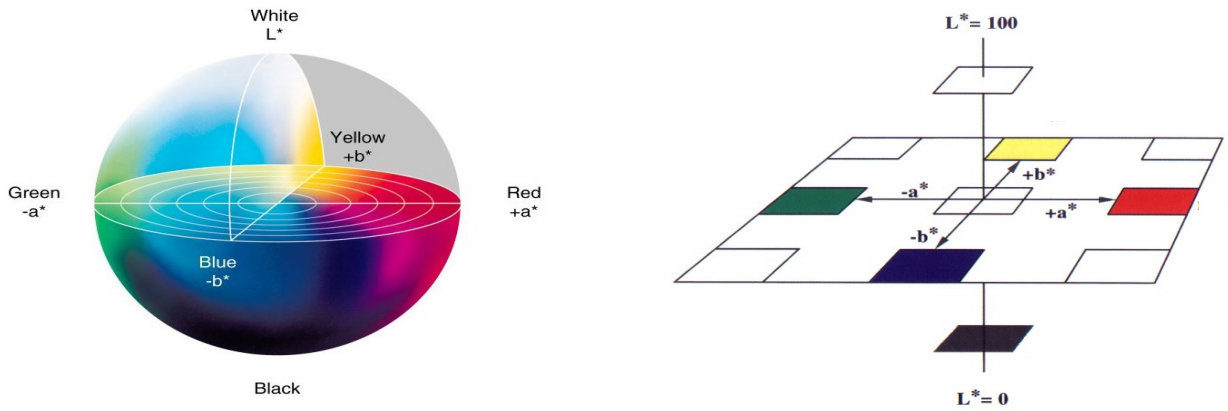

Fig. 4. The colour space of CIELab system.

Table 1. Results of color coordinate measurements of pigments.

Waste catalyst	T,°C	L*	a*	b*
8 %	1000°C	91.4	-4.3	-4.6
8 %	1100°C	85.1	-7.5	-14.5
8 %	1200°C	82.6	-8.7	-12.7
15 %	1000°C	86.4	-5.3	-6.9
15 %	1100°C	76.5	-9.4	-22.8
15 %	1200°C	75.7	-9.8	-19.5
30 %	1000°C	82.4	-8.3	-7.4
30 %	1100°C	77.5	-8.7	-20.4
30 %	1200°C	73.6	-9.4	-18.4

The color space of the CIELab system is shown in Fig. 4.

The results of the measured color coordinates of the synthesized pigments with waste are presented in Table 1.

The presented data in Table 1 show that with the increasing of both parameters - amount of waste and firing temperature a tendency to decreasing of brightness (L*) is observed. At the same time the colour coordinates (a*) and (b*) initially increase their values with the increasing of the amount of pigment and the firing temperature, then a tendency of decreasing of these value is observed.

It can be seen from the data presented that the amount of blue colour (- b*) was highest for the pigment containing 15 % waste catalyst with sintering temperature of 1100°C (b = - 22.8).

Electron microscopic study of the pigments

Electron microscopy is a method for direct study of the structure of the samples studied.

For this purpose, a one-stage method of replica preparation was employed. The latter is obtained by deposition of thin film of certain material onto the sample and then the film replica is detached from the surface and is observed by electron microscope.

Electron microscope has high resolution and wide range of magnification which provides opportunity to observe directly the characteristics of materials' structure. Instead of light, it uses a beam of fast electrons.

The samples were observed on a transmission electron - EM- 400, PHILIPS. The objects were deposited directly onto the electron microscope nets using carbon substrate. The accelerating voltage between the anode and the cathode was 80 kV. The particles are impervious for the electron beam and the photographs allow making conclusions only for the shape and size of the crystals, as well as their affinity to aggregation.

Microphotographs of the pigments synthesized are shown in Fig. 5(A, B).

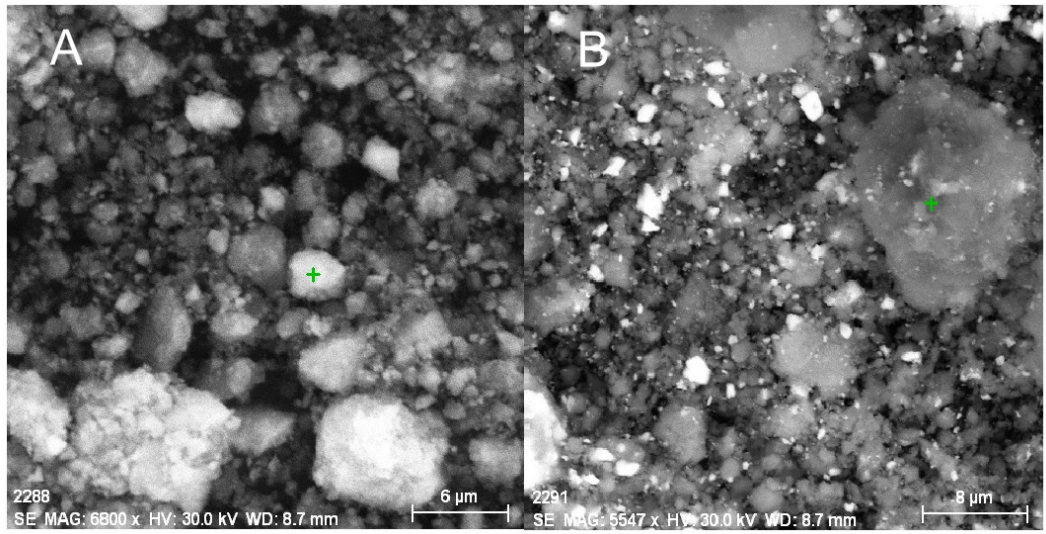

Fig. 5. Microphotographs of pigment containing: A) 8 % and B)15 % waste catalyst and sintered at 1100°C.

SEM results show that the samples were polydisperse and two types of crystals can be identified: with particle size 1 - 2 µm and between 5 - 10 µm.

CONCLUSIONS

Blue ceramic pigments containing waste catalysts from LUKOIL Neftohim Burgas AD were synthesized by the method of solid state sintering. The basic materials for the synthesis of zircon pigments were ZrO_2, SiO_2. nH_2O, MgO, Na_2SiF_6 and the corresponding quantity of catalyst. The optimal parameters of the synthesis process were established. The color characteristics of the garnet pigments synthesized were determined using the color measuring system CIELab. The most intense blue color (- b * = - 22.8) was found for the pigment containing 15 % waste catalyst and synthesized at 1100°C. The pigments synthesized are suitable and can successfully be used as glaziers for ceramic tiles and sanitary ceramics.

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