VILNIUS UNIVERSITY

INSTITUTE OF CHEMISTRY, CENTER FOR PHYSICAL SCIENCES AND TECHNOLOGY

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SYNTHESIS AND CHARACTERIZATION OF NOVEL BLACK PIGMENTS

Summary of doctoral dissertation

Physical sciences, Chemistry (03 P)

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The work was carried out in Vilnius University in the period 2007–2011.

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VILNIAUS UNIVERSITETAS
FIZINIŲ IR TECHNOLOGIJOS MOKSLŲ CENTRO CHEMIJOS INSTITUTAS

Aurelija Gatelytė

NAUJŲ JUODŲJŲ PIGMENTŲ SINTEZĖ IR TYRIMAS

Daktaro disertacija

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1. INTRODUCTION

Both synthetic and natural inorganic black pigments are widely used in the ceramics industry as colourants either for glazes and for ceramic bodies. Indeed 25% of pigments used in the ceramic industry are black and these are obtained from two main crystalline structures, namely, hematite and spinel. Some of the black pigments contain the oxides of cobalt, manganese, nickel or copper with iron and chromium. Commercial black pigments normally have a spinel structure, owing to its higher stability and are derived from irone-cobalt chromite $(Fe,Co)(Fe,Cr)_2O_4$ and chromium-iron-nickel $(Ni,Fe)(Fe,Cr)_2O_4$ black spinels. There has been a great interest within the ceramic industry in the development of high stability pigments that show intense tonality and which satisfy both technological and environmental requirements. The way to obtain colour in a vitreous matrix is to disperse in the matrix an insoluble crystal or crystals that are coloured and known as pigments. The colour of the crystal is then imparted to the transparent matrix. Ceramic pigments must have the following properties such as thermal stability, insolubility in the glazes, resistance to attack by chemical agents (acids and bases) and should not produce gases to form faults in the glazes.

Carbon black is the accepted generic name for a family of small particle size carbon pigments which are formed in the gas phase by thermal decomposition of hydrocarbons. Carbon blacks are currently sold in the form of hundreds of commercial grades which vary in particle size, aggregate size and shape, porosity, and surface chemistry. Their most important properties for inks, coatings, and plastics are related to the final product appearance (e.g., blackness, tone, and tint), UV protection, and electrical conductivity.

For this doctoral dissertation there were synthesized and observed the black pigments which are important in both – in art and industry. It was the first time when using the sol-gel method in our laboratory were synthesized $YFeO_3$, $Y_3Fe_5O_{12}$, $CoFe_2O_4$, $NiFe_2O_4$, $ZnFe_2O_4$ nanocompounds, which latter were fitted for the black pigmentation of the ceramic glazes. Using the sol-gel method the initial materials are dissolved in a water, and in solutions reaction is going in molecular level. So using that method of synthesis it is possible to synthesize high quality inorganic materials very effectively, and that materials have a very high phasic purity, that was proven by research of ferrate pigments synthesis. Producing the ceramic glazes it was assured because new compounds have chromatic characteristic of the pigments. Also one of the purpose of this doctoral dissertation it was to create different compositions of oily various carbon forms black colourant. It was the first time when carbon nanoderivatives were used as one of the black colourant component. So regarding to that the topic of this doctoral thesis is new, the experimental results worked out of the research process and their interpretation are original.

The main aim of this doctoral thesis: to investigate the synthesized carbon oily colourants and also to synthesize and to characterize the new pigments and glazes containing metal ferrites. For this reason there were formulated tasks as follows:

1. To synthesize and characterize various compositions of black carbon pigments, which would be used for oil paintings.
2. To synthesize and investigate the black nanocarbon oily pigments.
3. For the first time to use an aqueous sol–gel method to synthesize and characterize the nanostructured metal ferrites: $YFeO_3$, $Y_3Fe_5O_{12}$, $CoFe_2O_4$, $NiFe_2O_4$, $ZnFe_2O_4$.
4. To adjust these ferrite pigments to black glazes production and to characterize them in detail.

Statements for defence

1) Various carbon materials might be used for the black pigments, which are intendent for oil painting production.
2) For the first time synthesized the black nanocarbon oily pigments, characterized by necessary chromatic characteristics and original surface morphology.
3) This is the first time of proving an aqueous sol–gel method is favourable for the preparation of various metal ferrites.
4) The new black pigments and glazes created with synthesized ferrites have very good chromatic characteristics.

2. EXPERIMENTAL

2.1 Materials and reagents

For the synthesis of black carbon pigments these reagents were used: charcoal, C (soot), K_2CO_3, $Ca_3(PO_4)_2$, $CaCO_3$, $Mg_3(PO_4)_2$, flax oil, graphite, graphited soot (refined), and graphited soot, synthesized by different techniques. For the sol-gel synthesis stoichiometric amounts of Y_2O_3, $Fe(NO_3)_3\cdot 9H_2O$, $Co(NO_3)_2\cdot 6H_2O$, $Ni(CH_3COO)_2\cdot 4H_2O$, $Zn(CH_3COO)_2\cdot 2H_2O$ were used as starting compounds, ethane-1,2-diol ($HOCH_2CH_2OH$) as complexing agent, all of them analytical grade.

2.2 Methods of synthesis

The black carbon oily colourant were produced by mixing carbon with other inorganic compounds and adding flax oil. Mixtures of C with K_2CO_3, C with $Mg_3(PO_4)_2$ and C with $CaCO_3$ were producing by molar proportions 1:1, 1:0.1, 1:0.01. Mixtures C with $Ca_3(PO_4)_2$ and $CaCO_3$, C with $Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2$, C with $CaCO_3$, and $Mg_3(PO_4)_2$ were producing by molar proportions 1:1:1, 1:0.1:0.1, 1:0.01:0.01. Also the mixtures of C with $Ca_3(PO_4)_2$, $CaCO_3$, $Mg_3(PO_4)_2$ were producing by molar proportions 1:1:1:1, 1:0.1:0.1:0.1 and 1:0.01:0.01:0.01. To each mixture the 0.25 ml flax oil was added. The produced mixtures were evenly spread on the plastic saucer or terracotta plaques. The carbon oily colorants were dried for two weeks in air at room temperature.

Graphitized soot were synthesized at 400–700 °C temperatures. As initial substance the CO was used, and as catalyst in GSI case was used Fe, and in GSII case Ni. Refined graphitized soot were synthesized using Fe catalyst. The iron, which left after the reaction, was eliminated from GSR, by washing with hot concentrated hydrochloric acid through the chromatographic column. Refined GSR were washed with distilled water till universal indicator did not show the acidic medium of the solution.

All mixed-metal ferrites were synthesized by separately dissolving the initial materials in a distilled water, except Y_2O_3, which was dissolving in 0.2 M acetic acid solution at 55-60 ^{o}C temperature. The obtained transparent metal nitrate and acetate solutions were poured into the same glass and were stirred for 1 h at the same temperature. Finaly, 2 ml of 1,2 – ethanediol was added to the solution. The resulting sols were stirred in the covered beakers for another 30 min. Transparent solutions were concentrated in an open beakers at 60-65 °C temperature. The resulting greenish, reddish or yellowish fluffy gels were dried for 24 h at 110 ^{o}C. After drying, fluffy gels were accurately crushed in an agate mortar. Dried gels heated for 2 h at 800 °C temperature into the heating furnace. The heating rate was 10 °C/min. The obtained intermediate substances were squashed in an agate mortar and again heated at 1000 °C for 10 h.

The components of each glaze were carefully stirred in a little amount of water. Saturated compound was gradually spread by the paintbrush on the terracotta platę (3x2 cm). The glazes were obtained by the heating at 800 °C, 900 °C and 1000 °C for 5 h gradually raising the temperature and cooling inside the oven.

2.3. Characterization and techniques

The black oily colorants and synthesized compounds were characterized by infrared spectroscopy (FTIR) using the Perkin-Elmer FT-IR Spectrum BX II spectroscope. The samples for FTIR analysis were pressed with KBr (1.5%). The phase purity of the synthesized compounds was evaluated using X-ray diffractometer Bruker AXE D8 Focus with LynxEye detector (CuKα). The morphology and microstructure of compounds were analyzed using scanning electron microscopes (SEM) EVO 50 XVP and Zeiss EVO50 EP. Atomic force microscope (AFM) Nanoscope V Catalyst and optical microscope Olympus IX71 were also used for the characterization of obtained compounds. The chromatic characteristics of the black oily colorants evaluated by using spectrophotometer Perkin Elmer Lambda 35 UV VIS. All ceramic glazes samples were photographed by digital camera Canon EOS 300 D and optical Leitz microscope. For the contact angle measurements the KAM2 device was used.

3. RESULTS AND DISCUSSION

3.1 Synthesis and characterization of black carbon pigments

According to the IR spectroscopic measurements the historical charcoal contains different carbonates and phosphates. Therefore, for the synthesis of new black pigments the carbon C (soot), $Mg_3(PO_4)_2$, K_2CO_3, $Ca_3(PO_4)_2$ and $CaCO_3$ were chosen as initial materials and additionally characterized by the IR method.

3.1.1 IR characterization of black carbon pigments having various composition

In the first part the IR spectroscopy analysis data of mixtures of comercial carbon soot with $Mg_3(PO_4)_2$, K_2CO_3, $Ca_3(PO_4)_2$ and $CaCO_3$ are represented. The aim of these analyses was to determine the minimum amount inorganic salts comparing to carbon amount suitable for the preparation of black pigments. The IR spectra of mixtures of C soot with $Ca_3(PO_4)_2$ and $CaCO_3$ having different ratios (1:1:1; 1:0.1:0.1; 1:0.01:0.01) are shown in Fig. 1.

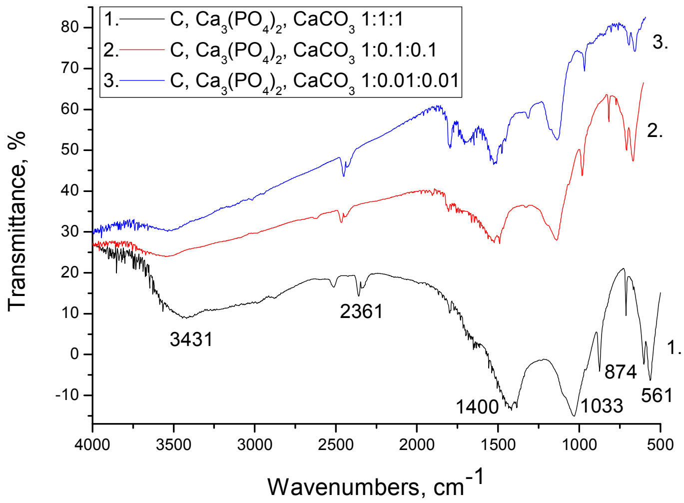

Fig. 1. IR spectra of C soot with $Ca_3(PO_4)_2$ and $CaCO_3$.

From the IR spectra it is clear, that quite intensive typical peaks for PO_4^{3-} located at 1033 cm^{-1} and 561 cm^{-1}, for CO_3^{2-} at 1400 cm^{-1} and 874 cm^{-1} and for H_2O at 3408 cm^{-1} are observed even when the smallest amount of salts (1:0.01:0.01) was used. These results from IR spectroscopic measurements of mixtures having various compositions of C soot with K_2CO_3, $Ca_3(PO_4)_2$, $CaCO_3$ and/or $Mg_3(PO_4)_2$ let us to conclude that intensity of typical absorption peaks apparently depends on the quantitative ratio of components in the mixtures. Besides, in all cases intensity of vibrations of O-H, PO_4^{3-} and CO_3^{2-} groups decreases with increasing amount of C in the black carbon pigments.

3.1.2 The characterization of the black carbon pigments for oil painting

For the preparation of black carbon pigments used for oil painting, the mixtures of the carbon soot with $Mg_3(PO_4)_2$, K_2CO_3, $Ca_3(PO_4)_2$ and $CaCO_3$ were mixed with flax oil. The micrographs of optical microscopy let us approximately to evaluate the dependence of oily black colorants quality on the carbon pigments chemical composition. It was demonstrated that the highest quality of the chromatic black tone of black oily colorants is when molar ratio of C : inorganic component was 1 : 0.01 (Fig. 2).

Fig. 2. The picture of black oily colorants produced from C soot and $CaCO_3$ having different ratios (from left): 1:1; 1:0.1 and 1:0.01.

The best black colorants were obtained from mixtures of C : K_2CO_3, or C : $CaCO_3$: $Mg_3(PO_4)_2$, or C : $CaCO_3$: $CaCO_3$: $Mg_3(PO_4)_2$ with oil. Interestingly, the IR spectra of these oily colorants contains absorption peaks attributable not only for oil, but also carbonate and phosphate typical absorption peaks.

3.2 Synthesis and characterization of the black nanocarbon oily pigments

In the first part of dissertation the optimal carbon and K_2CO_3, $Ca_3(PO_4)_2$, $CaCO_3$, $Mg_3(PO_4)_2$ proportion in the pigments was determined. In this part for the preparation of black pigments different modifications of nanocarbon (graphite, graphitized soot (refined) and graphitized soot, synthesized by different techniques (graphitized soot I and graphitized soot II) were used.

3.2.1 Characterization of black nanocarbon pigments by SEM method

All mixtures of nanostructured carbon with K_2CO_3, $Ca_3(PO_4)_2$, $CaCO_3$ and $Mg_3(PO_4)_2$ were obtained in optimal proportions. The SEM micrographs of graphite are shown in Fig. 3. Evidently graphite consists of very thin sheets with size from 1 to 3 μm. Therefore this material could be attributed to 2-dimensional nanostructures. The obtained black pigments using mixtures of graphite : $CaCO_3$: $Mg_3(PO_4)_2$, graphite : $CaCO_3$ and graphite : $Ca_3(PO_4)_2$: $Mg_3(PO_4)_2$ were moistened with flax oil and gradually spread on the terracotta plates. The SEM images of black oily pigments having nanostructured graphite are shown in Fig. 4. As seen, the spherical particles with size of ~2-10 μm are dominating on the surface of painting. However, the sheets of graphite are also visible.

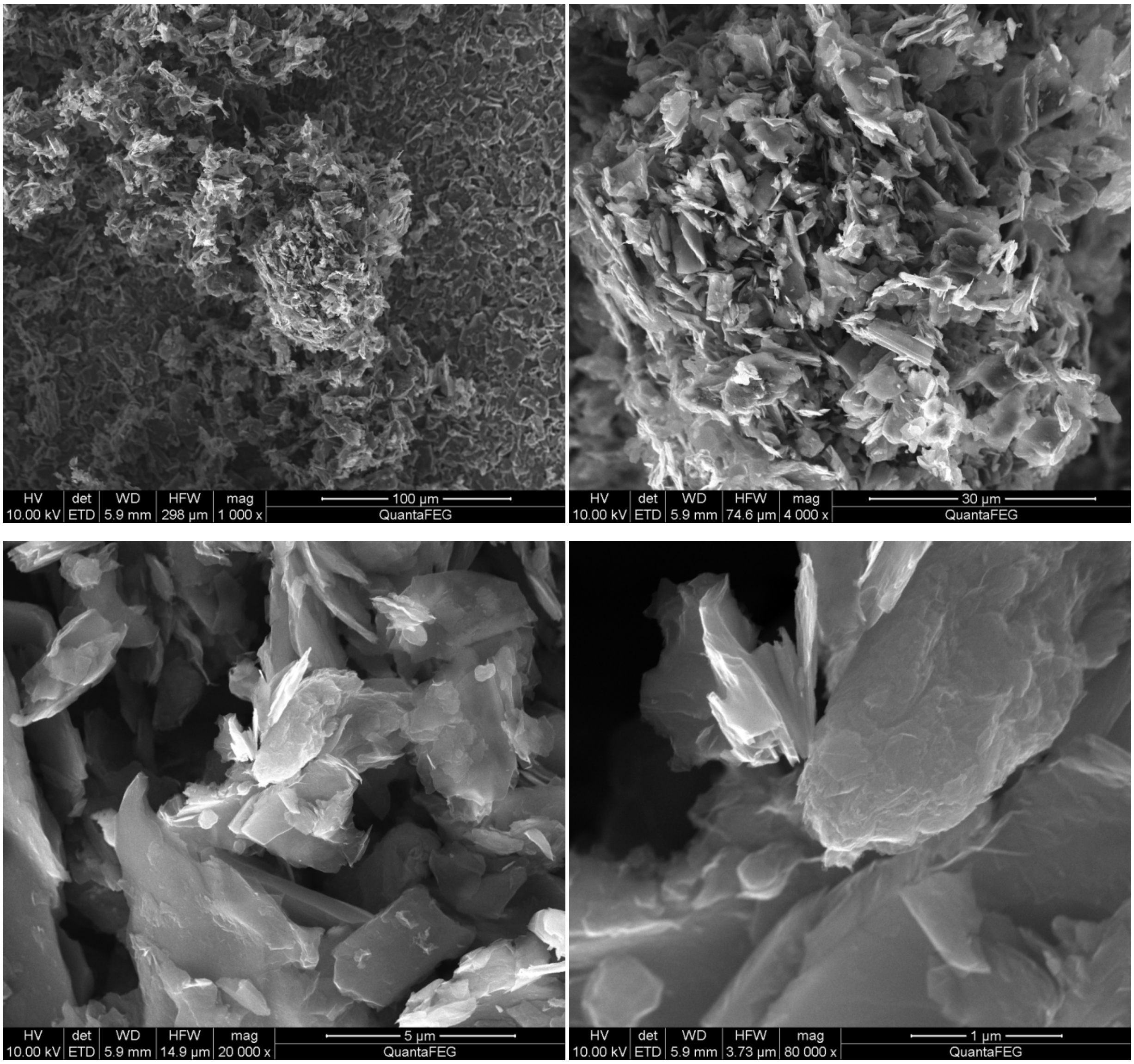

Fig. 3. SEM micrographs of graphite. Magnification 1000x, 4000x, 20000x and 80000x.

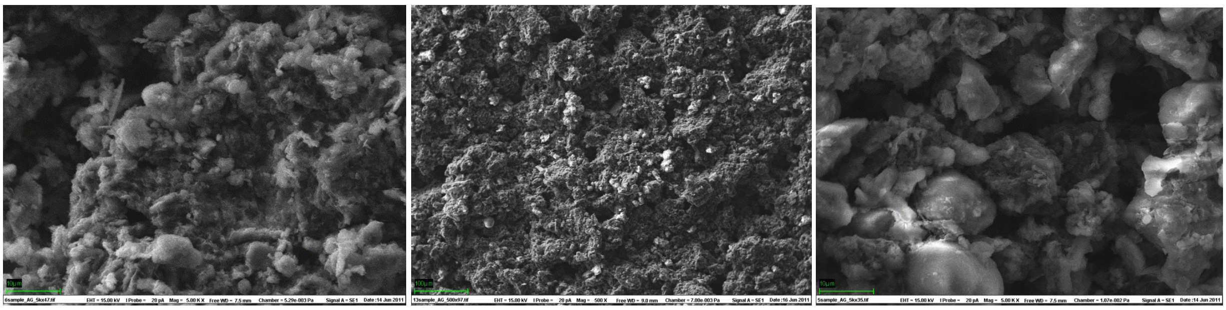

Fig. 4. SEM micrographs of black oily pigments: (left) graphite : $CaCO_3$: $Mg_3(PO_4)_2$, (middle) graphite : $CaCO_3$ and (right) graphite : $Ca_3(PO_4)_2$: $Mg_3(PO_4)_2$.

The SEM micrographs of refined graphitized soot are shown in Fig. 5.

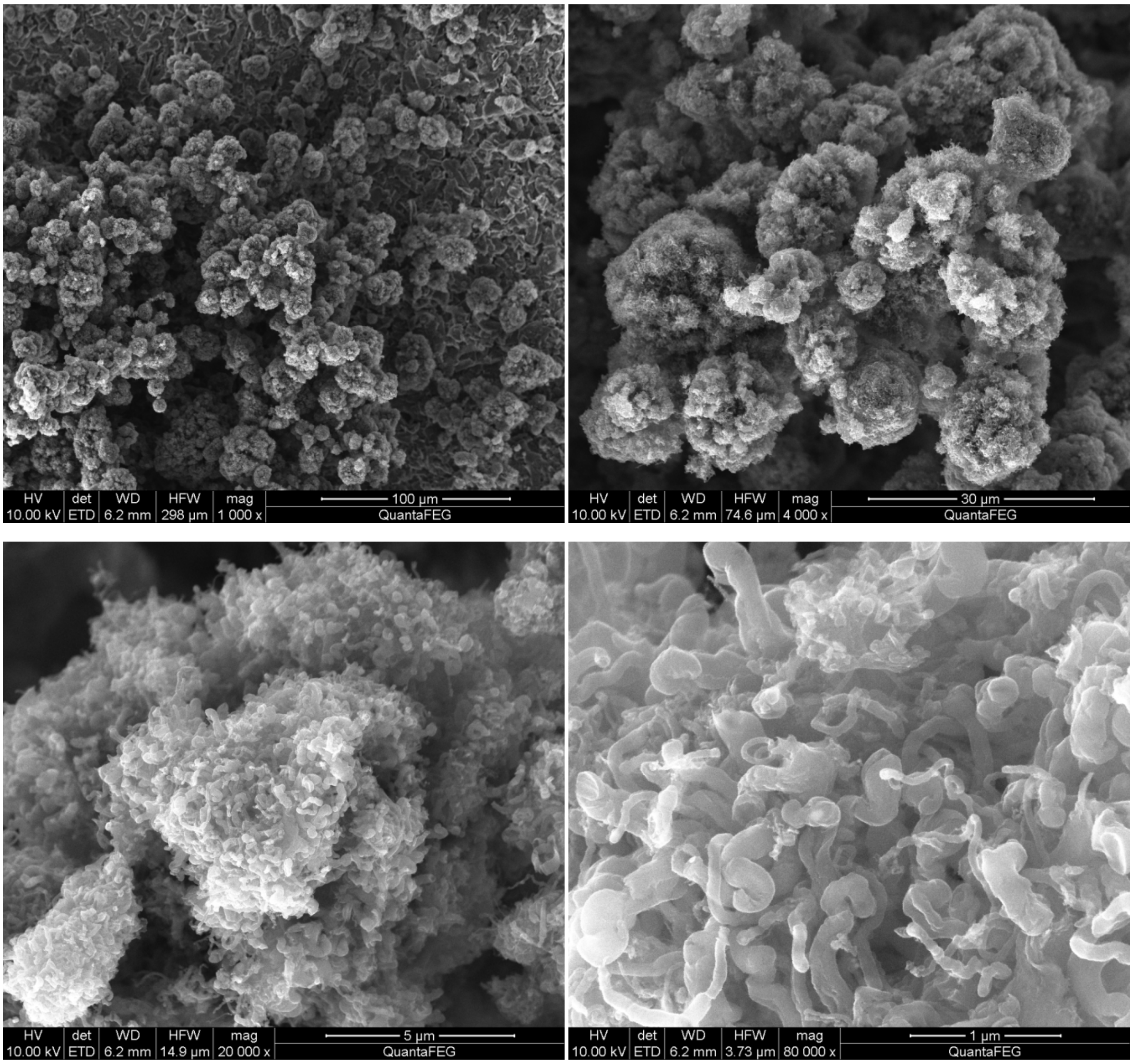

Fig. 5. SEM micrographs of refined graphitized soot. Magnification 1000x, 4000x, 20000x and 80000x.

Fig. 5 shows that surface morphology of refined graphitized soot is quite different from that of graphite. Evidently, the refined graphitized soot show 1-dimensional nanostructure (carbon nanotubes). The length of carbon nanotubes is about 1 μm, and diameter varies from 20 up to100 nm. The refined graphitized soot were also used for the fabrication of black oily pigments using the same methodology as above. The SEM images of black oily pigments having nanostructured refined graphitized soot are shown in Fig. 6. The SEM analysis shows that synthesized black oily colorants on the base of nanostructured carbon architectures are monolithic nanostructures. The components of black pigment in the black colorants are mixed very gradually. Such surface microstructure is promising for good chromatic characteristics of the obtained paintings.

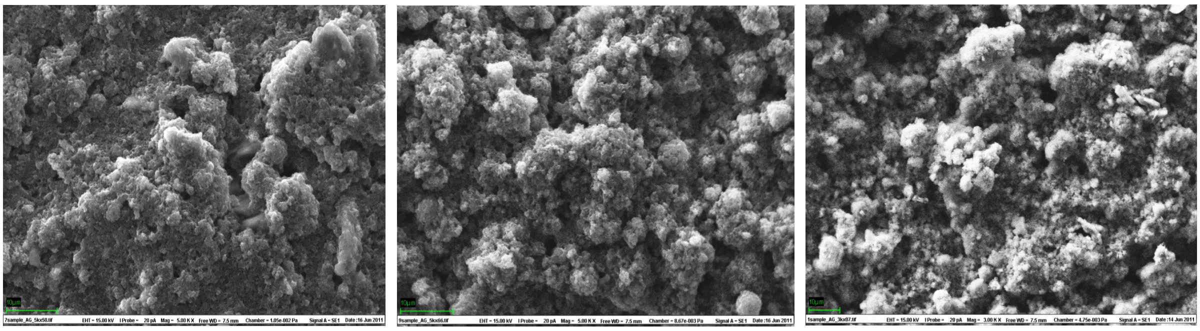

Fig. 6. SEM micrographs of black oily pigments: (left) graphitized soot (refined) : $CaCO_3$: $Mg_3(PO_4)_2$, (middle) graphitized soot (refined) : $CaCO_3$ and (right) graphitized soot (refined) : $Ca_3(PO_4)_2$: $Mg_3(PO_4)_2$.

The graphitized soot, synthesized by different techniques (graphitized soot I and graphitized soot II) were also used for the preparation of black oily pigments. Both materials were also composed of carbon nanotubes. These graphitized soot were mixed in the same way with inorganic salts and flax oil to obtain the black oily colorants. However, the obtained SEM results let us to conclude that black oily colorants obtained from refined graphitized soot showed slightly better quality. The prepared oily black colorants, spread on the terracotta plates, SEM photographs are shown in Fig. 3.

3.2.2 Determination of surface contact angle of black nanocarbon pigments

In this part of dissertation the results of contact angle measurements on various oily colorants surfaces are presented. For example, it was demonstrated that hydrophobicity of black oily colorants is higher when pigments are synthesized using nanostructured carbon. The water drops photographs on the surfaces of the black oily colorants obtained from refined graphitized soot are shown in Figs. 7-9. As seen, the hydrophobicity of obtained surfaces of black oily colorants also depends on the chemical composition of black carbon pigment. The curves of degradation of contact angle in time are presented in Fig. 10. It seems, that contact angle decreases slightly faster on the surfaces of black oily colorants containing metal phosphates.

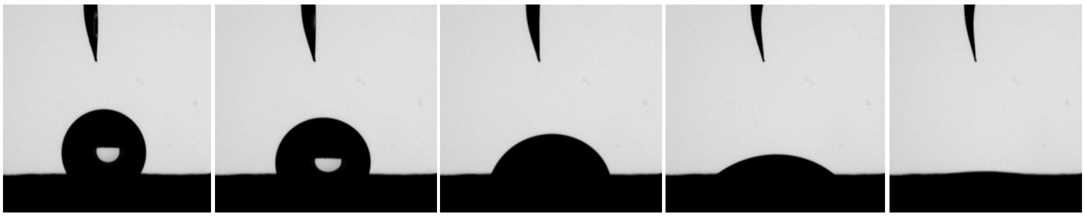

Fig. 7. The water drops photographs on the surface obtained from refined graphitized soot : $CaCO_3$: $Mg_3(PO_4)_2$.

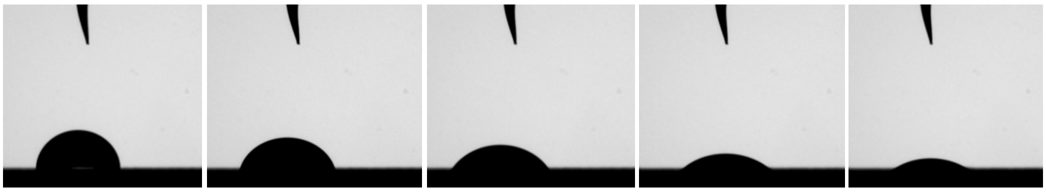

Fig. 8. The water drops photographs on the surface obtained from refined graphitized soot : $CaCO_3$.

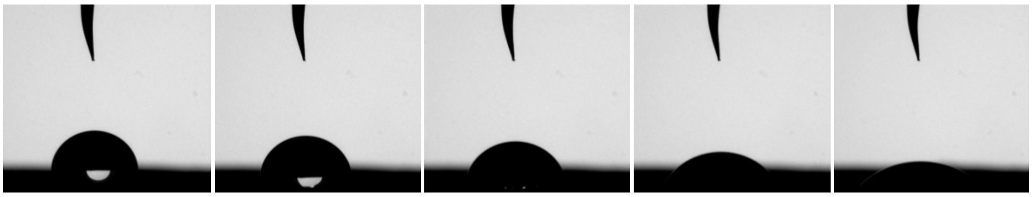

Fig. 9. The water drops photographs on the surface obtained from refined graphitized soot : $Ca_3(PO_4)_2$: $Mg_3(PO_4)_2$.

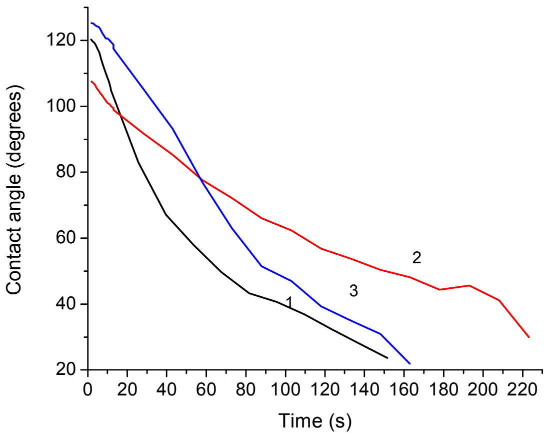

Fig. 10. Time dependences of contact angle on the surfaces obtained from graphitized soot II : $CaCO_3$: $Mg_3(PO_4)_2$ (1), graphitized soot II : $CaCO_3$ (2) and graphitized soot II : $Ca_3(PO_4)_2$: $Mg_3(PO_4)_2$ (3).

3.3 Synthesis and characterization of black ceramic pigments

In this part will be characterized mixed metals nanoferrites $YFeO_3$, $Y_3Fe_5O_{12}$, $CoFe_2O_4$, $NiFe_2O_4$, $ZnFe_2O_4$ synthesized by sol-gel technique. These nanoferrites for the first time were used as black ceramic pigments for the preparation of new black glazes.

3.3.1 Sol-gel synthesis and characterization of various mixed metals ferrites

The phase purity of the synthesis products is evaluated by X-ray diffraction analysis method. According to the XRD analysis, a fully crystallized single-phase oxide $YFeO_3$ with well pronounced perovskite crystal structure has formed (PDF No. 39-1489). The most intensive lines (121), (002) and (123) are observed at $2\theta \approx 33.1$ (100

%), 33.9 (31 %) and 60.2 (27 %), respectively. The monophasic yttrium iron garnet has also formed during heating the Y-Fe-O (Y : Fe = 3 : 5) precursor gel at 1000 °C (see Fig. 11).

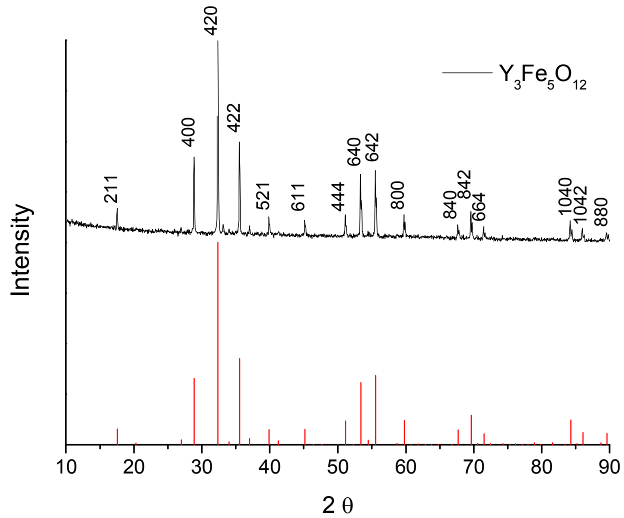

Fig. 11. X-ray diffraction pattern of $Y_3Fe_5O_{12}$ ceramics synthesized using sol-gel method at 1000 °C. The Miller indices of $Y_3Fe_5O_{12}$ phase are marked. The vertical red lines belong to standard PDF of $Y_3Fe_5O_{12}$ phase.

The XRD pattern completely corresponds to the reference data (PDF No. 43-507). For the synthesized $Y_3Fe_5O_{12}$ the most intensive lines (420), (642) and (422) are observed at 2θ ≈ 32.3 (100 %), 55.5 (48 %) and 35.5 (46 %), respectively.

All the samples obtained after heating of Co-Fe-O, Ni-Fe-O and Zn-Fe-O precursor gels at 1000 °C are monophasic materials. The XRD data clearly confirmed the crystalline spinel structure of cobalt ferrite ($CoFe_2O_4$) to be the main crystalline component (PDF No. 22-1086). For the sol-gel derived $CoFe_2O_4$ the most intensive lines (311), (440) and (220) are observed at 2θ ≈ 35.5 (100 %), 62.7 (41 %) and 30.2 (32 %), respectively. With the substituting cobalt for nickel the obtained X-ray diffraction results consist very well with reference data (PDF No. 10-325). For the spinel structure nickel ferrite $NiFe_2O_4$ the most intensive lines (311), (220) and (440) are observed at 2θ ≈ 35.8 (100 %), 30.3 (42 %) and 63.0 (37 %), respectively. Fully crystalline single-phase oxide $ZnFe_2O_4$ with well pronounced spinel crystal structure have also formed at 1000 °C using the same sol-gel technique (PDF No. 22–1012). For the zinc ferrite $ZnFe_2O_4$ the most intensive lines (311), (220) and (440) are observed at 2θ ≈ 35.4 (100 %), 29.8 (39

%) and 62.3 (34 %), respectively (Fig. 12).

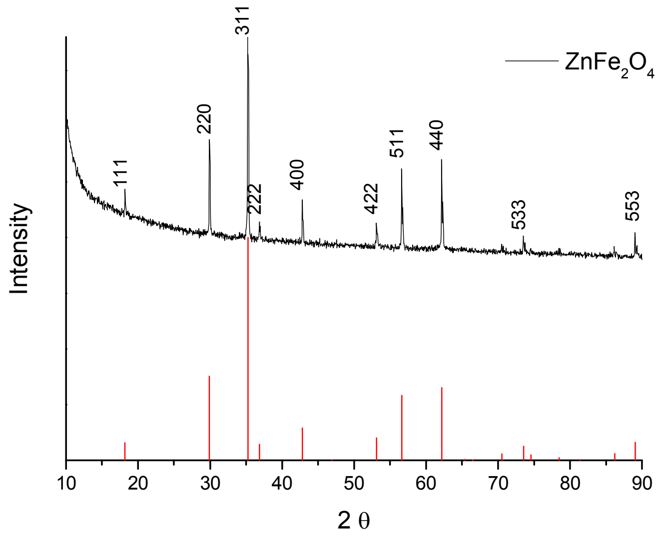

Fig. 12. X-ray diffraction pattern of $ZnFe_2O_4$ ceramics synthesized using sol-gel method at 1000 °C. The Miller indices of $ZnFe_2O_4$ phase are marked. The vertical red lines belong to standard PDF of $ZnFe_2O_4$ phase.

Scanning electron microscopy was used for the characterization of morphology of synthesized ferrites. The representative SEM micrographs of selected sol-gel derived ferrites are presented in Fig. 13. As seen, the surface of $YFeO_3$ is composed of ~200-1000 nm necked to each other nanocrystallites.

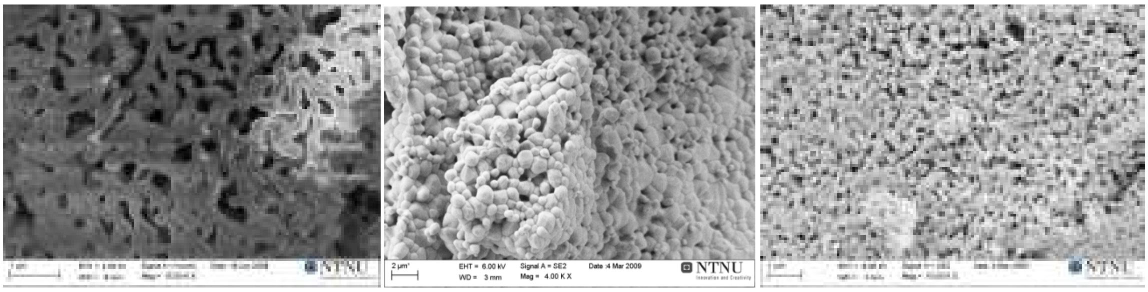

Fig. 13. SEM micrographs of sol-gel derived $YFeO_3$ (left), $CoFe_2O_4$ (middle) and $ZnFe_2O_4$ (right).

In the case of $Y_3Fe_5O_{12}$ ceramics more prononced agglomeration of nanocrystallites was observed. The scanning electron micrograph indicated that the particle size of spinels depends on the nature of transition metal ($CoFe_2O_4$ (~1000 nm) > $ZnFe_2O_4$ (200-500 nm) > $NiFe_2O_4$ (100-150 nm)). Moreover, all three spinels have formed with mesoporous structure.

IR spectroscopy was used as additional tool for the structural characterization of the ceramic materials obtained by the aqueous sol-gel method. The IR spectrum of synthesized $YFeO_3$ ceramics show broad absorption bands arising from O–H stretching and bending vibration of water due to the exposure of the sample to the atmosphere at ~ 3500 cm^{-1} and ~ 1600 cm^{-1}, respectively. Importantly, in the 1300 cm^{-1}–400 cm^{-1} fingerprint region, one sharp band was presented at around 564 cm^{-1} is typical metal-oxygen absorption for the perovskite-type compounds. Evidently, the character of this region of IR spectrum for Y : Fe = 3 : 5 sample (see Fig. 14) is a little different.

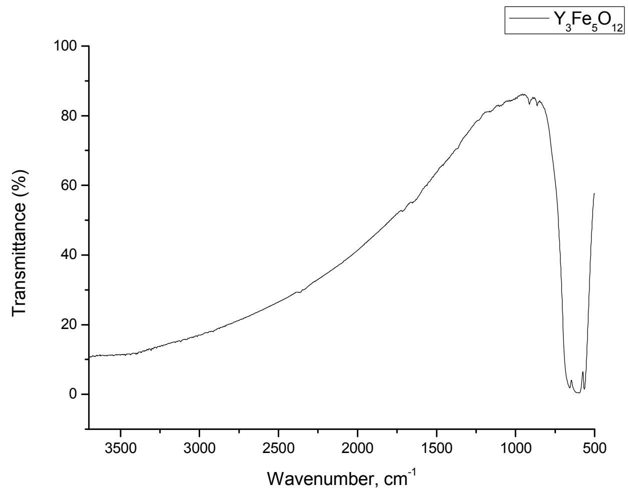

Fig. 14. Infrared spectrum of $Y_3Fe_5O_{12}$

The most important feature is that several intensive bands are determined in the region of 900 cm^{-1}–450 cm^{-1}, which may be attributed to the stretching modes of the isolated [AlO_4] tetrahedra and [AlO_6] octahedra in the garnet structure, i. e. these bands correspond to the formation of crystalline IAG. All three IR spectra of Co-Fe-O, Ni-Fe-O and Zn-Fe-O nitrate-acetate-glycolate gels heated at 1000 °C are almost identical with characteristic intensive absorption band located nearly 600 cm^{-1}. The observed peaks are M–O vibrations and probably are characteristic for spinel structure compounds.

3.3.2 Application of various mixed metals ferrites for the preparation of black ceramic pigments

The sol-gel derived nanoferrites $YFeO_3$, $Y_3Fe_5O_{12}$, $CoFe_2O_4$, $NiFe_2O_4$, $ZnFe_2O_4$ were used for the preparation of new black ceramic pigments. Initially these materials were mixed with Pb_3O_4 and SiO_2. The pigments were heated at 800, 900 and 1000 °C temperatures. After evaluating visually it was made a conclusion that the highest quality of glazes were obtained by heating pigments at 800 ˚C. However the synthesized glazes had black brownish colours. Therefore, copper oxide (CuO) (0,000128 mol) was additionally added to the previous mixtures. The surface morphology of pigments containing nanosized transition metal ferrites was analyzed using SEM method. The representative SEM micrograph of black ceramic pigment with $YFeO_3$ is shown in Fig. 15.

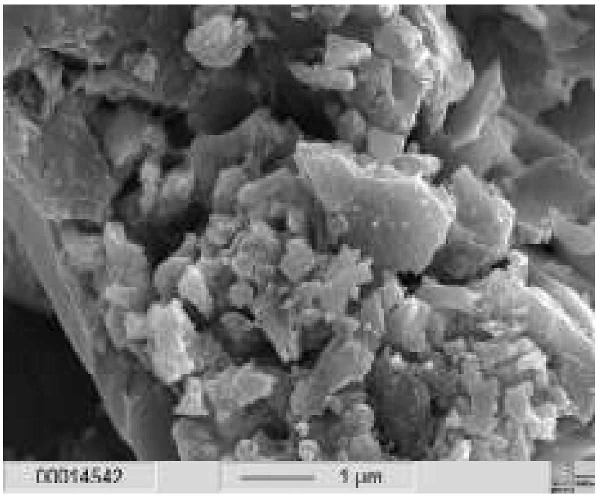

Fig. 15. The SEM micrograph of black pigment in which composition is $YFeO_3$.

The particle size of blank pigments varies from 100 nm to 3 µm, and that confirms the wide distribution of the particle size in the pigments. This fact may be explain by that blank pigments besides nanoferrites containes large amount of other ingredients (Pb_3O_4, SiO_2, CuO). Interestingely, the surface morphology of all synthesized black pigments was almost identical. So, we can conclude that surface morphology of different black pigments is not dependent on the sol-gel derived $YFeO_3$, $Y_3Fe_5O_{12}$, $CoFe_2O_4$, $NiFe_2O_4$ and $ZnFe_2O_4$ but is determined by the other components.

3.3.3 Investigation and characterization of new black glazes

The black pigments having modified chemical composition were spread on the terracotta surface and heated only at 800˚C temperature. The picture of obtained glazes is presented in Fig.16.

Fig.16. The pictures of black ceramic glazes obtained using nanoferrites: $YFeO_3$ (top, left), $Y_3Fe_5O_{12}$ (top, middle), $ZnFe_2O_4$ (top, right), $NiFe_2O_4$ (bottom, left) and $CoFe_2O_4$ (bottom, right).

It is clear, that all ceramic glazes have an intense and rich dark black colour. Addition of CuO improved the black undertone of the nanoferrites pigments very well. The SEM images of the obtained representative glazes are shown in Fig. 17.

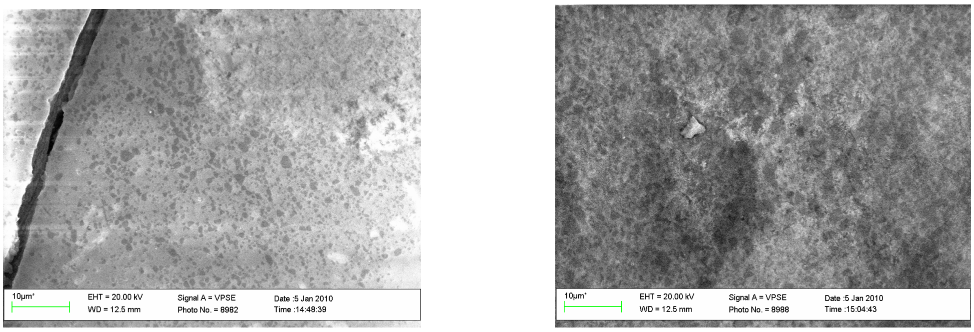

Fig. 17. SEM images of black glazes with $NiFe_2O_4$ (left) and $ZnFe_2O_4$ (right).

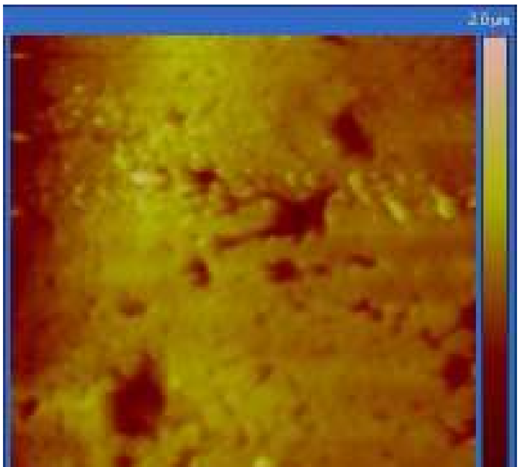

Fig. 18. AFM micrograph of the glaze with $Y_3Fe_5O_{12}$.

The SEM micrographs of black glazes show fine microstructure with smooth surface. The surfaces of new black glazes were also analyzed by AFM method. No any crystallized big crystals on the glaze was determined on the AFM micrographs (see Fig. 18). The surface is homogeneous and quite smooth.

CONCLUSIONS

1. IR spectroscopic investigations revealed, that the charcoal contains carbonate and phosphate ions in the composition. Therefore, the models of the black pigments of the C soot and K_2CO_3, $Ca_3(PO_4)_2$, $CaCO_3$ and $Mg_3(PO_4)_2$ was formed. It was determined that peak intensities of OH^-, PO_4^{3-} and CO_3^{2-} absorptions in the IR spectra of C soot mixtures with K_2CO_3, $Ca_3(PO_4)_2$, $CaCO_3$ and $Mg_3(PO_4)_2$ are decreasing when the carbon soot amount in their composition increases.
2. The chromatic black tone of black oily colorants is the highest quality when carbon soot molar ratio with inorganic salts was 1: 0.01. Moreover, the quality of the black oily colorants also depends on the composition of used metal carbonates and phosphates.
3. Nanostructured refined and not refined graphitized soot were used for the first time for the fabrication of the black pigments. The SEM analysis showed that refined and not refined graphitized soot show one-dimensional nanostructured surface morphology. It was determined that the refined graphited soot are the most suitable for the preparation of high quality black oily colorants.
4. The hydrophobicity of synthesized new black oily colorants depends very much on the presence of nanostructured carbon in colorants. Thus, the nanostructured carbon determines the hydrophobic characteristics of oily colorants. The contact angle of black oily colorants obtained from the graphitized soot and $CaCO_3$ decreases rather slowly. The phosphated surfaces of the black oily colorants are more hydrophilic.
5. Different monophasic nanoferrites $YFeO_3$, $Y_3Fe_5O_{12}$, $CoFe_2O_4$, $NiFe_2O_4$ and $ZnFe_2O_4$ were synthesized by an aqueous sol-gel method. These nanoferrites for the first time were used for the fabrication of black ceramic pigments. The SEM analyses revealed, that surface of yttrium perovskitte ferrite is composed of 200-1000 nm nanocrystallites. In the case of yttrium iron garnet more intensive agglomeration of

nanocrystallites was observed. In the case of spinels the particle size slightly depends on the nature of transition metal ($CoFe_2O_4$ > $ZnFe_2O_4$ > $NiFe_2O_4$).

6. The new black ceramic pigments were obtained by mixing of sol-gel derived nanoferrites $YFeO_3$, $Y_3Fe_5O_{12}$, $CoFe_2O_4$, $NiFe_2O_4$ and $ZnFe_2O_4$ with Pb_3O_4, SiO_2 and CuO. There was proven, that surface morphology of different black pigments mostly is influenced by the other components, for example Pb_3O_4, SiO_2 and CuO, but not depend on the sol-gel synthesized nanoferrites.

7. The obtained black ceramic pigments were used for the preparation of new black glazes. It was determined that the surface of obtained glazes at 800 ˚C temperature is quite equal and glossy. The glazes obtained at 900 ˚C already contains crystalline phases which are forming during the annealing process. Moreover, the glazes are fusing with ceramic substrate during calcination at 1000 ˚C. In conclusion, the metals nanoferrites $YFeO_3$, $Y_3Fe_5O_{12}$, $CoFe_2O_4$, $NiFe_2O_4$ and $ZnFe_2O_4$ synthesized by the sol-gel method for the first time successfully used as black ceramic pigments for the preparation of new high quality black glazes.

The List of Original Publications by the Author

Articles in Journals

1. **A. Gatelytė**, D. Jasaitis, A. Beganskienė, A. Kareiva. Sol-Gel synthesis and characterization of selected transition metal nano-ferrites. *Medžiagotyra*, 17 (2011) 302-307.

2. **A. Gatelytė**, J. Senvaitienė, D. Jasaitis, A. Beganskienė, A. Kareiva. SEM characterization of sol-gel derived precursors, novel black pigments and glazes. *Chemija*, 22 (2011) 19-24.

3. **A. Gatelytė**, D. Jasaitis, A. Beganskienė, A. Kareiva. Sol-gel derived ferrites: synthesis and characterization. *Advanced Materials Research*, 222 (2011) 235-238.

Published Contributions to Academic Conferences

1. **A. Gatelyte**, D. Jasaitis, A. Beganskiene, A. Kareiva. Sol-gel preparation and characterization of nanosized iron-containing oxide ceramic. 11th International Conference-School, Palanga, Lithuania, August 27-31, (2009) 71.

2. **A. Gatelyte**, D. Jasaitis, A. Beganskiene, A. Kareiva. Sol-gel preparation and characterization of nanosized iron-containing oxide ceramic pigments. 9th National Lithuanian Conference „Chemistry 2009“, Vilnius, Lithuania, October 16, (2009) 20.

3. **A. Gatelyte**, D. Jasaitis, A. Beganskiene, A. Kareiva. Sol-gel preparation of nanosized iron-containing oxides as potential candidates for ceramic pigments. Conference ”Chemistry and Technology of Inorganic Compounds”. Kaunas, Lithuania, April, (2010) 20-22.

4. **A. Gatelyte**, D. Jasaitis, A. Beganskiene, A. Kareiva. Sol-gel derived ferrites: synthesis, characterization and application. 9th International Conference on Global Research and Education "Inter-Academia 2010", Riga, Latvia, August 9-12, (2010) 148-149.

5. **A. Gatelyte**, D. Jasaitis, A. Beganskiene, A. Kareiva. Nanosized iron-containing oxide ceramics prepared by sol-gel method. 9th International Conference "Solid State Chemistry", Prague, Czech Republic, September 10-15, (2010) 110.

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NAUJŲ JUODŲJŲ PIGMENTŲ SINTEZĖ IR TYRIMAS

SANTRAUKA

Buvo sudaryti modeliniai juodieji pigmentai iš C suodžių ir K_2CO_3, $Ca_3(PO_4)_2$, $CaCO_3$ bei $Mg_3(PO_4)_2$. Pagal IR spektroskopinius duomenis buvo nustatyta, kad C suodžių su K_2CO_3, $Ca_3(PO_4)_2$, $CaCO_3$ ir $Mg_3(PO_4)_2$ įvairios sudėties mišinių IR spektruose OH^-, PO_4^{3-} ir CO_3^{2-} grupėms charakteringųjų smailių intensyvumas mažėja didėjant juose

anglies suodžių kiekiui. Modeliniai juodieji pigmentai buvo panaudoti juodųjų aliejinių dažų kūrimui. Buvo nustatyta, kad juodųjų aliejinių dažų spalvinis juodasis tonas yra kokybiškiausias, kai su linų aliejumi buvo maišomi anglies suodžiai, pagaminti tokiu moliniu santykiu C: neorganinė druska : 1: 0,01. Juodųjų aliejinių dažų kokybė priklauso ir nuo naudojamų karbonatų bei fosfatų mišinio sudėties. Visi angliniai dariniai su $Ca_3(PO_4)_2$, $CaCO_3$ ir $Mg_3(PO_4)_2$ buvo maišomi optimaliu santykiu. Pirmą kartą juodiesiems pigmentams gaminti panaudoti sintetiniai valyti ir nevalyti grafitizuoti suodžiai. Nustatyta, kad valyti grafitizuoti suodžiai yra tinkamiausi kokybiškiems juodiesiems aliejiniams dažams gaminti. Susintetintų naujų juodųjų aliejinių dažų hidrofobiškumas labai priklauso nuo nanostruktūrintos anglies buvimo dažuose. Juodųjų aliejinių dažų, gautų iš grafitizuotų suodžių ir $CaCO_3$, paviršių kontaktinis kampas kinta lėčiausiai. Fosfatiniai juodųjų aliejinių dažų paviršiai išlieka hidrofiliškesni. Susintetintų nauji juodieji aliejiniai dažai buvo tirti kontaktinio kampo metodu. Buvo parodyta, kad dažų hidrofobiškumas labai priklauso nuo nanostruktūrintos anglies buvimo dažuose. Juodųjų aliejinių dažų, gautų iš grafitizuotų suodžių ir $CaCO_3$, paviršių kontaktinis kampas kinta lėčiausiai. Fosfatiniai juodųjų aliejinių dažų paviršiai išlieka hidrofiliškesni. Vandeniniu zolių-gelių metodu buvo susintetinti įvairūs metalų vienfaziai nanoferatai $YFeO_3$, $Y_3Fe_5O_{12}$, $CoFe_2O_4$, $NiFe_2O_4$, $ZnFe_2O_4$, kurie pirmą kartą panaudoti juodaisiais keraminiais pigmentais. Nauji juodieji keraminiai pigmentai buvo maišomi su Pb_3O_4, SiO_2 ir CuO. Įrodyta, kad skirtingų juodųjų pigmentų paviršiaus morfologija labiau priklauso ne nuo zolių–gelių metodu susintetintų $YFeO_3$, $Y_3Fe_5O_{12}$, $CoFe_2O_4$, $NiFe_2O_4$ ir $ZnFe_2O_4$, o nuo kitų sudedamųjų dalių, t.y. Pb_3O_4, SiO_2 ir CuO. Gauti juodieji keraminiai pigmentai buvo panaudoti naujoms juodosioms glazūroms sintetinti. Nustatyta, jog 800 ˚C temperatūroje gautų glazūrų paviršius yra pakankamai tolygus ir blizgus. 900 ˚C temperatūroje gautų glazūrų paviršiuje jau pastebimos atsirandančių kristalitų fazės, o 1000 ˚C temperatūroje pigmentai jau sukepa su keramika. Taigi galima teigti, kad zolių-gelių metodu susintetinti metalų nanoferatai $YFeO_3$, $Y_3Fe_5O_{12}$, $CoFe_2O_4$, $NiFe_2O_4$ ir $ZnFe_2O_4$ pirmą kartą sėkmingai panaudoti juodaisiais keraminiais pigmentais naujoms, kokybiškoms juodosioms glazūroms gauti.