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**CHARACTERIZATION OF SPECIAL OXIDIC
ANTICORROSIVE PIGMENTS
BY XRD AND XFR ANALYSIS**

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Spinel type pigments were analyzed by X-ray fluorescence spectrometry and X-ray powder diffraction. X-ray fluorescence spectrometry determined the contents of specific elements and X-ray diffraction determined the crystalline structure of the samples. Three samples of spinel pigments were analyzed as such and after their application to aluminum and carbon core. The results of XRD showed the presence of crystalline phase of the pigment and also small amount of Fe₂O₃ and also the diffraction lines of the cores. The XRF analysis showed the presence of the elements from which were the pigments prepared and also trace amounts of impurities (P₂O₅, SO₃).

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Introduction

Interaction of X-rays with solid substances could be used for determination of their composition and also for determination of their crystal structure. X-ray diffraction analysis uses the phenomenon of diffraction of X-rays by crystals. Monochromatic X-ray diffraction on powder crystalline materials was used for identification, and also for quantitative analysis of crystalline compounds. X-ray spectral analysis allows the determination of the composition of inorganic substances based on the excitation of secondary X-rays. X-ray spectral analysis and X-ray diffraction analysis belong to the non-destructive analytical methods [1]. The advantages of X-ray methods are their relative simplicity and speed.

Spinel-Type Pigments

The general formula of these pigments was AB_2O_4 , at point A could be elements Mg, Ca, Zn, Co, Fe, Cu and Mn, at point B elements Al, Fe, Cr, Co and Ti. Pigments $ZnFe_2O_4$ and $CaFe_2O_4$ were used commercially [2]. Mechanism of action of anti-corrosive spinel type pigments is based on the formation of zinc or calcium soaps by reaction with a suitable binder, which improves the mechanical properties of the protective film and also reduces its permeability to aggressive agents. Pigments based on spinels have also neutralizing properties because their aqueous extract of pH = 9.8 helps to neutralize the acidic binders; this shifts the pH to the range that is less favorable to corrosion. On the film-substrate interface the spinel type pigments can form insoluble complex compounds, which passivate the surface. Physiological safety of this type of pigments determines them to the position of a good alternative to the toxic pigments [3].

Structure and Types of Spinel Pigments

The crystal structure of spinel pigments is derived from mineral spinel $MgAl_2O_4$. This structure can be considered as a combination of alternating cubes ZnS and $NaCl$. Structure is determined by grouping bulky oxygen anions and face-centered cubic arrangement. Free cavities for placement of cations are octahedral (coordination number 6) and tetrahedral (coordination number 4).

Elementary cell of spinel contains 32 oxygen anions, 8 cations in the tetrahedral positions and 16 cations in octahedral positions. In a normal spinel structure A^{2+} cations occupy one eighth of tetrahedral cavities and B^{3+} cations a half of octahedral cavities. In the inverse spinel structure all A^{2+} cations and half of B^{3+} cations occupy octahedral positions. The second half of B^{3+} cations occupy tetrahedral cavities. Inverse spinels can be expressed by formula $B(AB)O_4$. The

transition between the two types are mixed oxides ($A_{1-x}B_x$) [$A_{1-x}B_x$], where the parameter x expresses the normal arrangement rate. Factors that influence the type of spinel structure are different (ligand field stabilization energy, Madelung constant for the normal and inverse structures, ligand field stabilization energy for octahedral and tetrahedral arrangement, polarization and covalent effects). Inverse spinels have disordered and defective structure, because crystallographically identical positions within the elementary cell are not occupied by the same cation [4].

Formation and Properties of Spinel-type Pigments

Properties of spinel pigments are characterized by their crystalline structure that depends on the properties and host lattices. Typical property of this kind of mixed oxides is their mutual miscibility and almost unlimited creation of solid solutions. From simple spinels or ferrites can be derived mixed spinel compounds, which means the substitution solid solutions of single spinels. Isomorphic substituted structures consist of a continuous range of compounds, from compounds with defined stoichiometric ratio of substituents to the compounds in which structure are foreign ions only as incidental impurities.

Thermally stable structure formation involves actions that take place at high temperatures in the solid phase. The term reaction in the solid phase can be used in two main cases. First are actions, when two chemical compounds form a new one and the second are actions when from one substance are formed the other substances. Formation of ferrites can be placed into this group of reactions. Theories, which explain the origin of spinels, exist in several variants [5]. One of them is the case when the most mobile ions diffuse through the product layer in the same direction with the electrons [5]. Molecular oxygen is transported with the gaseous phase. It is assumed that the spaces between the grains are filled with air. For this reason, the burning was performed in an oxidizing atmosphere. There was a migration of particles of only one of the reactants due to the much smaller diffusion rate of the second substance. The kinetics of the reaction is affected by the rate of diffusion of faster ion through the layer of the product. The kinetics of reaction also depends on the amount of defects in the structure, more defects in the structure mean faster reaction. Three main phases can be distinguished for reactions in the solid phase, the phase of formation and growth of the new compound, the phase of diffusion of reactive components through the product layer and the phase of chemical reaction. Each of these phases could limit the kinetics of the reaction. The speed of this type of reactions could be affected by acceleration of the control process, improved contact of the particles.

Spinel-type pigments are characterized by high melting point, colour stability and hardness. Due to their great opacity and stability they are used as pigments in

ceramic glazes. Spinel is applied in cases which need heat-stable, non-toxic inert pigment (plastics, paints, ceramics). Interesting application have spinels in anticorrosive paints. A very interesting option of development of anticorrosive pigments based on ferrite, respectively ferrospinels, is their synthesis with lamellar, non isometric particles [6].

Experimental

Samples Preparation

Practical experience showed that the largest source of errors in X-ray analysis, especially fluorescence analysis, was the preparation of the samples. It was necessary to pay great attention to the sample preparation. For the measurements, several types of samples could be used: sprinkled, pressed, molded with a binder and melted. Liquid samples could be measured only in certain types of instruments. The results of fluorescence analysis were influenced by sample inhomogeneity (different chemical composition, different phase composition, uneven particle size, surface roughness of the sample). The influence of sample inhomogeneity was most considerable in sprinkled samples; for samples pressed or molded with a binder (cellulose was mostly used as a cement), the effect of surface roughness and of different granularity was suppressed. The samples melted (lithium or sodium tetraborate was used as a fluxing agent most often) in the form of beads or disks; the mineralogical effect (influence of phase composition) and the effects of surface roughness and different grain size of particles were suppressed. The melting temperature was between 1000 °C and 1300 °C; an induction furnace was generally used for the heating [7]. Completely homogeneous sample with particle size between 1 and 50 μm which showed no preferred orientation of the particles or stress distortion, was ideal for X-ray diffraction. Large particle size reduced the number of particles with a suitable spatial orientation which allowed diffraction of X-rays, which might result in an incorrect measurement of the intensity of diffracted radiation. Homogenization and dilution was usually carried out manually in an agate mortar, electric grinder was used for building materials or waste. In the case of pigments or fillers intended for the production of coatings, which were very fine, hand distribution of agglomerates in mortar was sufficient.

Description of Instrumentation

Diffraction phase analysis was performed on X-ray diffractometer Philips MPD 1880 (crystal monochromator) under standard apparatus conditions. Evaluation of

the diffraction data was carried out using a software package X'Pert (X'Pert HighScore Plus software version 2.1b and X'Pert Industry Software version 1.1g). Identification was performed by using the ICDD PDF 2 diffraction database, which contained about 107,000 standards.

X-ray spectral analysis was performed on X-ray spectrometer Philips PW 1404 (wavelength dispersive device), equipped with an analytical program UniQuant, which allowed semiquantitative determination of 74 elements (from fluorine to uranium) with the reported measurement uncertainty 5-10 %. This software used the method the basic parameters based on the Sherman formula [8].

Results and Discussion

For X-ray analysis, three types of anticorrosive pigments were chosen; they were analyzed as such and then after their application to aluminum and carbon core. In the following figures, we show the diffraction patterns of all samples, all crystalline phases found in the samples are summarized in Table I. Table II summarizes the contents of elements (expressed as oxides) quantified by X-ray fluorescence.

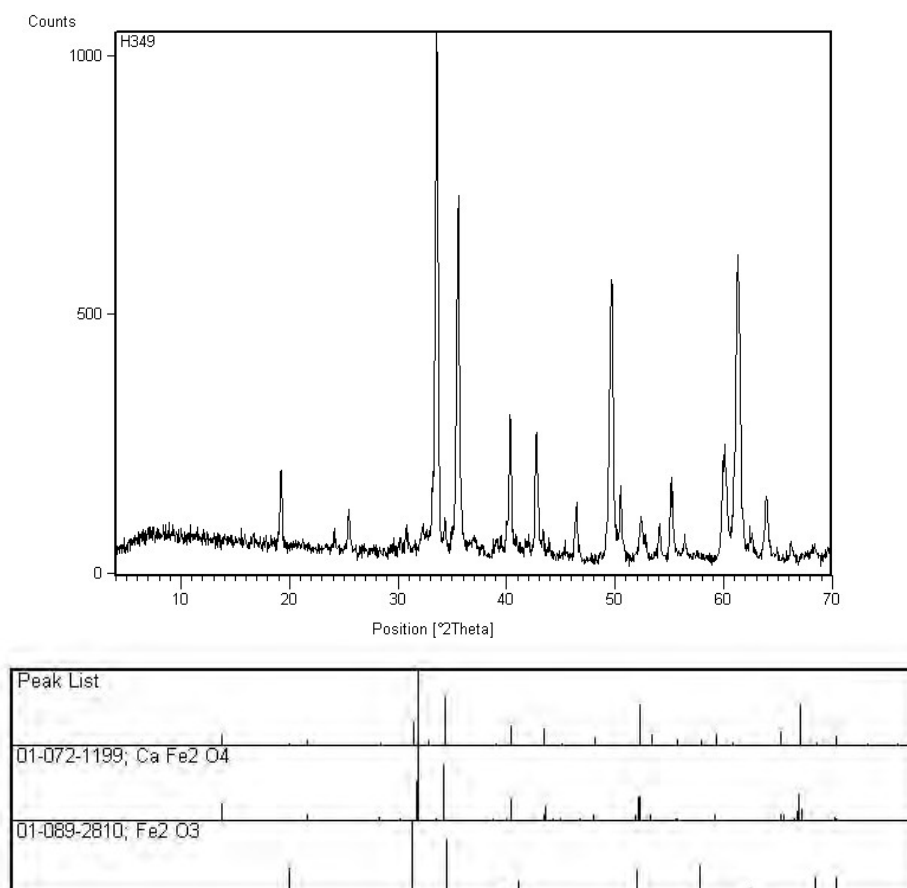
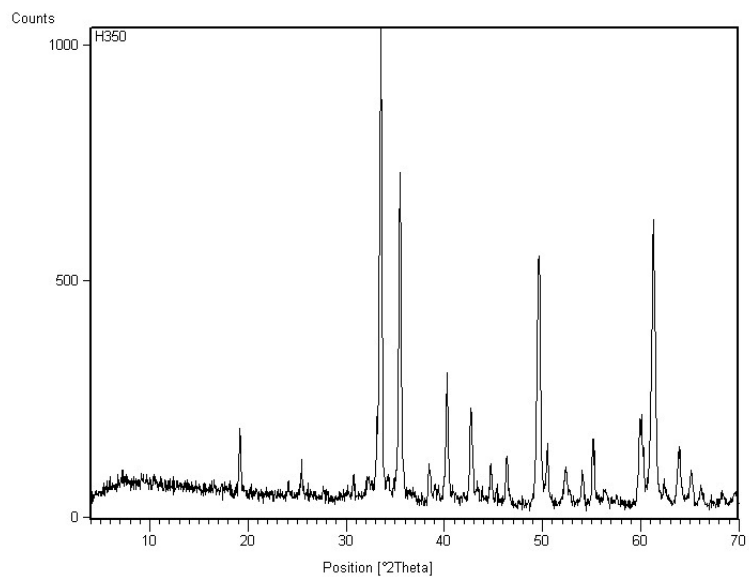
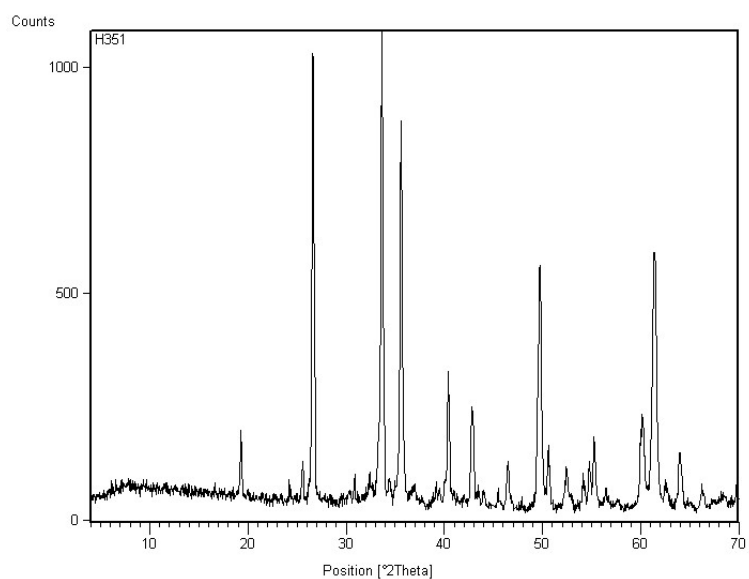


Fig. 1 Diffraction pattern of sample 1



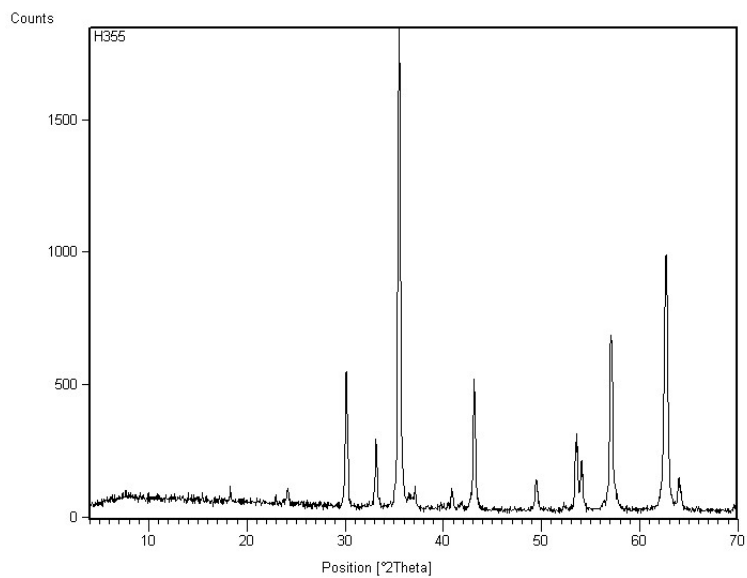
Peak List
01-072-1199; Ca Fe2 O4
00-001-1176; Al
01-072-0469; Fe2 O3

Fig. 2 Diffraction pattern of sample 1/A1



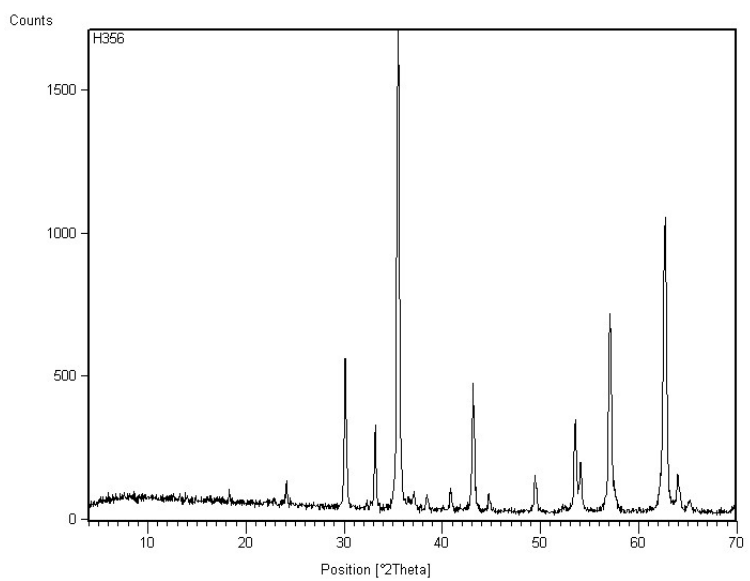
Peak List
01-074-2136; Fe2 Ca O4
00-026-1080; C
01-089-0599; Fe2 O3

Fig. 3 Diffraction pattern of sample 1/C



Peak List	
01-088-1936; Mg Fe ₂ O ₄	
01-089-0596; Fe ₂ O ₃	

Fig. 4 Diffraction pattern of sample 2



Peak List	
01-088-1936; Mg Fe ₂ O ₄	
00-024-0072; Fe ₂ O ₃	
03-065-2869; Al	

Fig. 5 Diffraction pattern of sample 2/Al

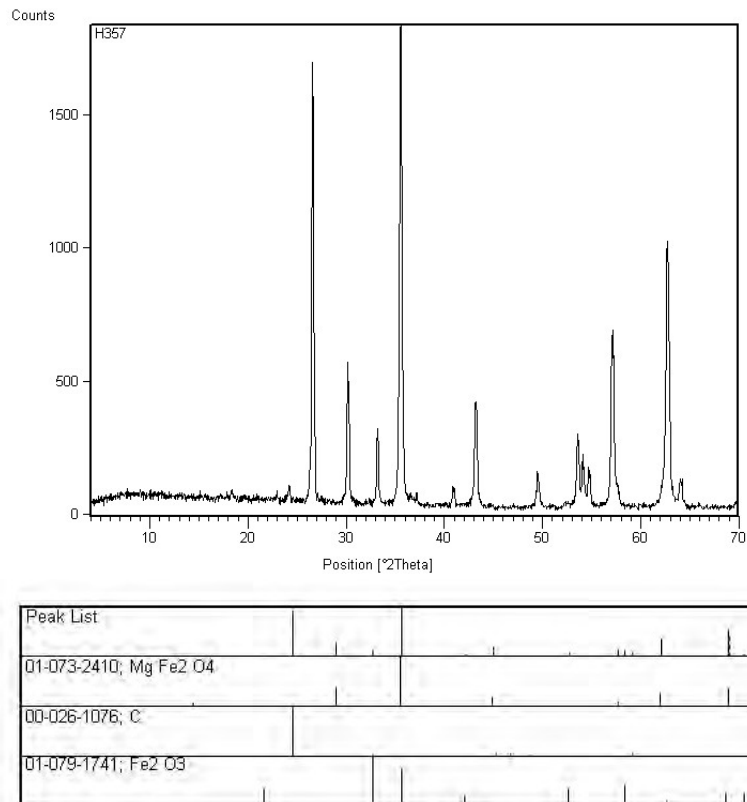


Fig. 6 Diffraction pattern of sample 2/C

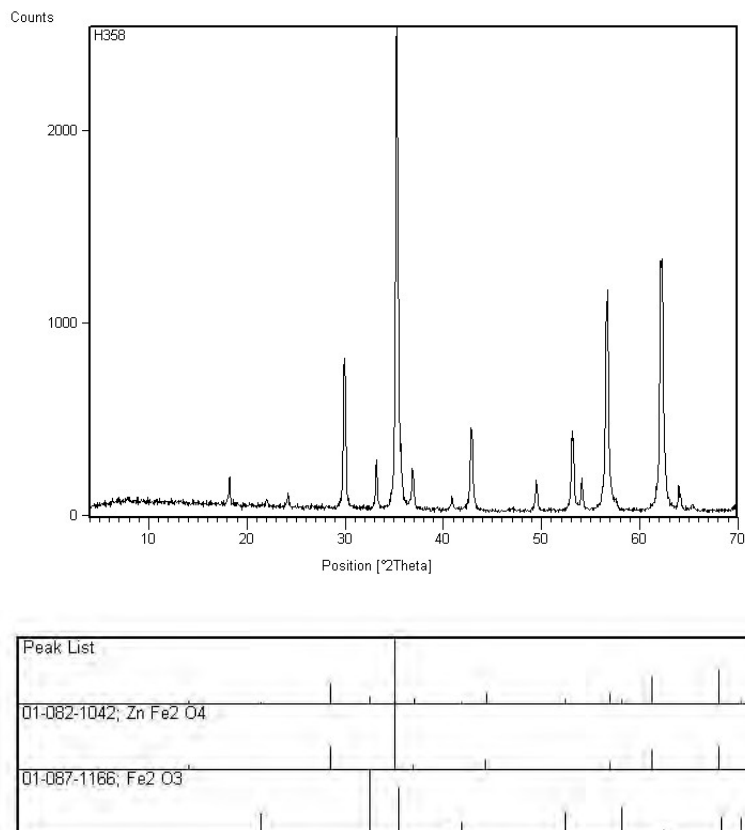
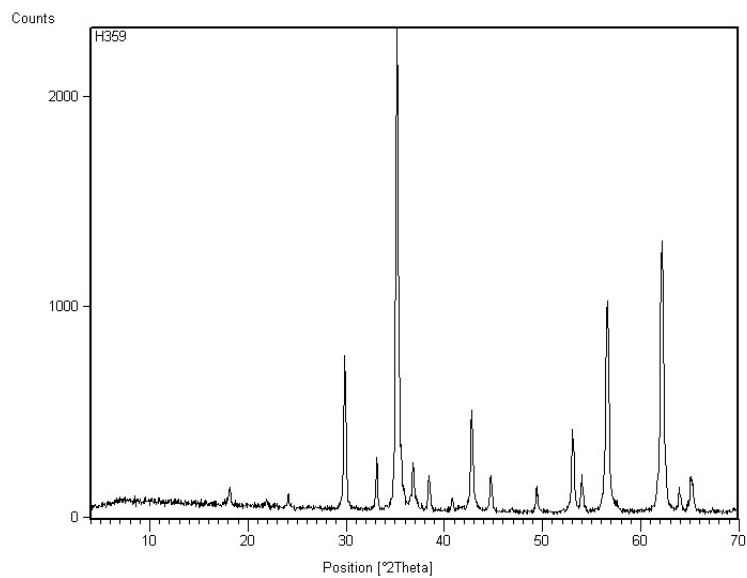
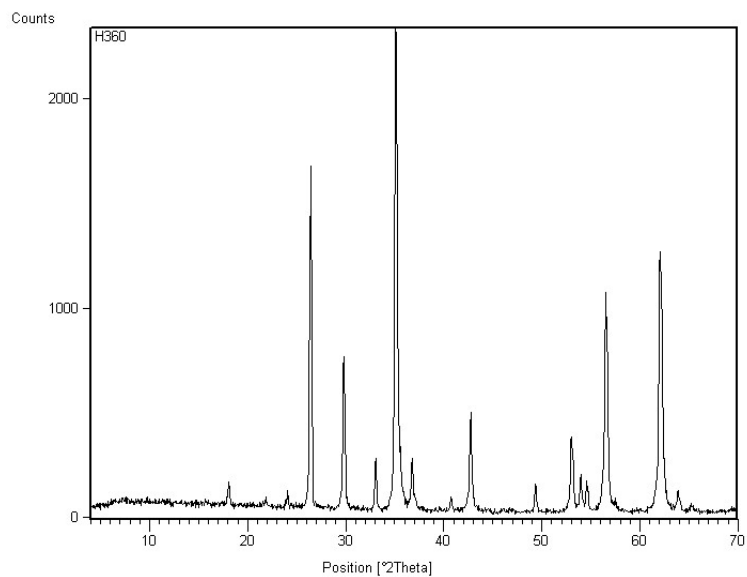


Fig. 7 Diffraction pattern of sample 3



Peak List	
01-079-1150; Zn Fe2 O4	
01-089-0598; Fe2 O3	
03-065-2869; Al	

Fig. 8 Diffraction pattern of sample 3/A1



Peak List	
01-082-1042; Zn Fe2 O4	
00-008-0415; C	
01-089-0598; Fe2 O3	

Fig. 9 Diffraction pattern of sample 3/C

Table I Crystalline phases determined by X-ray powder diffraction

Sample Number	Crystalline Phases
1	CaFe ₂ O ₄ Fe ₂ O ₃
1/Al	CaFe ₂ O ₄ Fe ₂ O ₃ Al
1/C	CaFe ₂ O ₄ Fe ₂ O ₃ C
2	MgFe ₂ O ₄ Fe ₂ O ₃
2/Al	MgFe ₂ O ₄ Fe ₂ O ₃ Al
2/C	MgFe ₂ O ₄ Fe ₂ O ₃ C
3	ZnFe ₂ O ₄ Fe ₂ O ₃
3/Al	ZnFe ₂ O ₄ Fe ₂ O ₃ Al
3/C	ZnFe ₂ O ₄ Fe ₂ O ₃ C

Sample 1 was anticorrosive pigment CaFe_2O_4 , the XRD pattern showed that the major phase was CaFe_2O_4 ; in the sample, a small amount of Fe_2O_3 was also found. Sample 1/Al was CaFe_2O_4 anticorrosive pigment, but now it was applied to an aluminum core; the diffraction lines of aluminum could be found in the diffraction pattern. Sample 1/C was applied to carbon core and the diffraction lines of carbon were present in the diffraction pattern. Sample 2 was anticorrosive pigment MgFe_2O_4 oxide, which was the major crystalline phase in the sample; there was found a small amount of crystalline Fe_2O_3 . This sample was applied to aluminum and carbon core, and diffraction lines of these elements were present in the diffraction patterns of samples 2/Al and 2/C. The last sample was ZnFe_2O_4 , whose major phase was ZnFe_2O_4 , and a small amount of Fe_2O_3 was found in the diffraction pattern. Samples 3/Al and 3/C were modifications of sample 3, and the lines of the new elements from the core were present in each diffraction pattern. XRF showed almost none impurities, except for a small amount of SiO_2 and trace amounts of P_2O_5 and SO_3 , in all the samples.

Table II Results of X-ray fluorescence analysis (the concentrations of elements were expressed in weight percent)

Component	Sample								
	1	1/Al	1/C	2	2/Al	2/C	3	3/Al	3/C
MgO	0.29	0.17	0.26	16.9	15.4	17.5	-	-	-
Al_2O_3	0.24	11.5	0.35	0.25	10.9	0.33	-	30.9	-
SiO_2	2.42	2.25	2.40	2.41	2.33	2.47	2.50	1.93	2.42
CaO	25.8	23.8	25.5	0.20	0.20	0.20	0.02	0.02	0.02
TiO_2	0.60	0.54	0.60	0.71	0.67	0.71	0.65	0.48	0.63
Fe_2O_3	69.7	61.0	70.0	78.7	69.7	77.9	68.5	48.3	68.4
ZnO	-	-	-	-	-	-	27.8	17.8	27.8

Conclusion

The combination of both X-ray methods created a basic picture of the chemical and structural arrangement of anticorrosive pigments. For the complex characteristics of the pigments we had to add the particle size analysis and also methods for analysis of water-soluble substances (pH and conductivity of pigment extract) and the measurement of absorption of oil or water (according to the pigment use). For the X-ray analyses, we chose three types of anticorrosive spinel

pigments, which were analyzed as such and after their application to aluminum and carbon core. The results of XRD showed that small amounts of Fe_2O_3 were present in all the pigments; beside this impurity, the pigments contained crystalline phases which were expected. The results of XRF showed that the pigments were relatively pure, all of them contained only small amount of impurities (SiO_2 , P_2O_5 and SO_3).

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