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DOI: 10.15199/40.2024.9.5

# Unconventional EPR studies of powder coatings

## Niekonwencjonalne badania farb proszkowych metodą EPR

*This work presents electron paramagnetic resonance studies of powder coatings. These unconventional studies allow the analysis of paramagnetic centers (dopants, defects, local environment, etc.) for the identification and selection of appropriate components in the paint manufacturing process. The g-factor and all line parameters were calculated.*

**Keywords:** EPR, paints, free radicals, paramagnetic centers

*W artykule przedstawiono wstępne badania elektronowego rezonansu paramagnetycznego farb proszkowych. Te niekonwencjonalne badania pozwalają na analizę centrów paramagnetycznych (domieszek, defektów, lokalnego otoczenia itp.) pod kątem identyfikacji i doboru odpowiednich składników w procesie produkcji farb. Obliczono współczynnik g oraz wszystkie parametry linii.*

**Słowa kluczowe:** EPR, farby, wolne rodniki, centra paramagnetyczne

### 1. Introduction

Paint is one of the oldest human inventions and has been produced since prehistoric times. There are many types of paint, and they can be grouped according to the type of binder used, purpose, or number of layers. Any technology based on adhesion, such as painting, varnishing or sealing, uses elemental methods to achieve the desired energy state of the surface layer [1]. Adhesion properties are used in the application of protective coatings. Proper preparation of the surface layer is important [2, 3]. In all paint systems, the pigment always constitutes the dispersion phase. The colour of the paint depends on light scattering and absorption. Particle packing is important in determining the properties of the

paint film. Electrodeposited paints can be colloiddally stabilised by anionic, cationic or even non-ionic groups [4].

Electron paramagnetic resonance (EPR) spectroscopy is the best non-destructive method for testing paint components and is associated with the absorption of a high-frequency field that accompanies a change in the electron spin orientation field in an external magnetic field. It occurs in paramagnetic substances (atoms, molecules and molecular complexes with uncompensated, unpaired spin, so-called paramagnetic centres) in which the unpaired spin magnetic moments align in the direction of the magnetic field. EPR can detect any substance with paramagnetic electrons, including organic and inorganic radicals (e.g. superoxide radical in wine [5], phosphate transport in erythrocytes [6], transition metal complexes [7],

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■ Received / Otrzymano: 16.08.2024. Accepted / Przyjęto: 12.09.2024

metalloproteins [8], aerospace mullites and powders [9], multi-walled carbon nanotubes and nanowires [10]). EPR is also used by art conservators, historians and restorers, among others, to examine paintings. EPR spectroscopy has been used to study cave paintings [11], wall paintings [12], or individual pigments [13, 14].

The aim of this study is to analyse the EPR paramagnetic centres present in two types of powder coatings with a view to selecting the process parameters for the production of the coatings.

## 2. Research materials and methods

### 2.1. Basic information about the EPR method

Electron paramagnetic resonance (EPR) spectroscopy is based on the resonant absorption of microwave radiation  $E = h\nu$  by paramagnetic atoms or molecules placed in a strong magnetic field ( $B$ ). The relationship between  $\nu$  and  $B$  is given by equation:

$$E = h\nu = g\beta B, \quad (1)$$

where:  $\beta$  – Bohr magneton,  $h$  – Planck's constant,  $g$  – the Landé  $g$ -factor is the intrinsic constant of matter containing unpaired electrons. EPR spectra are usually recorded by sending a constant value of microwave radiation while scanning a magnetic field. Spectral absorption occurs when equation (1) is satisfied. Spectral absorptions appear as the first derivatives of absorption in the function of  $B$ , because magnetic field modulation and phase-sensitive detection at the modulation frequency are used to improve the signal-to-noise ratio [15]. Characteristic line parameters can be determined from the line shape, i.e. the value of the resonant field  $B_r$ , allows us to determine the effective spectroscopic partition coefficient  $g_{\text{eff}}$ , the width of the resonant line  $\Delta B_{pp}$ , and the intensity of the EPR line (Fig. 1).

EPR measurements were carried out on a model FT-EPR ElexSYS E-580 spectrometer (Bruker), operating at continuous wave in the X-band (approximately 9.5 GHz) using the following settings: central field – 3501.00 G, modulation amplitude – 1 G, modulation frequency – 100 kHz, microwave power – 94.64 mW, attenuation – 2.0 dB (94.64 mW), scan range – 7000 G, conversion time – 30 ms, registration time – 122.88 s. The temperature of the measurements was controlled from liquid nitrogen to room temperature (95–300 K) using a quartz nitrogen cryostat with a 41131 VT digital controller (Bruker). The spectrometer is equipped with a 10 inch magnet with a field uniformity of 10 mG, and a Hall controller calibrated from –18 kG to +18 kG with an accuracy of better than 500 mG. The temperature system allows the temperature to be determined to within 0.1 K. For data acquisition, as well as for the analysis of the EPR measurements, Xepr software (Bruker) was used. For the analysis and calculations, Easyspin software, which is an add-on to the MATLAB package (Natick), was used. For the determination of the  $g$ -factor and the analysis of the EPR spectrum, fitting and simulation were performed using VisualEPR [16] and Easyspin [17] software.

### 2.2. Paint

Paint plays an important role not only in the arts, but also in materials engineering, for example in vibration absorption [18], mechanical engineering [19], shipbuilding [20], defence or aerospace [21].

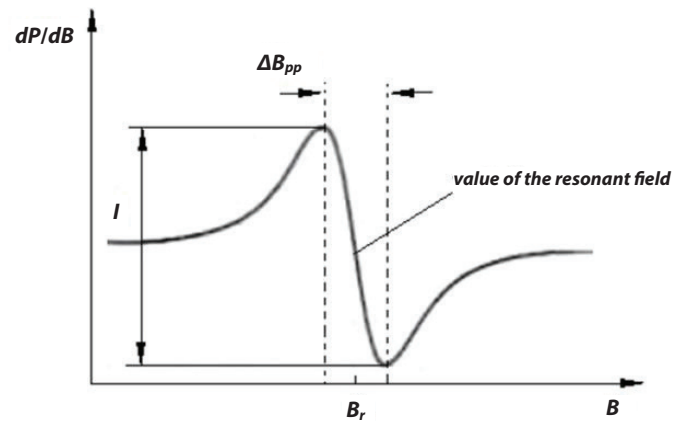


Fig. 1. Shape of EPR spectrum – characteristic line parameters marked

Rys. 1. Przykładowy kształt widma EPR – zaznaczono charakterystyczne parametry linii

The development of paint is strongly influenced by environmental protection, corrosion resistance and durability to weathering. The selection of components that are most sensitive to degradation is therefore very important [19]. Coatings produced by Inver Polska (Dębica, Poland), which is part of the Sherwin-William company (Cleveland, USA), were used in this study. The two polyester powder paint samples (hereafter referred to as sample 1, and sample 2) share a common base of polyester resin and hardener, which provides them with mechanical and chemical properties. They differ in several aspects described below, which affect their performance and specific applications. The rheology and anti-caking agent in sample 2 provides better control over the flow properties of the paint, which can be beneficial in applications requiring precise application [22]. The rheology and anti-caking agent in sample 1 is more geared towards preventing caking during storage [23]. Both samples contain black pigment, but these are different substances that affect the colour intensity and protective properties of the coating [24]. Sample 1 contains one anti-corrosion agent, while sample 2 has two, which may provide better corrosion protection [25]. In addition, sample 2 contains a filler that improves the mechanical properties of the coating, increasing its hardness and abrasion resistance [26]. Polyester resin is the primary component of the paint, which protects the surface from damage and corrosion. Its chemical structure allows it to form strong cross-links during curing, which gives the coating its strength and durability [27]. In order for the polyester resin to perform its role, a hardener is required to initiate the cross-linking reaction, transforming the liquid resin into a durable coating. The hardener ensures that the coating becomes resistant to mechanical damage and chemical attack [28]. Another ingredient included in the test samples is the slip agent. Its presence ensures that the powder remains easy to apply and does not form lumps during storage [23]. A defoamer prevents the formation of air bubbles in the coating, which can lead to surface defects. It allows for a uniform and aesthetically pleasing coating, which is crucial for the final appearance and protective properties of the paint [26]. The stabiliser protects the coating from thermal and oxidative degradation, which increases its life and effective-

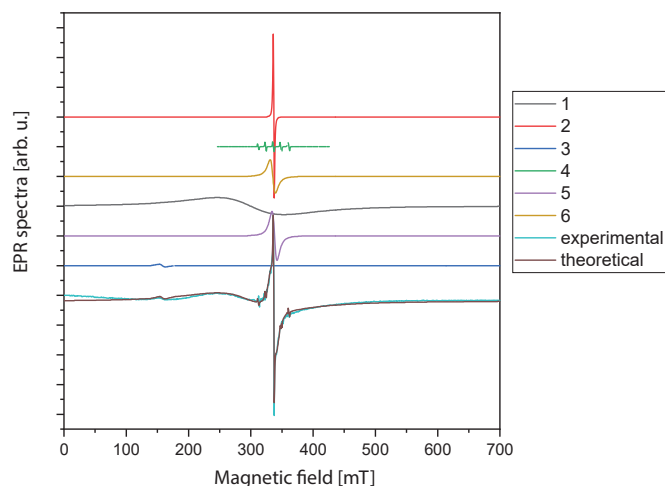


Fig. 2. Experimental spectrum for sample 1 and theoretical spectrum with individual components

Rys. 2. Widmo doświadczalne dla próbki 1 i widmo teoretyczne z poszczególnymi składowymi

ness [29]. Wax is added to the paint to improve surface properties such as scratch and abrasion resistance. Wax forms a thin layer on the surface of the coating, reduces friction and increases resistance to mechanical damage. This allows the paint to retain its protective properties for longer [30]. The final component is an anti-corrosive agent. Its function is to improve the corrosion resistance of the coating [25]. In addition, a filler improves the coating's mechanical properties. Fillers increase hardness and abrasion resistance, which is key to maintaining the durability of the coating under service conditions [26].

The polyester powder coatings tested, samples 1 and 2, are advanced, multi-component products whose properties result from the synergy of multiple components. Sample 1 is geared more towards general applications with good rheology and scratch resistance, while sample 2 offers better control of flow properties and enhanced corrosion and mechanical protection, thanks to additional agents and fillers.

### 3. Results and analysis

EPR spectra were measured for 2 powder paint samples, the obtained spectra are shown in Fig. 2 (sample 1) and Fig. 3 (sample 2). Analysing the obtained spectra, we notice very large differences in the intensity of the EPR spectra, and in the number of components. For sample 1, the intensity of the lines is much higher, and from the line distribution we get 6 component lines, while for sample 2 only 4 components. The  $g$  values for all the component lines were determined: for sample 1 –  $1-g = 2.340$ ,  $2-g = 1.999$ ,  $3-g = 4.236$ ,  $4-g = 1.998$ ,  $5-g = 1.988$ ,  $6-g = 2.004$ ; for sample 2 –  $1-g = 2.34$ ,  $2-g = 1.999$ ,  $3-g = 4.236$ ,  $4-g = 1.998$ . It was observed that the four components in sample 2 have their counterparts in sample 1, differing only in the intensity of the lines and therefore in the number of paramagnetic centres. Based on the literature, paramagnetic centres were assigned to individual lines. For line no. 1, with a large

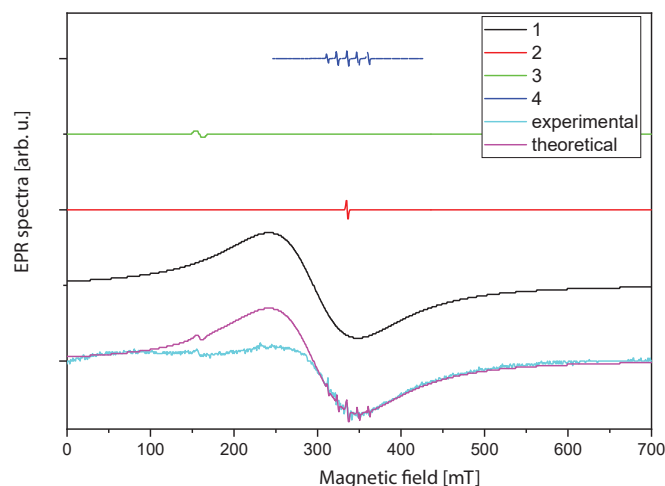


Fig. 3. Experimental spectrum for sample 2 and theoretical spectrum with individual components

Rys. 3. Widmo doświadczalne dla próbki 2 i widmo teoretyczne z poszczególnymi składowymi

width of  $g = 2.34$ , many different defects (vacancies, impurities, etc.) can be assigned, for line no. 2  $g = 1.999$  with a small width, most likely originating from carbon. The value  $g = 1.999$  is attributed to the interaction between conduction electrons in carbon nanoparticles trapped in defects or magnetic ions. The greater the deviation from the free electron  $g$  value, the greater the localisation due to defects [31, 32]. For line 3, analysis of the line positions suggests that  $g = 4.28$  and  $g = 2.00$  can be attributed to  $\text{Fe}^{3+}$  ( $S = 5/2$ ) ions, as they represent a typical spectrum for so-called disordered systems [33], which are in the form of glass [34]. The intensities of the lines decrease progressively showing the evolution of relative line shapes and intensities at  $g_{\text{eff}} = 4.3$  from isolated ions at local tetrahedral (and eventually octahedral) sites. For line 4,  $g = 1.998$ , we observe the hyperfine structure of the EPR spectrum which originates from the  $\text{Mn}^{2+}$  ion [35], while line 5 can be attributed to the  $\text{Cr}^{3+}$  ion and line 6 to the  $\text{Fe}^{2+}$  ion [36]. Temperature dependence of the EPR spectra was performed. Small changes in line 1, and line 3, were observed for both samples (Fig. 2 and 3). The intensity of the narrow line 1 increases approximately twofold with decreasing temperature, while the broad line 3, gently decreases in intensity, and slightly broadens, with decreasing temperature.

### 4. Conclusion

Key information on coatings and EPR spectroscopy is presented in the paper. EPR spectra were measured for two types of paint: sample 1 and sample 2. Temperature dependence of the spectra in the range 95–300 K was performed, which showed no significant differences, while comparison of the spectra of the two samples at room temperature shows differences, which were analysed using the specialist VisualFPR and EasySpin programs. The basic parameters of the EPR lines were determined, the most significant of which is the  $g$  factor, and based on this the individual lines were assigned to the paramagnetic centres described in the literature. It was

observed that the four components in sample 2 have their counterparts in sample 1 differing only in the intensity of the lines, with component 2 having a very high intensity in sample 1 compared to sample 2. The source of these differences is the relatively large amount of carbon in sample 1.

Due to the very high sensitivity and selectivity of the EPR method, we see very high potential in its application for paint testing. Particularly in planned studies aimed at assessing the durability of paints based on the detection of free radicals and active ions in individual components, the occurrence of which leads to paint degradation.

#### CRediT authorship contribution statement

**Piotr Pisiak:** Conceptualization, Formal analysis, Methodology, Software, Writing – original draft, Writing – review & editing.

**Bogumił Cieniek:** Conceptualization, Formal analysis, Investigation, Methodology, Software, Visualization, Writing – original draft, Writing – review & editing.

**Ireneusz Stefaniuk:** Conceptualization, Formal analysis, Methodology, Project administration, Software, Supervision, Validation, Writing – review & editing.

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