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Electron Magnetic Resonance Study of the Most Sensitive Metal Paint Components for Degradation

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ABSTRACT

The article presents an electron magnetic resonance study of metal paints in terms of identification and selection of appropriate pigment components based on the summation of spectral components. Research was carried out to assess the durability of paints on the basis of the detection of free radicals in individual components, the occurrence of which leads to paint degradation. Two types of acrylic resins, three types of organic pigments, and titanium white, hardener, and clearcoat were tested. The g-factor as well as all electron magnetic resonance line parameters were calculated. Electron magnetic resonance is found to be useful in the effort to eliminate a paint component that reduces color durability and to select components in terms of paint quality.

Keywords: electron magnetic resonance, paints, degradation.

INTRODUCTION

Paints are one of the oldest artefacts of man, and they have been made since prehistoric times. There are many different types of paints that can be grouped in different ways, such as the type of binder, the purpose or the number of coats. Each adhesion-based technology e.g. painting, varnishing or sealing uses methods of elements for obtaining the desired surface layer energy state [1]. The adhesive properties are used to apply protective coatings. Therefore, proper preparation of the surface layer of painted materials is so important [2-3]. In all paint systems, the pigment is always the dispersion phase; however, this cannot be the only dispersion phase. The color of the paint depends on light scattering and light absorption. The packing of continuous solid particles is important in determining the properties of the paint film. Electrodeposit inks can be colloidally stabilised by anionic or cationic groups, and even non-ionic [4]. Electron magnetic resonance (EMR) spectroscopy is the best nondestructive method for testing paint components, which is related to 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 where unpaired spin magnetic moments align in the direction of the magnetic field. Paramagnetic substances are: atoms, molecules and molecular complexes with uncompensated (unpaired) spin, the so-called paramagnetic centres. Spin, an intrinsic property of a particle, is the angular momentum of a nucleus or electron. EMR can detect any species with paramagnetic electrons, including organic and inorganic radicals (for example, a superoxide radical in wine [5], or phosphate transport in erythrocytes [6]), transition metal complexes [7], metalloproteins [8], biradicals [9], and more (for example, a mullite and powders used in aerospace industry [10], multi-walled carbon nanotubes and nanohorns [11], and zinc oxide thin films of dilute magnetic semiconductors [12]). EMR were also used by art restorers, historians, and restorers to study paintings. EMR spectroscopy has been used to study rock paintings [13], wall paintings [14], and individual pigments [15–19].

EMR BACKGROUND

Electron magnetic resonance spectroscopy is based on the resonant absorption of a microwave radiation ($E = h \cdot \nu$) by paramagnetic atoms or molecules when placed in a strong magnetic field (B). The relationship between ν and B is given by Equation (1):

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

where: β – Bohr magneton, h – Planck's constant, g – Landé factor is an intrinsic constant of matter containing unpaired electrons.

Continuous-wave EMR spectra are typically recorded by sending a fixed value of microware radiation, while scanning the magnetic field. A spectral absorption appears when Equation (1) is satisfied. Spectral absorptions appear as first derivatives of an absorption as a function of B because magnetic field modulation and phase sensitive detection at the modulation frequency are employed to improve the signal-to-noise ratio in a spectrum [20]. Characteristic line parameters can be determined from the shape of the line. The value of the resonant field B_r, which allows us to determine the effective spectroscopic splitting coefficient g_{ef}, the width of the resonant line ΔB_{pp}, and the intensity of EMR line I (see Fig. 1).

PAINTS

Paints play an important role not only in the arts, but also in materials engineering, for example, with vibration absorbing [21], in mechanical engineering [22, 23], shipbuilding [24], armaments [25] or aerospace [26]. The development of paints is strongly influenced by characteristics such as environmental protection, corrosion resistance, and durability against atmospheric agents; hence, the selection of components most sensitive to degradation is very important [21, 23].

Composition

Paint is a chemical product composed of many raw materials. The properties of paint are determined by the binder, the ingredient that forms the paint layer. The main substance of the binder is a synthetic resin. The binder gives the paint its film-forming properties (drying), physical characteristics (film durability and adhesion), and chemical characteristics (film durability and chemical resistance). Binders and film-forming substances are found in all types of paints, varnishes, and emulsions. They cause the formation of a thin film (known as a film-forming film) on the surface of the item to be painted and are intended to give the paint appropriate properties such as gloss, durability, adhesion, weather resistance, strength, and elasticity. Substances that can act as binders in paints are synthetic or natural resins, such as polyurethanes, polyesters, vinyl/ethylene acetate (VAE), silanes, epoxy resins, or oils, for example. Pigment prevents

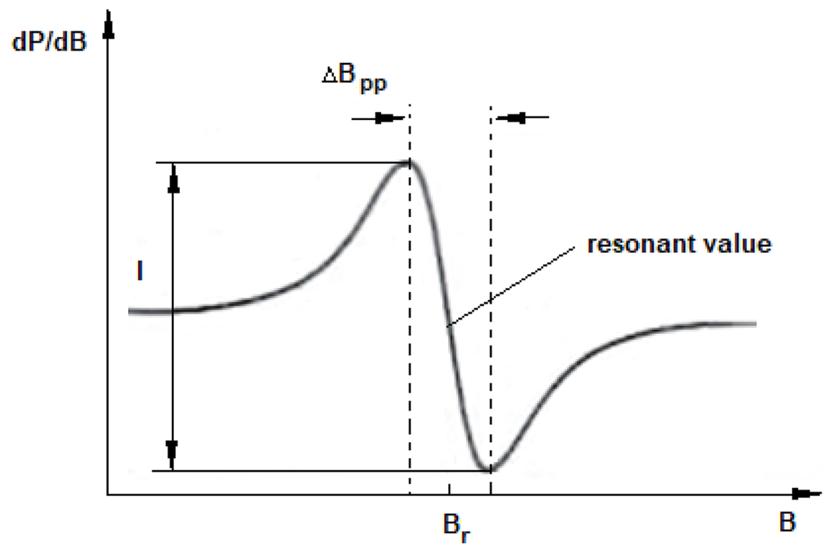

Figure 1. Parameters of the EMR line, the resonance field B_r, the width of the resonance line ΔB_{pp}, and intensity I

rusting and gives the paint its color. Pigments are fine, light-resistant coloring particles that do not dissolve in water or other solvents [27]. They can be divided into three classes: coloring pigments, anticorrosive pigments, and filler pigments. Color pigments impart color to paint, and include, for example, titanium white, carbon black, yellow ochre, carbon blue, cyanine green, and quinacridone red. Anticorrosion pigments include aluminium phosphate, zinc molybdate, and zinc dust. The filling pigments determine the properties of the film. Examples include matting pigments that affect the gloss of dried paint, functional pigments such as aluminium powder and fluorescent or phosphorescent pigments, and special pigments such as infrared reflectants and radio frequency absorbers [28]. Solvents and modifying additives are also important components of paints:

- Thinners are used to dissolve the polymer and reduce the viscosity of the binder. They are characterised by high volatility, so they easily evaporate during drying and do not become part of the paint. An additional task of thinners is to control the flow and application properties. They can also affect the stability of the paint in the liquid state. The main thinner for water-based paints is water. Oil-based paints (otherwise known as solvent-based paints) usually contain combinations of various organic solvents, such as aromatic compounds (toluene or other xylene derivatives), alcohols, or ketones [29].
- Modifying additives are ingredients added in small amounts that modify the properties of paints. Among other things, they can change surface tension, improve flow properties and pigment stability, control foaming, and prevent freezing [30].
- Emulsifiers help to form a durable and uniform emulsion, which directly translates into easier paint application on any surface [31].

Application type

Industrial paints for metals

Industrial paints have a protective function for the surfaces they cover (sunlight, precipitation, moisture, extreme temperatures, chemicals, mechanical damage, corrosion):

- Alkyd (or phthalic) – are solvent-based paints based on alkyd resins. They are resistant to mechanical damage and are often used as anticorrosive.
- Epoxy – two-component, made from epoxy resin and hardener. They form a hard and durable coating resistant to both moisture and chemicals, but also used as anticorrosive.
- Asphalt – asphalt varnishes are used for cast iron and steel surfaces.
- Acrylic contain high-quality acrylic resins in their composition. Used for metal surfaces clean, new and as a protection.
- Chloro-rubber, effectively protecting metal surfaces from corrosion, is also used as decorative. Resistant to harmful chemicals, both alkaline and acidic.
- Polyurethane – primers and topcoats. They protect against moisture and chemicals, including oil and grease.
- Polyvinyl is also used as decorative paints. Used for painting window sills and roofs.
- Silicone is used for any metal surface regardless of the type of metal.
- Nitro – based on nitrocellulose resin, flexible and durable. Resistant to harmful weather conditions [32, 33].

Car body paint:

- Urethane varnishes.
- Metallic varnishes.
- Acrylic varnishes.
- Matte, metallic, pearl, special (division by gloss).
- Division by composition:
  - clear varnish (clear) to protect the original varnish (colored) from chipping and scratches and road dirt.
  - acrylic varnish – two-part,
  - base varnish,
  - structural varnish – used for elements made of plastic,
  - water-based varnish.

1-component varnishes are formed after combining base resin with pigments and base thinner, and must additionally be protected with clear varnish. They can be divided into: base uni base color without additives, base metallic base resin + pigments + plus metallic additives, base pearl base resin + pigments + metallic-pearl additives, base xyralik base resin + pigments + metallic-pearl- xyralik additives, base special (three-layer) is a varnish in which the additional layer is tinted clearcoat.

2-component topcoats come in clear or colored versions with solvent and hardener. They do not require additional protection. These are acrylic varnishes, polyurethane varnishes, and polyacrylic varnishes. The components of these varnishes are: Lacquer + hardener + thinner in different proportions. Acrylic varnish, polyurethane varnish, polyacrylic varnish [30, 31, 34].

Characteristics of the paints

In order to assess the surface, internal structure, changes and deformations, and chemical composition, each of our paints was examined with a scanning electron microscope (SEM) FEI Quanta 3D 200i with an EDS (Energy Dispersive Spectroscopy) chemical analyser under high vacuum conditions. The accelerating voltage of 10kV was used to test the chemical composition. Microscopic images of the materials were obtained using the SE detector (secondary electrons) detector. The images obtained from the paints at a magnification of 109× to 120× are shown in Figures 2–9.

White polyurethane (car paint) – highly pigmented solvent-based polyurethane paint, chromium and lead-free. SEM with EDS analysis (Fig. 2) showed the presence of 40.44% carbon, 46.14% oxygen, 12.12% titanium and trace amounts of aluminium 1.29%. The presence of titanium increases the hardness of the coating.

Standard hardener for polyurethane products – SEM with EDS analysis showed the presence of 76.34% carbon, 23.66% oxygen. The cracks in the structure visible in the drawing were created during the taking of samples for testing.

Pigment paste – organic type dark blue (car paint). The pigment contains 71.41% carbon, 14.51% oxygen, 6.58% nitrogen, 3.85% calcium, 2.52 chlorine, and traces of silicon 0.61%, and sulphur 0.42%. In Fig. 4 the SEM image of the paint is shown. The presence of calcium increases the brittleness of the coating.

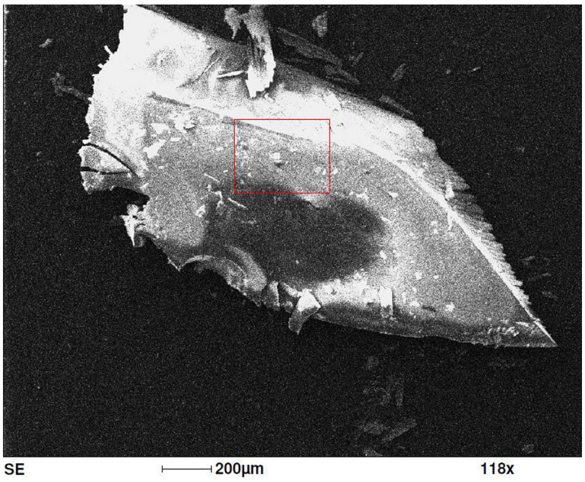

Figure 2. SEM image of white polyurethane paint

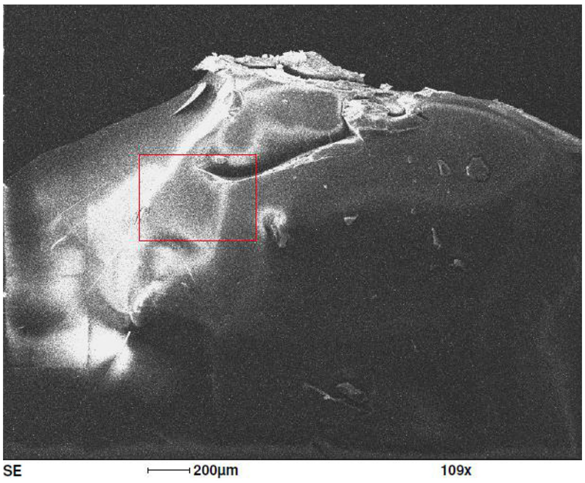

Figure 3. SEM image of standard hardener

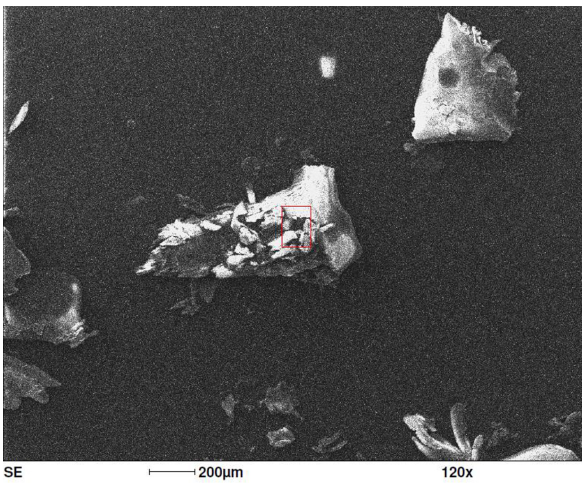

Figure 4. SEM image of dark blue pigment paste

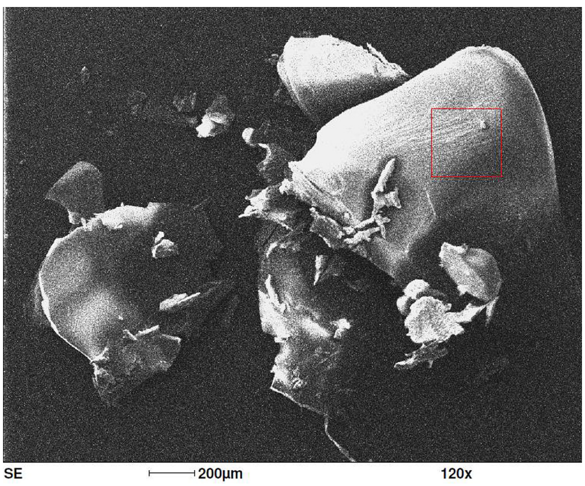

Figure 5. SEM image of pigment blue paste

Pigment paste – organic blue color type (car paint). Pigment contains 64.23% carbon, 22.61% oxygen, 10.68% nitrogen, and 2.30% calcium. In Fig. 5 a SEM image of the paint is shown.

Pigment paste – organic purple color type (car paint). The pigment contains 70.23% carbon, 25.51% oxygen, 3.28% nitrogen, and small amounts of silicon, 0.31% and chlorine, 0.67%. In Fig. 6 a SEM image of the paint is shown. The presence of silicon increases the hardness and brittleness of the coating.

Figure 7 shows SEM image of the silver metallic base coat (car paint) obtained by SEM. The lacquer contains 63.94% carbon, 20.77% oxygen, 13.33% aluminium, 1.37 silicon, and trace amounts of magnesium of the order of 0.59%. The presence of silicon makes the coating more brittle, and the brighter surface fragments visible in Fig. 7, indicate the presence of aluminium.

Black anticorrosion paint for metal – one-component paint for anticorrosive and decorative painting of ferrous metals (steel, cast iron), protecting against moisture and preventing rust. The paint contains 73.95% carbon, 17.83% oxygen, 5.62% nitrogen, 1.40% silicon, and trace amounts of calcium 0.78%. The SEM image (Fig. 8) shows the brittleness of the structure caused by the addition of silicon.

Ground enamel – primer for white metallic surfaces. It contains xylene and n-butanol. SEM with EDS analysis (Fig. 9) showed the presence of 58.41% carbon, 32.84% oxygen, 6% titanium, 0.7% calcium and trace amounts not exceeding 0.6% magnesium, aluminium, silicon, phosphorus, lead, and zinc. The titanium present in the paint will affect the curing of the material.

EMR measurements

EMR measurements of selected paints and their components (hardener and thinner) were

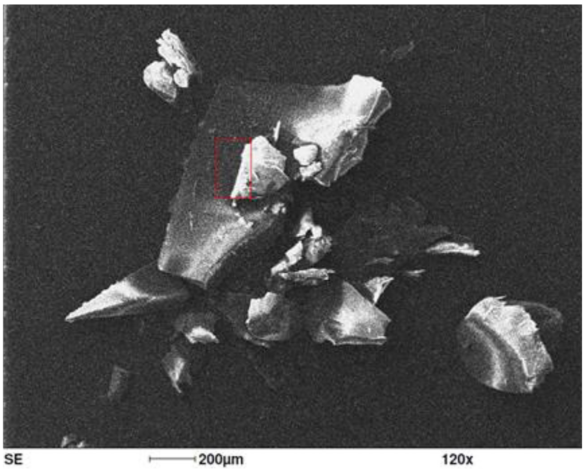

Figure 6. SEM image of purple pigment paste

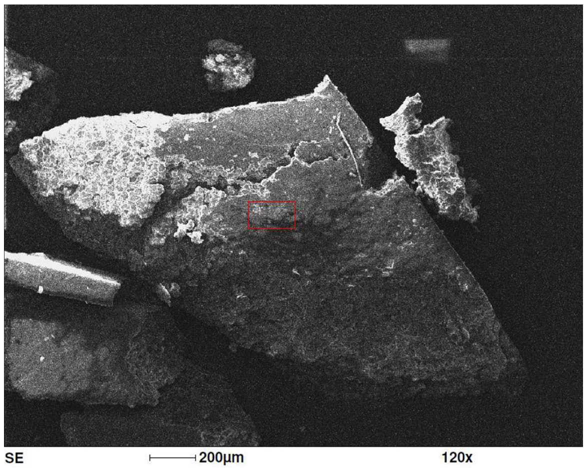

Figure 7. SEM image of the metallic base coat

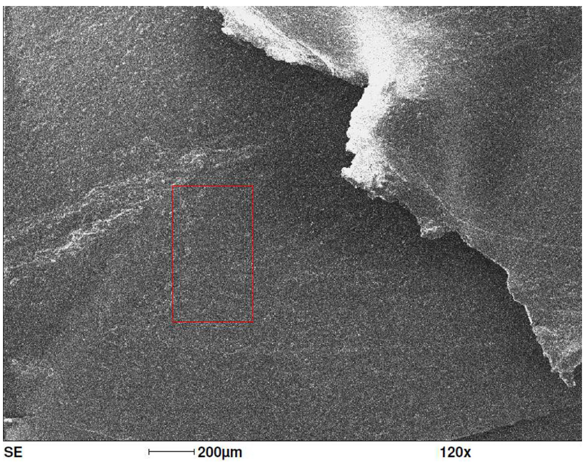

Figure 8. SEM image of black anticorrosion paint for metal

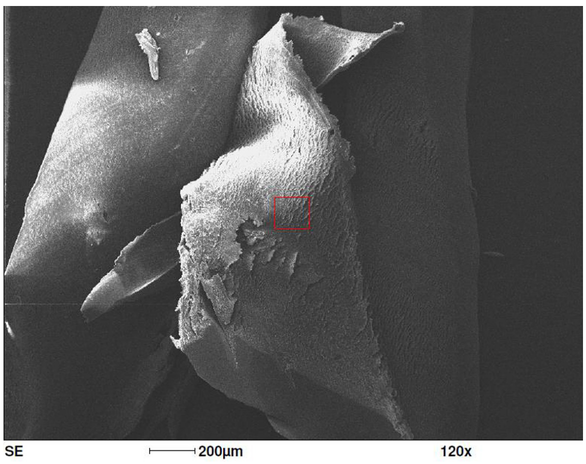

Figure 9. SEM image of ground enamel

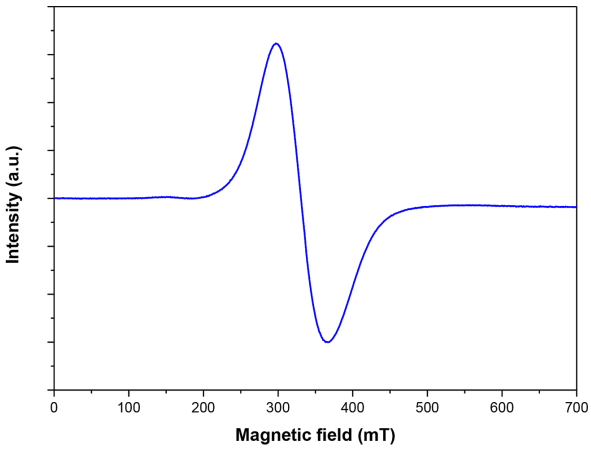

Figure 10. EPR spectra of white polyurethane paint

performed. The parameters of the EMR line were determined, such as intensity *I*, peak-to-peak width ΔB_{pp}, and the value of the resonant field H_r (according to Fig. 1). The determined values are summarised in Table 1.

1) White polyurethane (car paint)

Figures 10 and 11 show the EMR spectra of the white polyurethane paint. After the addition of thinner and hardener, a reduction in spectral intensity is observed compared to pure paint (Fig 10). The determined value of g_{ef} = 2.033 (see Table 1) is typical for typical free radicals.

2) 2K acrylic paint

Figure 11 shows the EMR spectra of 2K acrylic paints of three different pigments (dark blue, blue, and purple). Two separate lines are observed (this is most evident in the example of the dark blue pigment, where a very narrow line is seen in a field around 350 mT, and a wider line in a field around 340 mT. The value of the g_{ef} changes little between the pigments, while the intensity changes the most (see Table 1).

3) Metallic basecoat

Figure 13 shows the EMR spectrum of the metallic silver base coat. The intensity of the

Table 1. Overview of EMR line parameters

Paints	*I* (a.u.)	ΔB_{pp} (mT)	B_r (mT)	g_{ef}
White polyurethane (car paint)	12.466	69.39	331.16	2.033
White polyurethane with hardener (higher field)	0.0972	88.87	302.25	2.23
White polyurethane with hardener (lower field)	0.0254	45.46	156.98	4.29
White polyurethane with thinner	0.0421	85.62	179.03	3.76
Organic pigment paste (dark blue)	0.285	1.03	351.39	2
Organic pigment paste (blue)	1.649	5.81	342.57	2.052
Organic pigment paste (purple) r	0.585	7.86	341.9	2.055
Anticorrosion black paint for metal (narrow line)	3.445	1.02	336.09	2
Anti-corrosion black paint for metal (broad line)	4.179	28.03	323.44	2.079
Ground enamel – primer for metallic surfaces white	16.026	18.11	324.47	2.075

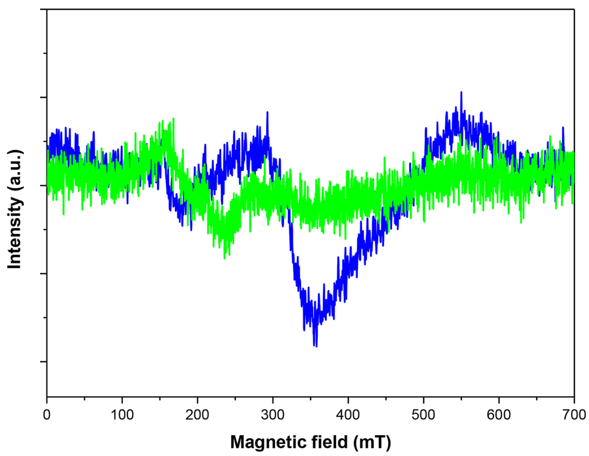

Figure 11. EPR spectra of white polyurethane with hardener (blue line) and white polyurethane with thinner (green line)

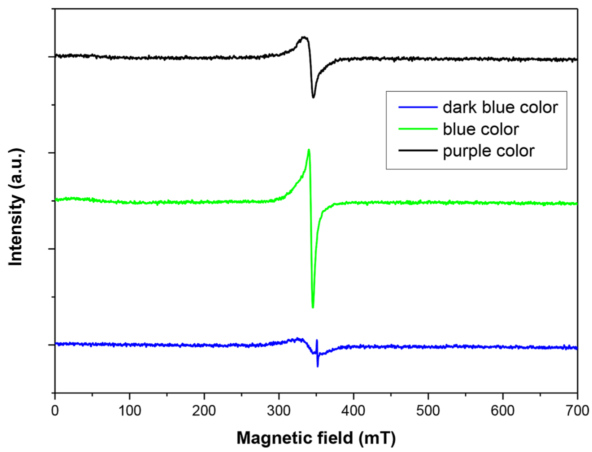

Figure 12. EPR spectra of 2K acrylic paint. Pigment paste: – dark blue (blue line), blue (grey line), purple (orange line)

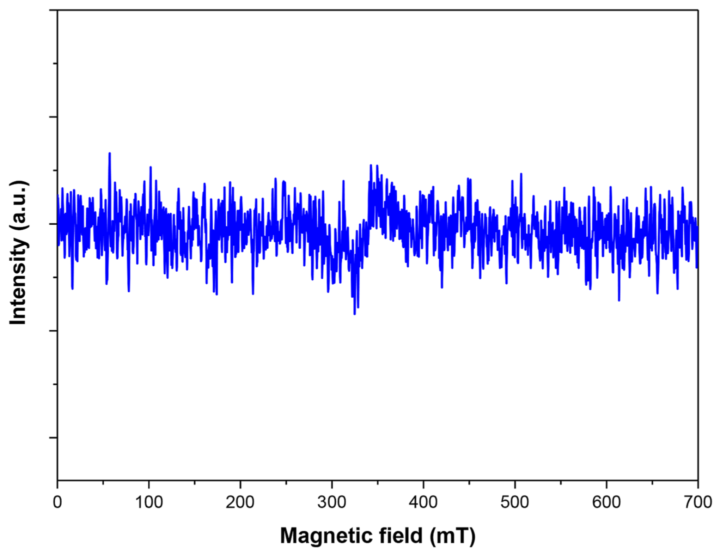

Figure 13. EPR spectra of metallic silver basecoat

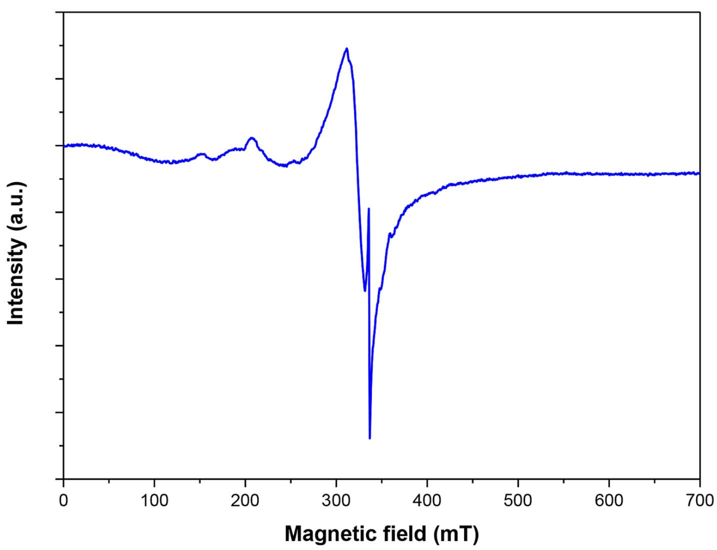

Figure 14. EPR spectra of anticorrosion black paint for metal

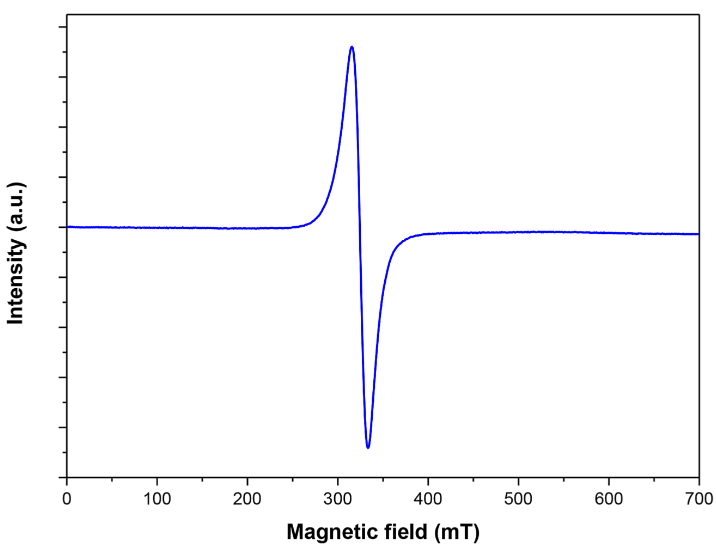

Figure 15. EPR spectra of ground enamel

signal is very weak, two weak lines can be seen, the origin of which is probably from the ions Ag^0 ($4d^{10}5s^1$) and/or Ag^{2+} and Ag^0 ($4d^9$) [9, 32] (while Ag + is inactive in the EMR signal).

4) Black anticorrosion paint for metal

Figure 14 shows EPR spectra of black anticorrosion paint for metal. The spectrum shows much more complexity compared to the previous ones, but the main feature of the spectrum shown is the similarity (at higher line intensities) to 2K acrylic paint, a dark blue pigment (Fig. 12). Two main lines are visible, a narrow line in a field of about 330 mT with $g_{ef} = 2$, and a wider line in a field of about 320 mT with $g_{ef} = 2.079$ (see Table 1).

5) Ground enamel – primer for white metallic surfaces. Contains xylene and n-butanol.

Figure 15 shows the EPR spectra of ground enamel. A single line with $g_{ef} = 2.075$ is visible. The spectrum is similar to the EPR spectra of white polyurethane paint (Fig. 10) but a shift of the line toward lower values of the magnetic field is observed.

CONCLUSIONS

In the work, EMR measurements of eight selected paint coatings were carried out. To determine their chemical composition, each of them was examined under high vacuum conditions using a scanning electron microscope (SEM). Measurements showed the diversity of the chemical composition of the elements included in the individual paints and their components.

The best and most sensitive method for studying paint components for degradation is electron magnetic resonance, which allows easy identification of pigments, and ability to control the correct selection of individual components of the finished color. The aim of the work was to develop tests of paint for the durability of the protective coating based on free radical trapping, including the detection of potential degradation centres, the possibility of eliminate a paint component that reduces color durability, and thus the possibility of selecting components for paint quality.

We successfully calculated the g-factor with high accuracy, as well as all EMR line parameters. Further on, it is planned by fitting simulations in MATLAB/Easyspin to calculate the full g-factor tensor. Thanks to EMR tests, it is possible to eliminate the paint component that reduces color durability and select components in terms of paint quality. The topic requires further work and will be continued.

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