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HAP:CO AS TUNABLE VIS-NIR REFLECTIVE PIGMENT

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Abstract: *Radar-absorbent materials, used in stealth technology for defense aircrafts, vehicles, satellites, etc. from radar detection, are commonly based on graphite or semiconductive particles embedded in a polymer matrix. In this study, we employed* Co^{2+} *ion-substitution to improve Vis-NIR reflectivity of hydroxyapatite (*$Ca_{10}(PO_4)_6(OH)_2$*, HAP) powder. HAP:Co with nominally 5 at.% of Co was prepared with hydrothermal processing of a precipitate. Synthesized powder was characterized by XRD, Raman and ATR–FTIR spectroscopy, FE–SEM and TEM. Thermal stability of HAP:Co powder was examined by simultaneous TG-DTA analyzer. To modify its optical properties and obtain powders with a varietty of color tone, the HAP:Co powder was calcined at 800, 1000, and 1100 °C, in an air atmosphere, for 1 hour. Afterward, the calcined particles were used to prepare composites with poly(vinyl butyral), (PVB); the concentration range was 1 wt.% of the HAP:Co in PVB. The composite coatings, in the form of thin films on glass, were prepared by the solvent-casting technique, using ethanol as a fast evaporating solvent. Firstly, the HAP:Co particles were dispersed in ethanol, then PVB was added (Mowital B30H) and dissolved. To evaporate the solvent before spectrophotometric measurements, the coatings on glass were dried at room temperature for 72 hours. To comprehend optical properties of the coatings, diffuse reflection, transmission, and color coordinates were determined. We found that calcined HAP:Co particles have potential to be used in the formulation of coatings for camouflage protection.*

Keywords: *HAP, cobalt, coatings, Vis-NIR reflectivity, corrosion.*

1. INTRODUCTION

The need for better camouflage to protect personnel and equipment from observation by enemy forces has become an essential part of new materials research in the military industry. What's more, the main goal is rather to obtain material with multispectral features, for different kinds of military applications, than just for camouflage application [1]. Development of non-toxic, environment friendly and reasonable priced material with tunable emissivity and excellent thermochromic properties is of great significance to improve combat capability for military equipment [2]. During the years different appropriate materials have been developed and tested. Among them nanoparticles and nanotubes of tungsten disulphide [3], cobalt doped zinc oxide [2], TiO_2 and Al_2O_3 [4] should be mentioned.

The aim of this research was to examine camouflage properties of hydroxyapatite-based ($Ca_{10}(PO_4)_6(OH)_2$, HAP) pigments since it is known that HAP is a non-corrosive material, non-toxic *via* ingestion and inhalation, beside, due to band gap at 220 nm it can absorb UV irradiation. Since calcium hydroxyapatite is white powder, a partial ion substitution of calcium ions by cobaltous ones was employed to gain powder chromaticity. Further variety of colors was attained by annealing of HAP:Co powder at different temperatures in range between 400 and 1200 °C. In order to observe spectrophotometric behavior and anticorrosion potential of HAP:Co pigments they were incorporated in a transparent polymer coating of poly(vinyl butyral), PVB. Due to its very good adhesion to different surfaces, such as metals, ceramics and other inorganic materials, this thermoplastic elastomer is often used in coatings. PVB finds application in various materials: in laminated glass, temporary binders, inks, paints, primers, laminated composite materials, binders for reflective sheet and binders for magnetic media, as a toughening agent for modification of other resins, like phenolic and epoxy [5-13]. PVB shows good toughness, flexibility, impact resistance, good tensile strength and elasticity. Besides these mechanical advantages, it is optically transparent, colorless, non-toxic, non-corrosive, and resistant to freezing and aging. Due to all above listed properties, PVB was chosen as a convenient polymer for the preparation of protective coatings with the addition of the HAP:Co particles.

2. EXPERIMENTAL

2.1. Samples preparation

HAP powder with nominally 5 at.% of cobalt were prepared by hydrothermal processing of a precipitate. Synthesized powder was additionally annealed in a tube furnace at 400, 800, 1000, 1100 and 1200 °C, in an air atmosphere, for 1 hour. Throughout the paper, the synthesized powder is designated as HAP:Co, while the numbers denote annealing temperature.

To prepare samples in the form of transparent coatings on glass and coatings on metal plates the following raw materials were used: HAP:Co particles annealed at different temperatures (Figure 1), fine-grained powder PVB Mowital B30H (Kuraray GMBH) and ethanol (Zorka, Šabac).

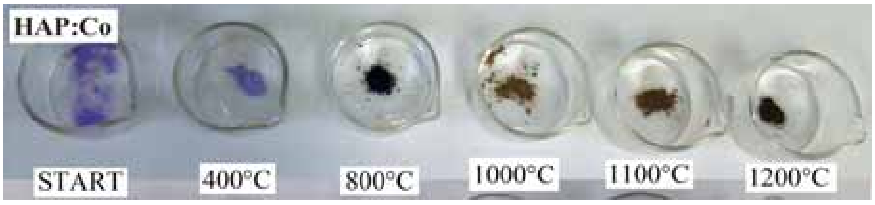

Figure 1. HAP:Co particles annealed at different temperatures in temperature range from 400 to 1200 °C.

PVB/HAP:Co coatings were prepared in the following procedure:

1) Since PVB is soluble in organic solvents, such as alcohols, ethanol was used to dissolve PVB powder in concentration 10 wt%.

2) HAP:Co particles in concentration of 1 wt.% were dispersed in solution of PVB in ethanol using ultrasonic probe Badelin SonoPuls during 15 min at 30 W.

3) Coatings on glass plates (40 mm × 100 mm) were formed by the solvent-casting technique: dissolved PVB with and without HAP:Co particles was cast over the glass and left for 72 hours so the solvent may evaporate completely at the room temperature. Solid thin films were formed on the glass plates (Figure 2).

4) Standard steel plates (5 mm × 20 mm) were half-dipped (immersed) into the solutions so after drying, only one half of the plate was coated with film of PVB/HAP:Co.

Beside, referent samples of pure PVB were prepared as well.

Figure 2. PVB/HAP:Co thin films on the glass plates.

2.2. Samples characterization

X-ray diffraction (XRD) data were collected using a Philips PW-1050 with Cu K$\alpha_{1,2}$ radiation (40 kV, 20 mA); 2θ range 10–90°, step of 0.05° and a counting time of 5 s per step. The room-temperature µ-Raman spectrum was collected in the frequency interval of 50–1800 cm^{-1} (DXR Raman microscope, Thermo Scientific) with a resolution of 4 cm^{-1}. The 532 nm line of a diode-pumped solid-state high-brightness laser was used as the excitation source. Fourier-transform infrared (FT–IR) spectra were recorded in the wavenumber region of 400–4000 cm^{-1}, with a resolution of 4 cm^{-1} using a Thermo Scientific™ Nicolet™ iS™10 FT–IR Spectrometer equipped with an attenuated total reflectance (ATR) accessory. A field emission scanning electron micrograph (FE–SEM) was recorded at Ultra plus, Carl Zeiss, Germany, while for a transmission electron micrograph (TEM) we used JEOL 2100, operating at 200 kV. A simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) was performed on a Setsys (SETARAM Instrumentation, Cailure, France) instrument, in the temperature range between 20 and 1200 °C under an air flow, in an Al_2O_3 pan at a constant heating rate of 10 °C min^{-1}

Diffuse reflectance, transmission and color coordinates of thin film coatings on glass plates were measured using the UV/VIS/NIR spectrophotometer with an integrated sphere (UV 3600, Shimadzu, Japan) [14]. For diffuse reflectance and transmittance measurements samples were measured in the visible and near-infrared regions of the electromagnetic spectrum (500-1600 nm) using UV Probe programme package, while color coordinates were measured in the visible range of the electromagnetic spectrum (380-780 nm) using Color program package with 10° and D65 observer [14]. Color coordinates were determined in the CIE Measurement Lab space. Samples were placed horizontally in the sample compartment of the device, which has a 2 cm aperture diameter.

The corrosion properties of thin film coatings on metal plates were determined using a three electrode cell. The samples were used as a working electrode, while platinum and saturated calomel were used as counter and reference electrodes, respectively. The electrochemical corrosion studies was carried out in 3.5% NaCl solution using potentiostat / galvanostat / FRA Vertex (Ivium Technologies) in potential range from -0.8 to -0.2 V vs. SCE at a scan rate of 10 $mV \cdot s^{-1}$. The measurements were done at room temperature.

3. RESULTS AND DISCUSSION

3.1. Powders characterization

The amount (in wt.%) of calcium and cobalt in the synthesized powder was determined by ICP emission spectroscopy analysis, with an error of ± 1 and ± 0.1, respectively. The number of Ca and Co atoms (in at.%, in relation to 10 atoms of calcium/cobalt in the HAP:Co) in the unit cell of HAP:Co was calculated to be 9.57 and 0.43, respectively; the stoichiometric formula is $Ca_{9.57}Co_{0.43}(PO_4)_6(OH)_2$.

Fig.3 shows XRD pattern of synthesized HAP:Co powder. All diffraction maximums correspond to those of single-phased hydroxyapatite (JCPDS Card No. 09–0432), beside, indicate a low crystallinity and small crystallite size. According to the XRD results, cobalt cations were incorporated in Ca^{2+} crystallographic positions in HAP structure [15,16]. This statement is also supported by Raman measurement. In the Raman spectrum of HAP:Co powder, presented in Figure 4, four bands appeared and can be assigned as: O–P–O doubly degenerated bending mode (ν_2) at 430 and 448 cm^{-1}, O–P–O triply degenerated bending mode (ν_4) at 582, 594 and 609 cm^{-1}, nondegenerated P–O symmetric stretching mode (ν_1) at 960 cm^{-1}, and triply degenerated P–O antisymmetric stretching mode (ν_3) at 1031, 1048, and 1080 cm^{-1}. All the Raman bands of HAP:Co coincide with those of pure HAP [15,16].

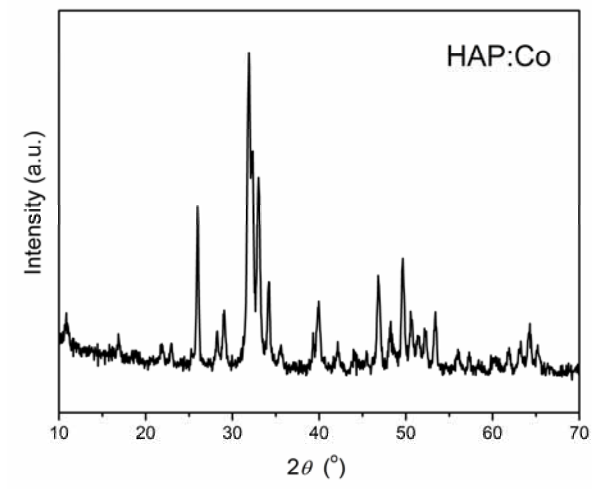

Figure 3. XRD pattern of HAP:Co powder.

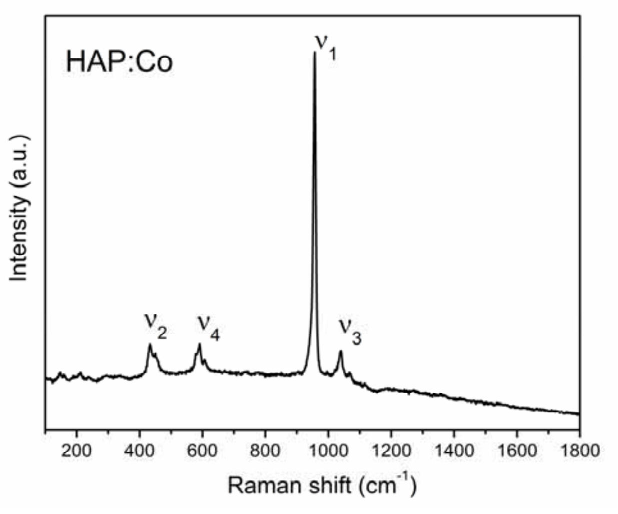

Figure 4. Raman spectrum of HAP:Co powder.

ATR/FT–IR spectroscopy was used to identify functional groups on the surface of HAP:Co particles. FT–IR spectrum of HAP:Co, presented in Figure 5, shows four phosphate (PO_4^{3-}) modes typical for apatite: double degenerative bending vibration (ν_2) characterized by a weak band at 473 cm^{-1}, double degenerative bending vibration (ν_4) with bands at 557 and 600 cm^{-1}, band at 962 cm^{-1} due to symmetric stretching vibration (ν_1), and a triple degenerative asymmetric stretching mode (ν_3) characterized by a strong, complex band in the 1000–1150 cm^{-1} region. The vibrational band of the OH libration mode appears at 631 cm^{-1}.

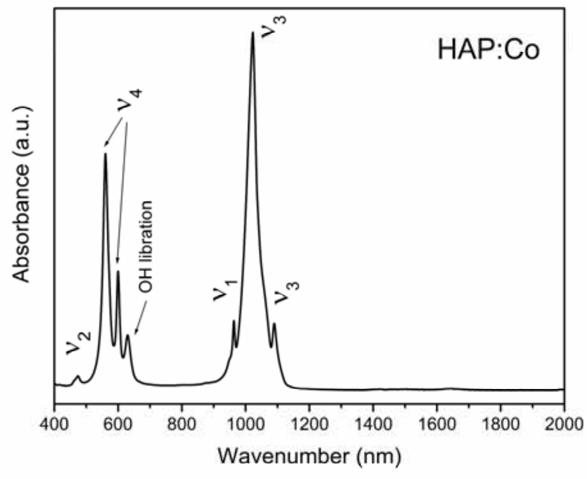

Figure 5. FT–IR spectrum of HAP:Co powder.

Therefore, XRD, Raman and FTIR spectroscopy showed that the synthesized HAP:Co powder is pure hydroxyapatite phase, without other calcium phosphate or cobalt oxide phases and impurities.

The morphology of HAP:Co particles was analyzed using field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) techniques. FE-SEM (Figure 6) and TEM (Figure 7) micrographs reveal that synthesized HAP:Co is uniform powder, consisting of elongated particles with sizes up to 100 nm and with negligible extent of agglomeration.

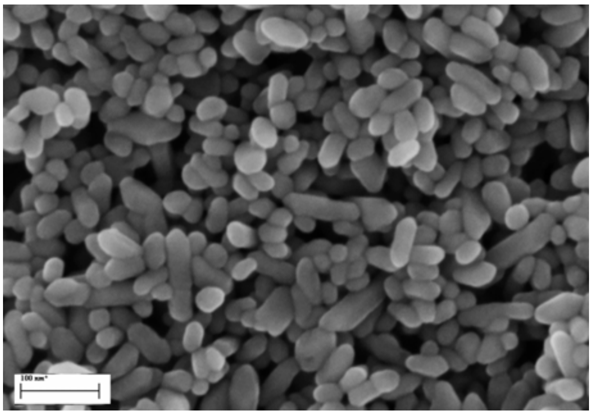

Figure 6. FE-SEM micrograph of the HAP:Co powder.

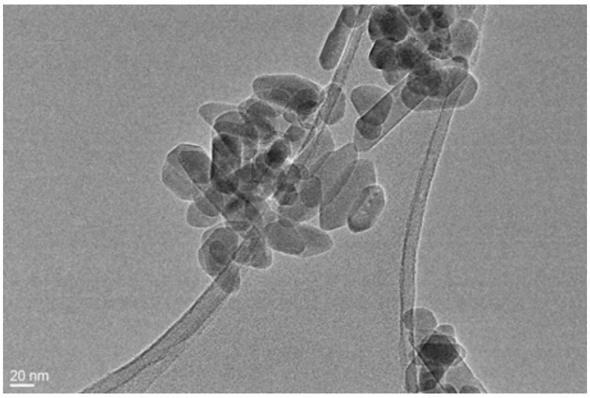

Figure 7. TEM micrograph of the HAP:Co powder.

Our intention was to modify optical properties and vary the color tone of hydrothermally synthesized HAP:Co powder *via* additional annealing at different temperatures. For that purpose, before annealing, we investigated a thermal stability of HAP:Co powder by simultaneous TG/DT analysis. TG/DTA plots of HAP:Co between 20 and 1200 °C are presented in Figure 8. Several steps of mass loss and corresponding thermal response can be observed from Fig. 8. The weight loss between 30 and 180 °C, of about 1.3 wt%, occurs due to the loss of surface water, and it is accompanied by a small endothermic feature on the DTA curve. The weight loss between 180 and 560 °C was due to the loss of lattice water, while a neglected weight loss, of 0.3 wt%, between 560 and 760 °C is due to evaporation of incorporated carbonates. Further heating is accompanied with constant dehydroxylation that yield phase transformation of HAP to β-TCP. The total mass loss of approximately 3.9 wt% suggests thermal stability of HAP:Co to 1200 °C.

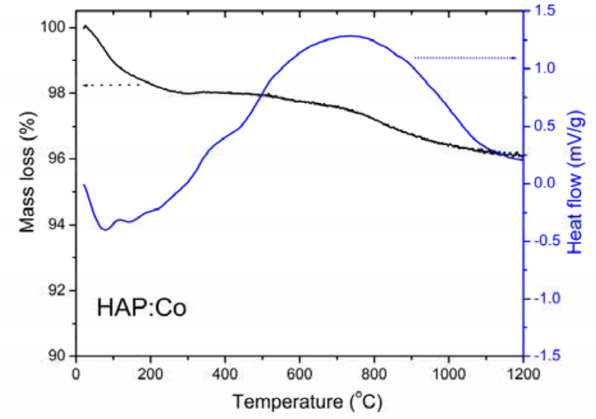

Figure 8. TG and DSC plots of the HAP:Co powder.

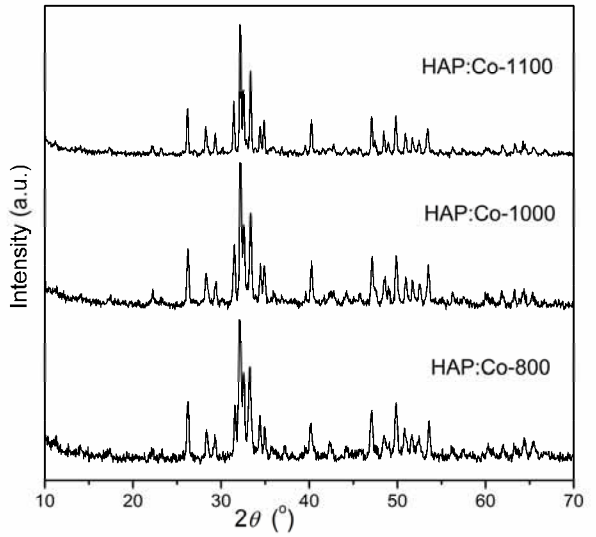

Figure 9. XRD patterns of annealed HAP:Co powders.

Since thermal stability was confirmed, HAP:Co powder was annealed at several temperatures in range between 400 and 1200 °C. As can be observed from Figure 1, annealing of HAP:Co at different temperature gives pigments with a variety of colors. In this paper we choose to present results for black, dark-green and brown pigments, i.e. HAP:Co samples annealed at 800, 1000 and 1100 °C, respectively. XRD patterns of samples calcined at 800, 1000 and 1100 °C are presented in Figure 9. Detailed analysis of XRD patterns shows that beside HAP crystal phase some amount of β-TCP is present in all annealed samples. This finding was confirmed by FTIR spectroscopy (Figure 10) and it is in accordance with results of TG-DTA which implicate dehydroxylation process above 760 °C.

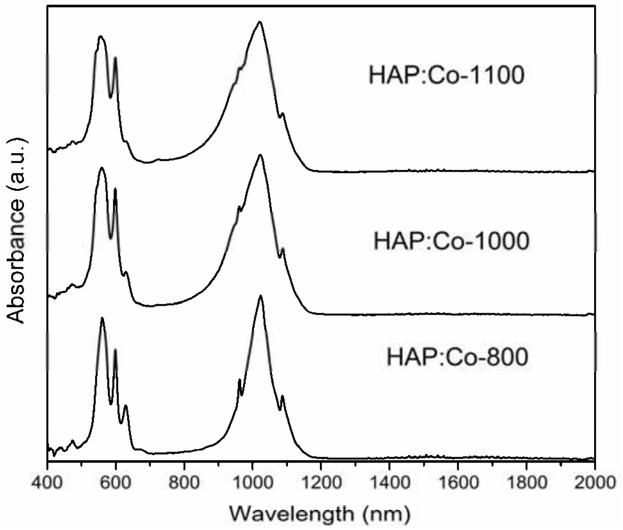

Figure 10. FTIR spectra of annealed HAP:Co powders.

3.2. Coatings characterization

Reflectance and transmission properties of PVB and PVB/HAC:Co coatings on glass were investigated in wavelength range between 500 and 1600 nm. The results of reflectance and transmission measurements are presented in Figures 11 and 12, respectively. As can be seen from Fig. 11, PVB/HAP:Co coatings prepared with different HAP:Co pigments have similar diffuse reflectance spectra. What's more, the diffuse reflection values are similar to those of the black shade and in accordance with the Serbian Military Standard [17]. However, the transmittance values are somewhat questionable because they show increase compared to regular glass [9].

Figure 11. Diffuse reflectance spectra of the PVB/HAP:Co coatings on glass.

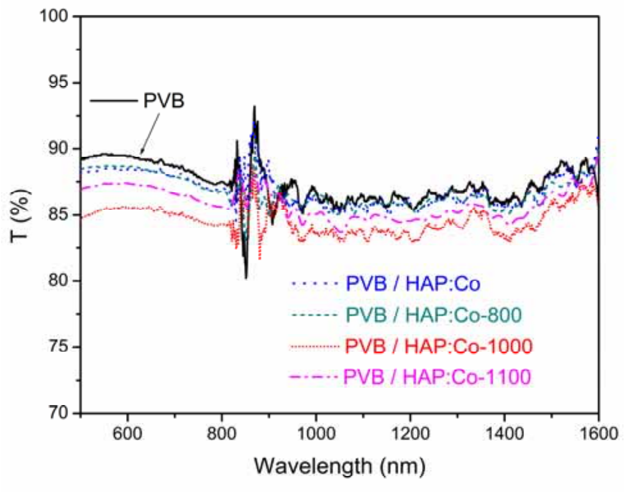

Figure 12. Transmittance spectra of the PVB/HAP:Co coatings on glass.

After all, color coordinates were measured, too. CIE Lab system color coordinates measured for pure PVB and PVB/Co:HAP coatings on glass are listed in Table 1. Considering the fact that all the powders obviously have different colors and that PVB-film samples are all transparent and almost colorless, the ΔE difference which indicates the difference in color shades was not of the interest for determination. Therefore, we analyzed the CIE Lab system color coordinates values alone.

Table 1. Color coordinates defined in CIE Lab system.

Samples	L*	a*	b*
PVB	10.37	-0.23	-1.78
PVB / HAP:Co	15.03	-0.40	-3.00
PVB / HAP:Co-800	12.53	-0.30	-1.77
PVB / HAP:Co-1000	18.29	-0.47	-0.99
PVB / HAP:Co-1100	13.64	-0.35	-1.14

The most interesting results were observed for the PVB/HAP:Co-1000 coating. It is intriguing that values for L* and b*coordinates are the highest and for a* coordinate is the lowest. These findings show that HAP:Co particles annealed at 1000 °C have promising camouflage properties but have to be further analyzed. Increase in concentration of particles dispersed in PVB and IR thermography could give more insight for more specific conclusion.

Corrosion properties of HAP:Co, HAP:Co-800, HAP:Co-1000 and HAP:Co-1100 were tested and potentiodynamic polarization curves are shown in Figure 13. Determined corrosion potential (*E*corr) of HAP:Co, HAP:Co-800, HAP:Co-1000 and HAP:Co-1100 are find to be -0.54, -0.40, -0.55 and -0.50 V vs. SCE, respectively. The corrosion study shows that, in 3.5% NaCl solution, the best corrosion resistance has the PVB coating prepared with HAP:Co pigment obtained by annealing at 800 °C.

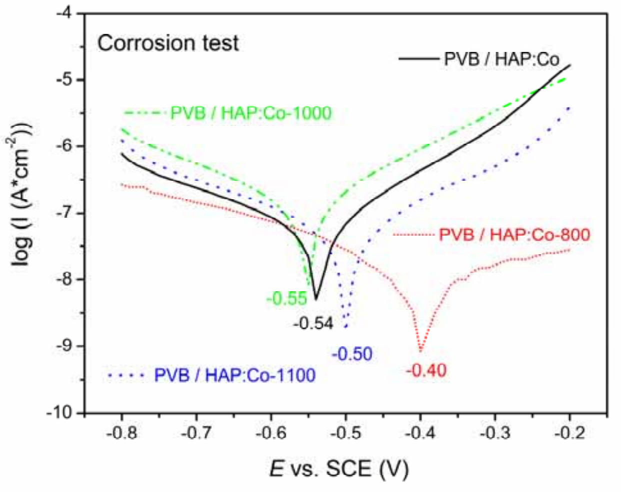

Figure 13. Potentiodynamic polarization curves of the PVB/HAP:Co coatings on steel plates, measured in 3.5% NaCl solution.

5. CONCLUSION

The present study revealed the possibility that the color of hydrothermally prepared HAP:Co powder can be easily modified by annealing in air atmosphere. The annealing of HAP:Co in temperature range from 400 *via* 800 to 1200 °C yields lilac, dark-green and dark-brown pigments, respectively. Variety of colors is determined by phase composition, position of cobaltous cation in the crystal structure of hydroxyapatite and stoichiometry. As important for bio-mimetic camouflage, dark-green and dark-brown HAP:Co pigments were used in combination with PVB for preparation of thin coatings on glass and metal plates and their optical properties were tested. It was shown that the diffuse reflection values are similar to those of the black shade and in accordance with the Serbian Military Standard. According to obtained results, HAP:Co-1000 pigment has promising camouflage properties on glass while HAP:Co-800 shows the best anticorrosion properties on metal plates. Thus, it is shown that PVB coatings with a small weight percentage of cobalt-hydroxyapatite pigments can have different camouflage and anticorrosion features.

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References

[1] Kumar, N., Dixit, A., *Nanotechnology for Defense Applications*, Cham, Switzerland, Springer Nature Switzerland AG, 2019.

[2] Zhang, B., Xu, C., Xu, G., Xiang, S., Zhu, Y., "Thermochromic and infrared emissivity characteristics of cobalt doped zinc oxide for smart stealth in visible-infrared region", Optical Materials, 86 (2018) 464–470.

[3] Lazić, D. S., Simić, D. M., Samolov, A. D., Jovanović D., "Properties of standard polymeric and water-based coatings for military camouflage protection with addition of inorganic fulerene-like tungsten disulphide (IF-WS_2) nanoparticles", Scientific Technical Review, 67 (1) (2017) 38-44.

[4] Jafari, H., Khajeh Mehrizi, M., Fattahi, S., "The effect of inorganic nanoparticles on camouflage properties of cotton/polyester fabrics", Progress in Color, Colorants and Coatings, 9 (2016) 29-40.

[5] Hooper, P. A., Blackman, B. R. K., Dear, J. P., "The mechanical behaviour of poly(vinyl butyral) at different strain magnitudes and strain rates", Journal of Materials Science, 47 (2012) 3564-76.

[6] http://www.kuraray.eu/en/produkte/product-groups/polyvinyl-butyral.

[7] Simić, D. M., Stojanović, D. B., Dimić, M., Totovski, Lj., Brzić, S., Uskoković, P. S., Aleksić, R. R., "Preliminary analysis of the possibility of preparing PVB/IF-WS_2 composites. Effect of nanoparticles addition on thermal and rheological behavior of PVB", Scientific Technical Review, 66 (4) (2016) 15-21.

[8] Simić, D., Stojanović, D. B., Kojović, A., Dimić, M., Totovski, Lj., Uskoković, P. S., Aleksić, R., "Inorganic fullerene-like IF-WS_2/PVB nanocomposites of improved thermo-mechanical and tribological properties", Materials Chemistry and Physics, 184 (2016) 335-344.

[9] Samolov A., Simić D., Totovski Lj., "Spectrophotometric properties of PVB/WS_2 thin films", Proceedings, 8th International Scientific Conference on Defensive Technologies OTEH 2018, Belgrade, 11-12 October 2018: 416-420.

[10] McKeen, L. W., *Polyolefins, Polyvinyls, and Acrylics*, in Plastics Design Library, ed. Laurence W. McKeen, Permeability Properties of Plastics and Elastomers (4th edition), William Andrew Publishing, 2017, pages 157-207.

[11] Froli, M., Lani, L., "Adhesion, creep and relaxation properties of PVB in laminated safety glass", Glass Performance Days 2011, pp.218-221. Tampere, Finland.

[12] Iwasaki, R., Sato, C., Lataillade, J. L., Viot, P., "Experimental study on the interface fracture toughness of PVB (polyvinyl butyral)/glass at high strain rates", International Journal of Crashworthiness, 12 (3) (2007) 293-298.

[13] Kwakernaak, A., Hofstede, J., Poulis, J., Benedictus, R., *Improvements in bonding metals for aerospace and other applications*, In M.C. Chaturverdi (Ed.), Welding and joining of aerospace materials, (2012) 235–287, Woodhead Publishing.

[14] Shimadzu, UV 3600 Tutorial, 2009.

[15] Stojanović, Z., Veselinović, Lj., Marković, S., Ignjatović, N., Uskoković, D., "Hydrothermal synthesis of nanosized pure and cobalt-exchanged hydroxyapatite", Materials and Manufacturing Processes, 24 (10) (2009) 1096-1103.

[16] Veselinović, Lj., Karanović, Lj., Stojanović, Z. Bračko, I., Marković, S., Ignjatović, N., Uskoković, D., "Crystal structure of cobalt-substituted calcium hydroxyapatite nano-powders prepared by hydrothermal processing", Journal of Applied Crystallography, 43 (2010) 320-327.

[17] SORS 7511/11 Diffuse reflection of camouflage materials in UV/VIS/NIR region of EM spectrum (In Serbian).