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Black coatings: a review

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Abstract

Black coatings are widely used in numerous applications e.g., decorative coatings, solar panels, optical instruments. The films are mostly prepared by liquid phase deposition or vapor phase deposition. In this paper we review the techniques of deposition and the properties of the most important black coatings. Optical properties are particularly presented and discussed.

Keywords: Black, coatings, solar, panels, decorative.

1-Introduction

A black object is made from a material that absorbs all incoming light (all the colors of the visible spectrum). In reality objects which look black reflect always some light and consequently the ideal black object does not exist. There is no material on Earth that absorbs 100% of light at all angles and over all wavelengths.

In the field of surface treatments, black coatings are widely used for decorative or solar absorbing functions. The films deposited should have high mechanical properties (resistance to wear), a good resistance to corrosion and, for solar absorbing application, an ultra high absorbance capacity.

Materials used as solar panel must be capable of absorbing, storing and transmitting energy from the sun to a transport medium (generally water or water-based fluid coolant) with minimum thermal losses. Consequently, for this application, one must maximize absorption ($\alpha > 0.95$) and minimize emittance ($\varepsilon < 0.10$) of the used material. In addition, as transmission is usually by conduction, a good thermal conductivity is necessary (1).

Black coatings used for both decorative and solar absorbing functions are mostly prepared by liquid phase deposition or vapor phase deposition. Black nickel and black chromium are the most important electrodeposited materials whereas the films elaborated by vapor phase deposition include mainly titanium alloys and carbon based materials.

The aim of this paper is to review both method of preparation and properties of the main black coatings.

2- Black coatings obtained by liquid phase deposition

Black nickel (2, 3), black zinc (4), black chromium (5), black phosphate (6) and black molybdenum (7, 8) based alloys are the most known black coatings obtained by liquid phase deposition. Among all, nickel based alloys and chromium based alloys have been particularly studied and are widely used for their efficient conversion of solar radiation into thermal energy.

2-1. Nickel and nickel based alloys

The black nickel coatings may be prepared by electroless (9) or electroplating techniques onto various metal substrates (10-13). Chemical conversion of a zinc-coated substrate is another way to obtain black nickel coatings (14-16).

Black nickel coatings have been prepared by chemical conversion of zinc-coated aluminum in the experimental conditions shown in Table 1 (17). The authors have studied the influence of the surface morphology of the base metal on the optical properties of the final coatings. They reported that the black nickel film prepared on a zinc-coated electropolished aluminum showed absorbance value of the order of 0.90 to 0.94 and emittance ranging from 0.08 to 0.15.

<i>Bath constituents and parameters</i>	<i>Quantity (g/l)</i>
NiSO ₄	75
Ni(NH ₄) ₂ SO ₄	45
ZnSO ₄	37.5
NaSCN	15

Table 1: Bath composition for chemical conversion of a zinc-coated aluminum to obtain black nickel coating (17).

Electrodeposited black nickel may be prepared using sulfate, chloride or sulfate and chloride based baths (Table 2) (18-19). The black color is due to the formation of ZnS and NiS particle in the films (20). Unfortunately, the obtained coatings do not present enough resistance to high humidity at elevated temperatures. To overcome this inconvenience more stable black coatings have been electrodeposited in nickel and sodium chloride aqueous solution (21-23). A solar absorptance and a thermal emittance of 0.96 and 0.10 respectively were reported by the authors and confirmed in another study (24). In this latter work the author used the bath composition and operating conditions shown in Table 2 to deposit a nickel black coating on aluminum and copper substrates. Using quite similar experimental conditions than in (24), black nickel has been electrodeposited on stainless steel substrate (25) (Table 2). The solar absorptance and thermal emittance values obtained were 0.91 and 0.1 respectively.

<i>Bath constituents and parameters</i>	<i>Quantity (g./l)</i>	<i>Quantity (g/l)</i>	<i>Quantity (g/l)</i>	<i>Quantity (g/l)</i>	<i>Quantity (M)</i>
NiSO ₄ , 6 H ₂ O	100				0.63
NiCl ₂ , 6 H ₂ O		75	75	75	0.09
H ₃ BO ₃					0.3
KNO ₃					0.2
NaCl			30	30	
(NH ₄) ₂ SO ₄	15				
(NH ₄ Cl)		30			
ZnSO ₄	22				
ZnCl ₂		30			
NaSCN	15	15			
pH	5.5-6	3.5-5.5			4.6
Temperature	26-32 °C	Room temperature	25-27°C	19-25°C	25°C
Current density (A.dm ⁻²)	0.2	0.15	0.14 (90s) + 0.26(60s)	0.07 (3-6 min) + 0.13(1-2 min) Or 0.11(3 min) + 0.22 (1 min)	0.5
Reference	18	18	25	24	19

Table 2: Compositions and experimental conditions for black nickel electrodeposition

Mechanical properties and corrosion resistance of black nickel coatings are greatly enhanced when phosphorus is co-deposited with nickel. Electroless black Ni-P with a phosphorus content ranged between 1% and 15% by weight may be obtained by using the composition and operation parameters of plating listed in Table 3. The black treatment was conducted by etching electroless plating nickel in oxidizing acid solution as follows. The samples were

immersed into 5.5 M sulfuric acid and 4.1 M sodium nitrate solution at 50°C after 10 s. After rinsing and drying, they were introduced into etching solution again for 5 s. (26).

Chemical composition and AFM morphology analysis of the pre-etched and post-etched electroless nickel at various phosphorus content showed that surface became smoother and the nodular structure of the pre-etched film evolved into small convex closure-like structure after black treatment. In addition, etching leads to increase phosphorus content in the film due to a preferential dissolution of nickel atoms. Visible reflectance measurements on the films showed that optimum phosphorus content range to prepare low reflectance black nickel from 3 to 7 wt %. In this case, the average reflectance measured at 633 nm was 0.46 ± 0.02 .

<i>Bath constituents and parameters</i>	<i>Quantity (mol/l)</i>
Nickel sulfate	0.10
Sodium hypophosphite	0.08, 0.1, 0.13, 0.15, 0.20, 0.25, 0.3, 0.35, 0.40
Sodium acetate	0.15
D,L-Malic acid	0.03
Citrate acid	0.02
Succinic acid	0.05
Lauryl sodium sulfate	8 mg/l
<i>Operating conditions</i>	
pH	5.8
Temperature	$85 \pm 2^\circ\text{C}$

Table 3: Bath composition and operating conditions of electroless Ni-P deposition (26)

In another study, an electroless Ni-P film deposited onto aluminum substrate overlaid with a zinc film has been obtained using the plating conditions shown in Table 4 (14). Blackening of electroless nickel was carried out by immersion in an acid solution. Three solutions at different concentrations were used: (a) nitric acid, (b) sulphuric acid + nitric acid, (c) nitric acid + sulfuric acid + potassium permanganate. Nitric acid (9M) was found to provide highest solar absorptance value of the order of 0.995. Surface analysis have shown that the pre-etched film contains 93.15% nickel and 6.81% phosphorus by weight whereas the etched coating showed lower nickel and phosphorus content (nickel 90.06%, phosphorus 5.75 and oxygen 4.19% by weight). The black nickel obtained after etching consists of oxides (NiO, Ni₂O₃) and some nickel phosphate. The black color is due to the chemical composition of the film and to its surface morphology which consists of a dense array of microscopic, conical pores perpendicular to the surface which act as light traps and is capable of absorbing 99.5% light in solar region. Since the thickness of electroless nickel decreases during etching a higher

thickness of electroless coating is required. The optimum coating thickness of electroless nickel is about $30 \pm 2 \mu\text{m}$ to achieve the ultra high solar absorbance after etching. The obtained electroless black coatings showed a good: (a) resistance to corrosion, (b) thermal stability (c) resistance to humidity. In addition the coatings have an excellent adhesion and a high Vickers hardness value of 575.

<i>Bath constituents and parameters</i>	<i>Quantity (g/l)</i>
Nickel sulphate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	30
Sodium hypophosphite, NaH_2PO_2	10
Sodium citrate, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$	12.5
Sodium acetate, CH_3COONa	5.0
Thiourea, NH_2CSNH_2	0.001
<i>Operating conditions</i>	
pH	4.7
Temperature	88 – 90 °C
Filtration	Continuous
Time	3h
Coating Thickness	$30 \pm 2 \mu\text{m}$
Water rinse	

Table 4: Solution used for Ni-P electroless deposition (14)

The influence of the substrate nature and its roughness on optical properties of black nickel coatings has been reported in numerous studies. In (27) the authors used a bath composed of nickel, nickel sulfate, nickel ammonium sulfate, zinc sulfate and sodium thiocyanate to electrodepose black nickel coatings on various substrates (aluminum, copper and stainless steel). Bead-blasted, polished and unfinished samples of the studied materials were used. The results showed that the maximum absorbance value depends on surface finish more heavily than the base metal. For bead blasted substrates, absorbance reaches 0.93 in some cases while it is lower for polished and unfinished samples.

Relation between plating time and optical properties of black nickel coatings has been studied in (16). It has been found that as the coating thickness increases from 1 to 10 microns, the solar absorbance changes from 0.96 to 0.90 whereas the emittance of the coating increases with thickness (from 0.11 to 0.87). A change of optical properties of black nickel coating with thickness has also been observed and discussed in (28-31).

Black nickel-cobalt and black nickel-copper alloys may also be obtained in black color by electrodeposition.

Black Ni-Co coatings have been electrodeposited using the experimental conditions shown in Table 5 (28-29). An optimized film has been produced at a current density of 3.5 A dm^{-2} for a duration of 30 seconds. The obtained film possesses a solar absorbance of 0.91 and a thermal emittance of 0.04 (28). This coating is constituted from particles of highly irregular shape, micro roughness and dendritic like structure. The high degree of solar absorption in this material has been attributed to optical interference and surface roughness which depends on the coating thickness. In addition it was pointed out that current density employed for deposition has a great influence on the optical properties of the coating since higher current densities require less deposition time to obtain a given coating thickness.

<i>Bath constituents and parameters</i>	<i>Quantity (g/l)</i>
Nickel sulfate	10
Cobalt sulfate	10
Ammonium acetate	10
<i>Operating conditions</i>	
pH	6.2
Temperature (°C)	35 °C
Current density (A.dm^{-2})	3-10

Table 5: Bath composition and operating conditions for black nickel-cobalt electrodeposition (28)

Electrodeposited black Ni-Cu on thin molybdenum foils has been studied in (30-31). Black films have been obtained from the bath solution given in Table 6. Table 7 shows that the optical properties of the films (α , ϵ) are increasing function of deposition time (30). Similar result was obtained with Ni-Co electrodeposited films (28). In another study, coherent, inclusion and pore free electrodeposited Ni-Cu black solar selective coatings with good optical properties ($\alpha = 0.94$ and $\epsilon = 0.10$) were obtained from triethanolamine complex bath solution containing ammonium persulfate (31).

<i>Bath constituents and parameters</i>	<i>Quantity (g/l)</i>	<i>Quantity (g/l)</i>
Cu(NO ₃) ₂	2.5	
(NH ₄) ₂ NiSO ₄ .6H ₂ O	20.0	
EDTA	2.5	
H ₃ BO ₃	10.0	10.0
CuSO ₄ .5H ₂ O		20.0
NiSO ₄ .6H ₂ O		20.0
(NH ₄) ₂ S ₂ O ₈		10.0
(HOCH ₂ CH ₂) ₃ N		20.0 ml/l
<i>Operating conditions</i>		
pH	5.2	5
Temperature (°C)	27 °C	27 °C
Current density (A.dm ⁻²)	0.5	0.5
Duration	30 s	30 s
Substrate	Mo-sheet	Mo-sheet
Reference	30	31

Table 6: Bath composition and operating conditions for black nickel-copper electrodeposition (30-31)

<i>Deposition time (s)</i>	<i>Absorption (α)</i>	<i>Emittance (ε)</i>
15	0.90	0.08
30	0.94	0.09
45	0.95	0.12
60	0.96	0.16
90	0.96	0.19

Table 7: Optical properties of the films obtained in the experimental conditions shown in Table 6 (30)

2.2- Chromium and chromium based alloys

Black chromium may be obtained by electrodeposition from hexavalent chromium processes based on chromic acid (CrO_3) (32) as well as by chromate conversion (33). Black chromium is known to offer better corrosion resistance than nickel films especially when formic acid is added to the solution used for the electrodeposition. Indeed it has been shown that surface modification with an adsorbed layer of formic acid significantly lowered the susceptibility of coatings to local corrosion (32).

Black chromate conversion films have been deposited on Zn and Co-Zn plated steel substrate by immersion in the chromating baths presented in Table 8 (33). Zn and Zn-Co sublayers have been deposited in acidic solution as shown in Table 9 (33). The plating has been conducted at room temperature and under a cathodic current density of 1.5 A.dm^{-2} . The obtained film contains 0.25-1.0% cobalt by weight. A comparative study between the reflective spectra of black films formed in chromating solutions with different compositions (Table 8) has been conducted. The investigation showed that the presence of an organic additive, ethoxylated aliphatic alcohols $\text{C}_{12}\text{-C}_{14}$ with 18 ethoxy groups, as well as Na_2SiO_3 in the formulation affects adsorption properties of the coatings. In addition, the obtained results showed that black coating deposited on the zinc sublayer presented a coefficient of solar absorption of $\alpha = 0.88 - 0.90$. When the zinc sublayer contains small amounts of cobalt (up to 1 wt %), a coefficient of absorption of $\alpha = 0.90 - 0.93$ was obtained. This high absorption coefficient is due to the inclusions of cobalt which penetrates from the metal sublayer into the chromate film. In addition, it has been shown that the presence of Co increases the corrosion resistance of the coating (33).

<i>Component (g/l)</i>	<i>Solution</i>							
	1	2	3	4	5	6	7	8
CrO_3	18	18	18	18	18	18	18	18
SO_4^{-2}	9	9	9	9	9	9	9	9
AgNO_3	0.4	-	-	-	0.4	0.4	0.4	-
Na_2SiO_3	-	-	5	5	5	-	5	-
Organic additive	-	0.1	-	0.1	-	0.1	0.1	-

Table 8: Bath compositions of chromating solutions (33)

<i>Component (g/l)</i>	<i>Electrolyte 1 (Zn film)</i>	<i>Electrolyte 2 (Zn- Co film)</i>
Zinc chloride	80	80
Ammonium chloride	180	180
Boric acid	20	20
Cobalt chloride	-	20-80
Basic additive	50	50
Brightener	10	6

Table 9: Bath compositions of Zn and Zn-Co films electrodeposition (33)

Electrodeposition of black chromium is mainly achieved in the conditions shown in Table 10 (32, 34-36). Characterization of black chromium coatings studied in (34) has shown that the most external layers were formed mainly by Cr₂O₃ with a selectivity of 3.41. After thermal treatment of the black chromium samples the composition of external layers changes with increasing amount of Cr₂O₃ and the selectivity increased to 3.91. Another study (37) has also pointed out that thermal annealing at 400°C leads to the conversion of the hydroxide present at the surface into Cr₂O₃. In addition no evidence for metallic chromium was found.

<i>Bath constituents</i>	<i>Concentration (g/l)</i>			
CrO ₃	200	364	250	250 - 400
NaNO ₃	2			
Na ₂ SiF ₆	0.2			
CH ₃ COOH				5 - 10
KNO ₃		2.3		
BaCO ₃		9.1		
CH ₃ COOH				
H ₂ SiF ₆		1.8	0.5	
Operating conditions				
Temperature (°C)	20		20 – 25	30
Current density (A.dm ⁻²)			25 - 30	80 - 100
Reference	32	34	35	36

Table 10: Bath composition and operating conditions for black chromium electrodeposition

However, although chromate is an excellent corrosion inhibitor, it has been recognized a highly toxic, sensitizing and carcinogenic. Since trivalent chromium is not toxic and closely resembles the characteristics of hexavalent chromium it represents the suitable alternative for hexavalent chromium replacement. Recently, a formulation mainly based on a trivalent chromium plating solution was proposed to electrodeposit black chromium (Table 11) (38).

<i>Bath constituents</i>	<i>Quantity (g/l)</i>
CrCl ₃ .6H ₂ O	266
CoCl ₂ .6H ₂ O	15
H ₂ SiF ₆	8-12
NaH ₂ PO ₄	4
NaF	21
Operating conditions	
Temperature (°C)	Room temperature (25°C)
Current density (mA.cm ⁻²)	200-500
Time (min)	1

Table 11: Bath compositions and operating conditions of black trivalent chromium electrodeposition (38)

In this study, the influence of hexafluorosilicic acid (H₂SiF₆) was particularly analyzed. It has been found that it was not easy to produce a black deposit without the presence of H₂SiF₆ and a minimum concentration (8 g/l) has to be attained in order to favor the formation of black chromium. The obtained coating was a mixture of Cr, Cr₂O₃, CrO₃ and Cr (OH)₃ with a solar absorbance of 0.97. In addition, it has been reported that a cobalt addition to electroplating bath improves its efficiency and the optical properties of black chromium coating. The author reported also that the thermal treatment of the black chromium coating up to 400°C has a slight effect on the absorbance properties.

Black coatings using chromium trivalent ions instead of its hexavalent ions were also obtained with an optimized design of the bath (Table 12). The obtained black coating had an absorption coefficient of 0.96. In this study, the authors have investigated the role of various additives and concluded that fluoride and dihydrogen phosphate anions are suitable additive materials (39).

<i>Bath constituents</i>	<i>Quantity</i>
Cr ⁺³ ion concentration	1M
Co ⁺² ion concentration	15g/l
Sodium hypophosphite concentration	0.75M
Sodium dihydrogen phosphate concentration	4g/l
Sodium fluoride concentration	0.5M
<i>Working conditions</i>	
Electroplating temperature	30°C
Electroplating time	1 minute
Electroplating current density	0.35 A/cm ²
pH of the electrolyte	Natural (0.5-1)

Table 12: Bath compositions and operating conditions of black trivalent chromium electrodeposition (39)

3- Black coatings obtained by vapor phase deposition technique

Black coatings elaborated by PVD or PECD techniques are widely used in decorative applications. Among them, carbon and titanium based compounds are the most important.

While the concept of absorption (or absorptance) introduced by the parameter α is the most widely used in the case of materials for solar applications, in the field of decoration one defines the color by using the CIE system which is based on human perception of color. In this case, black color is estimated from the value of the parameter L* which is a measure of lightness of an object and which indicates its reflecting properties. The parameters α and L* measure the same property but there is no link between these standards.

Let us remind that the CIE system has been introduced by the International Lighting Committee (*Comité International de l'Eclairage*). With this system, color is expressed using three parameters or coordinates L*, a* and b*.

The coordinate L*, which expresses luminosity, ranges from 0 for a black object to 100 for a white object and varies continuously between these extremes. L* is represented as a vertical axis, whereas the horizontal plane comprises the two axes a* and b*. The coordinate a* indicates position between red and green (positive values of a* indicate red while negative values of a* indicate green), whereas the coordinate b* indicates position between yellow and blue (positive values of b* indicate yellow while negative values of b* indicate blue)

3.1. Black titanium based compounds

TiCO coatings obtained using CO₂ as a reactive gas show a black color but insufficient hardness and wear resistance (hardness = 400 HV). Mechanical properties of these coatings were improved by using TiAlCO (hardness = 13 GPa) and TiAlCON (hardness = 11 to 17 GPa depending on nitrogen content) compounds. A hardness of 13 GPa was obtained for an ideal black color TiAlCON film (L* = 40, a, b < 1) (40). In another study TiCON coatings produced by PVD have permitted to obtain several tones of black for decorative applications (41). A titanium target was sputtered in an argon (working gas) + gas mixture (oxygen and nitrogen source) + acetylene (carbon source) atmosphere. The results reported in this study showed that with increasing the oxygen content in the film, the metallic dark grey color of

titanium carbide became very dark or black with the increase of the oxygen content in the films. In addition when the partial pressure PO_2+N_2 exceeds 0.11 Pa the brightness situates between 45 and 50 and $\{a^*, b^*\}$ tends to be closer to $\{0,0\}$.

3.2. Carbon and carbon based compounds

Diamond-like Carbon (DLC) films are also used as black coatings. These films combine high values for hardness (2000 -10 000 HV) with a low friction coefficient (0.1- 0.2) and great chemical stability (42-45).

DLC is made from a mixture of graphite (sp^2 hybridization state) and diamond (sp^3 hybridization state). Its properties can vary considerably as a function of the graphite/diamond ratio and the proportion of hydrogen it contains. Its mechanical properties can be rapidly degraded when the temperature exceeds 400°C (46). In this case, there is a sharp drop in the coating hardness due to the dehydrogenation of the material and the transformation of the carbon atoms from the sp^3 to the sp^2 form.

Recently, a nano-structured multilayer coating of a combination of a soft (a-C:H) produced by PECVD together with a hard layer ($\text{Cr/Cr}_{3-x}\text{C}_x$) produced by PVD allows to obtain colors between black and metallic Cr like depending on the thickness of the top Cr layer. It has been found that black color is obtained with 5 nm thick Cr layer whereas higher Cr film thickness (> 30 nm) gives a metallic Cr like (47).

The world's blackest material that absorbs 99.95% of light with a total reflectance of 0.045% has been created two years ago from carbon nanotubes (average diameter of 8-10 nm) produced by water-assisted chemical vapor deposition (CVD) process (48).

The surface of a carbon nanotube carpet was turned irregular and rough to minimize its optical reflectance. It has been shown that the obtained optical properties are the combination of the low density array, the nanometer-size nanotubes, and the random surface profile that makes the material an ideal black object.

The total reflective index of this material is about 0.045%, which is three times lower than the nickel-phosphorus alloy considered till now as the blackest material in the world. Basic black paint, by comparison, has a reflective index of 5% to 10 % (49-50). "This material is almost 30 times darker than a carbon substance used by the US National Institute of Standard and Technology as the current benchmark of blackness" (51).

3.3. Comparison between carbon and titanium based compounds

To choose the most resistance black coating to abrasion for an application in watch industry, a comparative study resistance to abrasion has been conducted between TiAlCON, DLC and DLC coated CrN or TiAlN films deposited on an austenitic stainless steels 316L which is the most common steel used for coverings in the watch industry (40).

Figure 1 presents the results of the coatings resistance to abrasion after a period of 48 h of testing using an abrasive wear test by vibration according to standard ISO 3160-3. The coatings were classified on a scale of 0 to 10, 10 being the value attributed to the sample not

used. The TiAlCON layers were compared to two DLC market coatings (DLC1 and DLC2). The effect of a hard underlayer (CrN (hardness = 1 800-2 000 HV) or TiAlN (hardness = 2 500-3 000) on the resistance to DLC (hardness = 1300 – 1500 HV) films to abrasion was also analyzed.

The results show that: (i) the presence of a hard underlayer enhance greatly the DLC resistance to abrasion, (ii) TiAlCON film is more resistance to abrasion than DLC.

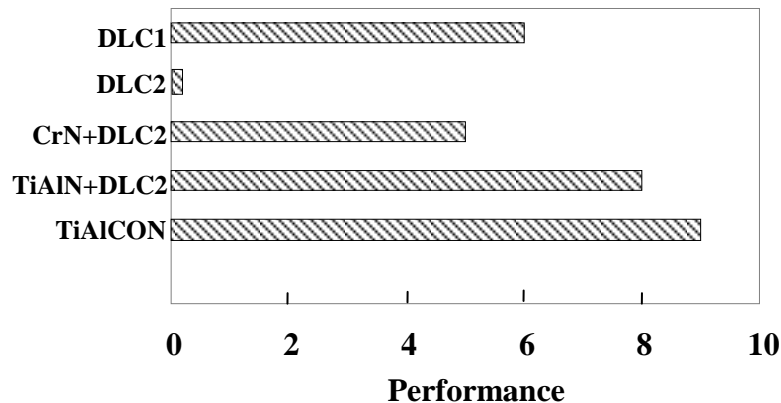


Figure 1. Performance of several black coatings after 48 h of wear by vibrations testing (40)

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