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# On the phenomenon of Co(III) adsorption at the surface of ABS plastics from colloidal solutions

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The greatest amounts of Co compounds onto the surface of ABS plastics were shown to be present after exposure of the plastics to Co(III) colloidal solutions. Co(III) colloidal particles resulted from the oxidation of Co(II) with H<sub>2</sub>O<sub>2</sub> in an acetate solution followed by their stabilization with ammonium ions. CoOOH and an unidentified cobalt substance were detected on the nonconductor surface after the treatment. The charge of colloidal particles in the solution depended on the concentration of cobalt compounds. The colloidal particles were found to be charged negatively at lower and positively at higher concentrations of cobalt compounds and ammonia, respectively.

**Key words:** cobalt colloidal solution, cobalt compounds, adsorption

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## INTRODUCTION

Co(II) aminoperoxocomplexes [Co(NH<sub>3</sub>)<sub>5</sub>O<sub>2</sub>]<sup>2+</sup> and [(NH<sub>3</sub>)<sub>5</sub>CoO<sub>2</sub>Co(NH<sub>3</sub>)<sub>5</sub>]<sup>4+</sup> [1–3], or under specific conditions, the Co(III) complex [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> [4] have been known to result from Co(II) aminocomplex oxidation with H<sub>2</sub>O<sub>2</sub>.

H<sub>2</sub>O<sub>2</sub> and even atmospheric oxygen oxidize easily Co(OH)<sub>2</sub> to rather stable Co(OH)<sub>3</sub> [5]. It is clear that such an oxidation should be faster when Co(OH)<sub>2</sub> exists as colloidal particles.

In the current study, it has been shown that the greatest amounts of Co onto the ABS surface are deposited after treatment with Co(III) colloidal solutions. In this regard these solutions are similar to Sn(II)–Sn(IV) colloidal solutions [6–9], which are used to treat the surface of nonconductors before metal deposition from an electroless plating solution.

## EXPERIMENTAL

The experiments were carried out using ABS plastics. Specimens of ABS plastics were pretreated for 0.5 min in a solution containing 0.06 M KMnO<sub>4</sub> and 10 M H<sub>3</sub>PO<sub>4</sub> at 20 °C. Short-time etching and room temperature were used with the aim to obtain a maximum smooth surface of plastics after etching and to minimize its influence on the determination of the elemental composition of the surface. The

specimens pretreated in such a way were treated for 2 min under stirring in cobalt complex solutions (Table 1), then were rinsed with the background solution (solution without Co(II) ions) or with distilled water and finally dried.

The cobalt complex solutions prepared by various means were studied spectrophotometrically. The UV-visible spectra were recorded with a Perkin Elmer Lambda 35 UV/VIS spectrophotometer at 20 °C in 1.0 cm path length quartz cells. The optically blank solution was the background solution.

The surface of ABS specimens after its pretreatment and treatment in the cobalt aminocomplex solution was investigated by a X-ray photoelectron spectroscopy (XPS). Photoelectron spectra were recorded on a Escalab MK II spectrometer (VG Scientific, Great Britain) with a Mg K<sub>α</sub> radiation source (1253.6 eV) operated at 300 W, at a fixed pass energy of 20 eV. The pressure of 1.33 · 10<sup>-6</sup> Pa was kept in the UHV analysis chamber. An Ar<sup>+</sup> ion beam was used to sputter-etch the surface (20 μA, ~2 nm/min, 30 s) at 6 · 10<sup>-3</sup> Pa. Maximum accuracy of the measurements was ±0.1 at. %.

The Co 2p<sub>3/2</sub>, O 1s, S 2p, N 1s and C 1s spectra were recorded when investigating the elemental composition of the coatings. Empirical elemental sensitivity factors were taken from literature, and the spectra obtained were compared with the standard spectra [10–12].

The distribution of elements through the whole depth of the surface was shown to be even for cer-

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**Table 1. Dependence of Co quantity on the ABS surface on cobalt solution composition and the sequence the solution's components are added**

The concentration of  $\text{H}_2\text{O}_2$  was  $4 \cdot 10^{-2}$  M in all experiments. The study was carried out the same day the solutions were prepared.

The XPS investigation data are for the case when 30 s etching with  $\text{Ar}^+$  was used (at a depth of  $\sim 1$  nm)

Trial No.	The initial solution contains			The sequence the solution's components are added	Quantity of Co, at. %
	Co(II), $\text{M} \cdot 10^3$	$\text{NaOOCCH}_3$ , M (NaAc)	$\text{NH}_4\text{OH}$ , M		
1	7	0.45	0.0	Co(II) →NaAc	3.9
2	7	0.45	0.34	→ $\text{H}_2\text{O}_2$ Co(II) →NaAc	2.1
3	7	0.45	4.7	→ $\text{H}_2\text{O}_2$ → $\text{NH}_4\text{OH}$ Co(II)	2.0
4	7	0.45	4.7	→NaAc → $\text{H}_2\text{O}_2$ → $\text{NH}_4\text{OH}$ Co(II)	Traces
5	7	0.00	4.7	→NaAc → $\text{H}_2\text{O}_2$ Co(II)	Traces
6	35	0.45	4.7	→ $\text{H}_2\text{O}_2$ → $\text{NH}_4\text{OH}$ Co(II) →NaAc → $\text{NH}_4\text{OH}$	Traces

tain specimens. The distribution was somewhat less uniform only on the outer surface. Hence, the XPS data obtained after 30 s sputtering, *i.e.* at a depth of  $\sim 1$  nm, are most often presented in our work.

The charge of the particles was determined by electrophoresis [13], performing the measurements at a constant voltage of 100 V for 15 min.

Analytical grade chemicals and distilled water were used to prepare the solutions. The solution pH was measured using a universal Mettler Toledo MP 200 pH-meter (Germany).

## RESULTS AND DISCUSSION

The experiments showed that when the ABS plastic surface was treated in a solution containing a sufficiently high cobalt(II) aminocomplex concentration (0.18 M) and then rinsed not with water but with the background solution, no cobalt was found on the surface. On the other hand, when ABS specimens after treatment in Co(II) aminocomplex solution were rinsed with water, the Co complex ions adsorbed at the surface or present in the solution layer adjacent to the surface were hydrolyzed. The products of the hydrolysis of compounds present in the solution layer adjacent to the surface

are thought to undergo conglomeration into fine colloidal particles, which might adhere to the surface, analogously as for copper [14]. The hydrolysis process mentioned above cannot occur in the background solution, and the cobalt ions adsorbed at the surface, if at all, are desorbed. Consequently, no cobalt ions are present at the surface. The products of hydrolysis, namely Co(II) hydroxides, can be rapidly oxidized by atmospheric oxygen [15, 16]. Such an oxidation has been shown to be possible thermodynamically [5]. Moreover, this oxidation has been confirmed by the results obtained earlier – cobalt(III) substance as  $\text{CoSOH}$  has been determined along with other Co substances on glassy carbon [17].

In all instances discussed below, the surface of ABS plastics after its treatment in cobalt compound solutions was rinsed with the background solution. In such a manner, the hydrolysis stage was excluded. The exclusion of the hydrolysis stage and employment of rather low concentrations (*e. g.*  $7 \cdot 10^{-3}$  M) of cobalt compounds in the experiments as well made the interpretation of the experimental results much easier.

Well previously, an efficiency of the adsorption of colloidal particles of tin compounds at various

surfaces in sensitizing  $\text{SnCl}_2$  solutions has already been investigated and described thoroughly [6]. One can see from data presented in Tables 1 and 2 that also in Co solutions (at low concentrations of Co(II) compounds, *e. g.*,  $7 \cdot 10^{-3}$  M) ABS surface adsorbs cobalt substances mostly in the case when these Co substances are in the colloidal state. This was achieved by adding  $\text{H}_2\text{O}_2$  (Table 1). Once a colloid is formed, the aggregation of the colloidal particles proceeds slowly (the Tindall cone becomes more distinct) and, as time elapses, the coagulation of the colloidal particles starts to occur (the solution becomes turbid). In the case when, after adding  $\text{H}_2\text{O}_2$ , ammonia is added immediately, the solution becomes stabilized. Ammonia substances appear to take place in the formation of the outer layer of colloidal particles. Similar phenomena are also characteristic of  $\text{SnCl}_2$  solutions [7].

The largest amounts of cobalt compounds were found when the plastic surface was treated in an acetate solution without ammonia. With increasing the  $\text{NH}_4\text{OH}$  concentration, their amount was found to decrease, most likely due to the dispersity of the particles.

When the sequence of the addition of  $\text{H}_2\text{O}_2$  and  $\text{NH}_4\text{OH}$  was changed, *i. e.* first  $\text{NH}_4\text{OH}$  and then  $\text{H}_2\text{O}_2$  were added to the Co(II) acetate solution, no cobalt was obtained. The spectrum of such a solution shows two different peaks, at 360 and 510 nm (Fig. 1a), while no peak is observed in the spectra of the colloidal solution, even in the UV region, despite the fact that the solutions are of an intensive reddish brown color.

Only traces of cobalt were found on ABS treated in solutions without acetate, *i. e.* when only  $\text{H}_2\text{O}_2$  and  $\text{NH}_4\text{OH}$  were added to Co(II) sulphate solution. Negative results were also obtained in the absence of an oxidizing agent; in this instance, no colloidal particles were formed, the solution was clear and reddish brown, the spectrum had the maximum at 360 nm (Fig. 1c).

By the way, in the Co(II) aminocomplex solution, spontaneous oxidation by atmospheric oxygen proceeds progressively as well, analogously as in Co(II) ethylenediamine solutions [18], as confirmed by increase in the intensity of the reddish brown coloring of the solution. However, in this case there was no movement of the colloidal particles in the electric field and no cobalt was found on the ABS surface after rinsing with the background solution.

The pH of Co(II) acetate solution is about 7 (Table 2). Under such conditions, the hydrolysis of Co(II) compounds is fast. The resulting Co(II) oxides and hydroxides as shown thermodynamically, in the presence of  $\text{H}_2\text{O}_2$  can be easily oxidized, into Co(III) [5]. The colloidal particles of Co(III) sub-

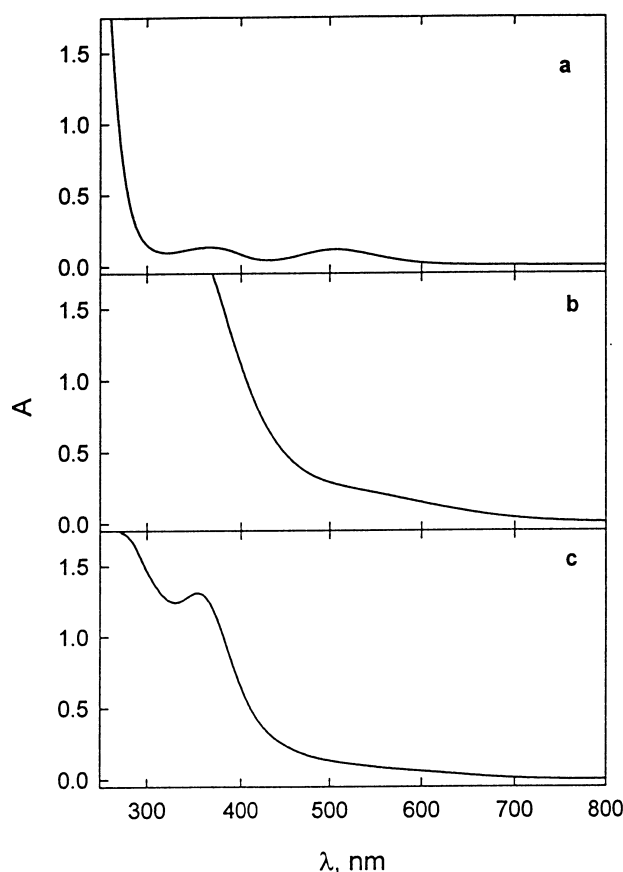
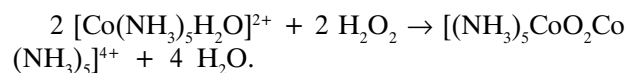


Figure. Spectra of the solutions containing (initial concentration):  $1.8 \cdot 10^{-3}$  M Co(II), 0.45 M NaAc,  $\text{H}_2\text{O}_2$   $4 \cdot 10^{-2}$  M and  $\text{NH}_4\text{OH}$  4.7 M.

The sequence the components were added: (a) Co(II) → NaAc →  $\text{NH}_4\text{OH}$  →  $\text{H}_2\text{O}_2$ ; (b) Co(II) → NaAc →  $\text{H}_2\text{O}_2$  →  $\text{NH}_4\text{OH}$ ; (c) Co(II) → NaAc →  $\text{NH}_4\text{OH}$

stances appear to be stabilized by the  $\text{NH}_4\text{OH}$  added.

If a large excess of  $\text{NH}_4\text{OH}$  ( $40 \times$  or more) was added instantaneously to the Co(II) acetate solution prepared (pH  $10 \div 12$ ), total Co(II) was complexed into a  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{2+}$  species [20]. When  $\text{H}_2\text{O}_2$  was added to such a solution, a Co(II) peroxocomplex was formed instead of colloidal Co(III) [1–3]:



The background solution in this case washed off the Co substances from the ABS plastic surface exposed to this solution.

It has been known that the adsorption of the colloidal particles of tin and iron compounds at hydrophobic surfaces of seven different polymers occurs only when these particles are charged positively [8]. The sign of the charge of the particles of cobalt substances determined by the electrophoresis

**Table 2. The charge of colloidal particles in the cobalt compound solutions**

The concentration of  $\text{H}_2\text{O}_2$  was  $4 \cdot 10^{-2}$  M and NaAc 0.45 M in all experiments

The study was carried out the same day the solutions were prepared.

The sequence the components were added: Co(II)  $\rightarrow$  NaAc  $\rightarrow$   $\text{H}_2\text{O}_2$ , or then  $\text{NH}_4\text{OH}$  was added

Trial No.	The initial solution contained		Solution pH	Charge sign
	Co(II), M $\cdot$ $10^3$	$\text{NH}_4\text{OH}$ , M		
1.	7	0.0	7.1	Negative
2.	14	0.0	6.9	Positive
3.	1.8	0.34	11.4	Negative
4.	3.5	0.34	11.2	Positive
5.	7	0.34	10.43	Positive
6.	17.8	0.34	10.65	Positive
7.	1.8	4.74	12.1	Positive
8.	3.5	4.74	12.0	Positive
9.	7	4.74	11.7	Positive

technique (Table 2) was shown to be negative at lower concentrations of cobalt and positive at higher ones. In the absence of  $\text{NH}_4\text{OH}$ , this change in the charge occurs at higher concentrations of cobalt substances than in the presence of ammonia. The higher the concentration of ammonium ions in the solution, the lower the concentrations of cobalt compounds at which the positive charge can be observed. The electrophoresis technique confirmed only that there were no colloidal particles in the solu-

**Table 3. The elements' atomic % on the ABS surface depending on the age of the most active solutions of cobalt compounds**

The initial solution contains (M):  $7 \cdot 10^{-3}$   $\text{CoSO}_4$ , 0.45 NaAc and  $4 \cdot 10^{-2}$   $\text{H}_2\text{O}_2$ .

The sequence the components were added: Co(II)  $\rightarrow$  NaAc  $\rightarrow$   $\text{H}_2\text{O}_2$ , or then  $\text{NH}_4\text{OH}$  was added.

The XPS investigation data are for the case when 30-s etching with  $\text{Ar}^+$  was used (at a depth of  $\sim 1$  nm)

Trial No.	Days after the solution was prepared	Quantity of Co, at. %
<b>Without <math>\text{NH}_4\text{OH}</math></b>		
1	0	3.9
2	1	4.0
3	2	3.9
4	3	2.0
5	4	Precipitate appeared
<b><math>\text{NH}_4\text{OH} = 4.74</math> M</b>		
6	0	1.7
7	1	1.9
8	2	2.0
9	3	2.0
10	4	3.2

tions whose application did not further lead to the presence of appreciable amounts of cobalt on the surface.

The colloidal solutions, on standing, undergo certain changes evidenced by the data on the amounts of cobalt on the plastic surface (Table 3). If the colloid has not been stabilized by ammonia in the cobalt acetate solution, aggregation of the particles is observed as time passes, and the amount of cobalt at the surface decreases. In the case of colloidal solutions stabilized by ammonia, an opposite picture is observed – the more prolonged the storage of the solution, the larger the amount of cobalt at the plastic surface. The efficiency of the process appears to be dependent on the dispersity of the particles. In all instances, if the col-

loidal particles are formed in advance, the solutions with much lower concentrations of cobalt compounds can be used, in comparison with those solutions where the colloid is formed only by rinsing the plastic surface treated in a solution of cobalt compounds with water.

As can be seen from the data of XPS analysis (Table 4), after the treatment of plastic surface in Co(III) colloidal solutions,  $\text{CoOOH}$  [12] and also an unidentified cobalt complex substance were detected in the surface layer at a depth of  $\sim 1$  nm. Hence, the amount of oxygen increases as compared to that found at the surface before treatment in Co(III) colloidal solutions. With increasing the cobalt concentration in the solutions, the amount of cobalt increases rather slightly.

Some assumptions as to the nature of colloidal particles can be made on the basis of  $\text{CoOOH}$ , which was found at the surface after treatment in colloidal solution and also from the experimental results of electrophoresis measurements (Table 2). The nucleus of the colloidal particles seems to be composed of  $\text{CoOOH}$  or  $\text{Co}(\text{OH})_3$ , while the outer layer contains  $\text{CH}_3\text{COO}^-$  (the negatively charged particle) or  $\text{CoCH}_3\text{COO}^+$  (the positively charged particle) at lower or higher concentrations of cobalt ions, respectively. In the case of ammonia solutions with sufficient concentrations of cobalt and ammonium ions, the outer layer consists of  $\text{Co}(\text{NH}_3)_5^{3+}$ .

Co(III) compounds to be adsorbed by the surface should be in a state of colloidal particles. If a Co(III) compound,  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ , synthesized according to [4] and dissolved in an  $\text{NH}_4\text{OH}$  solution, is applied for ABS treatment, no cobalt is found on

Table 4. Data of XPS analysis for the surface ABS plastic

The initial solution contains (M): 0.45 NaAc,  $4 \cdot 10^{-2}$  H<sub>2</sub>O<sub>2</sub> and 0.34 NH<sub>4</sub>OH.The sequence the components were added: Co(II) → NaAc → H<sub>2</sub>O<sub>2</sub> → NH<sub>4</sub>OH.The XPS investigation data are for the case when 30-s etching with Ar<sup>+</sup> was used (at a depth of ~1 nm)

Trial No.	Initial Co(II) concentration in the solution, M · 10 <sup>3</sup>	Element	* Quantity at. %	Binding energy, eV	Most probable composition of the compounds
After etching					
1	0	O	3.6	531.8 + 530.8	**
		N	3.7	399.6 + 398.8 + 401.9	Organic oxy- and hydroxy-compounds
After treatment of the surface in Co(II) amminocomplex solution					
2	1.8	Co	2.1	778.5	Co <sub>complex</sub> , CoOOH,
		O	4.7	531.7 + 533.2	
		N	3.8	398.9 + 400.3	
3	7	Co	2.1	778.7	Co <sub>complex</sub> , CoOOH,
		O	5.1	531.5 + 532.9	
		N	3.7	398.1 + 399.2+400.2	
4	17.8	Co	2.3	778.4	Co <sub>complex</sub> , CoOOH,
		O	4.8	531.5 + 533.3	
		N	3.7	399.4 + 398.2 + 400.6	

\* Atomic % of carbon consist residual part up to 100%.  
 \*\* Small amounts of the compounds mentioned are present in all other samples.

the surface thereafter, even though the specimen has been rinsed with water instead of the background solution. This indicates that in this instance no hydrolysis occurs (the complex species are too stable).

## CONCLUSIONS

1. To obtain an appreciable layer of cobalt substances on the ABS surface, the presence of Co(III) colloidal particles in the solution is necessary.

2. Co(III) colloidal particles result from the oxidation of Co(II) with H<sub>2</sub>O<sub>2</sub> in acetate solution, followed by their stabilization with ammonium ions.

3. CoOOH and an unidentified cobalt complex substance were detected at the plastic surface after exposure to a colloidal solution.

4. The colloidal particles are charged negatively at lower and positively at higher Co(III) and ammonia concentrations, respectively.

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**APIE CO(III) ADSORBCIJOS ANT ABS PLASTIKO  
PAVIRŠIAUS REIŠKINIŲ KOLOIDINIUISE  
TIRPALUOSE**

**S a n t r a u k a**

Kad ABS plastiko paviršiuje susiformuotų apčiuopiamas kobalto junginių sluoksnis, reikalingi tirpalai su kobalto(III) junginių koloidinėmis dalelėmis. Tokios dalelės gautos oksiduojuojant acetatiniame tirpale Co(II) vandenilio peroksidu ir po to stabilizuojant koloidus amonio jonais. Apdorojant

plastiko paviršių tokiam koloidiniame tirpale galima naudoti daug mažesnės koncentracijos kobalto junginių tirpalus, palyginti su tirpalais, kai koloidai susidaro tik plaunant vandeniu plastiko paviršių po apdorojimo Co(II) amoniacinio komplekso tirpale. Apdorojus koloidinių Co(III) junginių tirpale, ant plastiko paviršiaus randama CoOOH ir neidentifikuotų kompleksinių junginių. Koloidinių dalelių krūvis priklauso nuo kobalto junginių koncentracijos tirpale. Koloidinių dalelių krūvis, esant tirpale mažesnėms kobalto junginių koncentracijoms, yra neigiamas, o didesnėms – teigiamas. Kuo didesnė amonio jonų koncentracija tirpale, tuo labiau, esant mažesnėms kobalto junginių koncentracijoms, koloidinių dalelių krūvis kinta iš neigiamo į teigiamą.