NEW SUBSTANCES, MATERIALS, AND COATINGS

Composition, Structure, and Photocatalytic Properties of Fe-Containing Oxide Layers on Titanium

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Abstract—The composition, optoelectronic properties, and surface and cross-section morphology of coatings formed by the method of plasma electrolytic oxidation in electrolytes containing sodium phosphate or silicate with or without addition of $K_3[Fe(CN)_6]$ have been investigated. The coatings were studied by the methods of spectrophotometry, X-ray diffraction analysis, electron microscopy, and X-ray photoelectron spectroscopy. The photocatalytic activity of oxide coatings was studied in the reaction of phenol degradation under ultraviolet irradiation in the presence of hydrogen peroxide. The highest photocatalytic activity in the reaction of phenol degradation in the presence of hydrogen peroxide was manifested by Fe-containing coatings formed in the silicate electrolyte with addition of 8.0 g/L of $K_3[Fe(CN)_6]$.

Keywords: plasma electrolytic oxidation, titanium oxide, iron oxide, band gap, modification, photocatalysis **DOI**: 10.1134/S2070205117050252

INTRODUCTION

At present, contamination of water objects by wastewater streams containing high-toxicity stable organic contaminants comprises an urgent problem. In view of this, there is substantial practical interest associated with the development of efficient reliable methods of their destruction. The most promising technologies of destruction of a wide range of toxic chemicals are those of nonchemical water treatment based on efficient oxidation processes (AOPs, Advanced Oxidation Processes), in particular, heterogeneous photocatalysis [1]. The substantial research and practical interest to heterogeneous photocatalysis in ecological terms is caused by the possibility of oxidation of organics with a high degree of mineralization at relatively low temperature, especially in the presence of oxygen, ozone, and hydrogen peroxide, and significant reduction of power consumption during water treatment when using sunlight.

At present, titanium dioxide (mostly in the anatase modification) is the most thoroughly studied and efficient photocatalyst for decomposition of a wide range of organic and inorganic toxic substances [2–6]. Nevertheless, the quantum output of TiO_2 photocatalysis is, as a rule, very low because of fast charge carriers'

recombination. Moreover, since TiO_2 can be effective only under UV-radiation of a wavelength lower than 386 nm, the efficiency of its functioning under sunlight is lower than 10%.

One of the promising directions of the efficiency increase of the TiO_2 photocatalyst consists in TiO_2 modification by transition metals (Zn, Fe, Mn, Ni, etc.) ions [7–9] and use of mixed double and triple metal-oxide systems [10–14]. In particular, a combination of titanium oxide with oxides of iron and/or silicon results in production of a more active photocatalyst as compared to individual oxides [11–14].

Here, photoactive materials immobilized on different substrates are more convenient in terms of application than are powder photocatalysts, since their separation by completion of the technological cycle is not necessary.

Plasma electrolytic oxidation (PEO) is one method that enables one to implement technologically sound deposition of multicomponent oxide coatings on metal substrates. It consists in electrochemical oxidation of the surface of a metal or alloy under effect of spark and arc discharges [15–17]. PEO enables one to obtain coatings containing titanium oxide with different ratios of anatase and rutile modifications, including doped or modified with various transition metals or in combination with their oxides, on a titanium surface [15, 18-34].

Recently, a significant number of publications devoted to application of coatings obtained by the PEO method on titanium as photocatalysts in the process of degradation of various organic contaminants have appeared [24–34]. According to them, the photocatalytic activity of oxide layers formed by the PEO method on the titanium surface depends on the phase composition, rutile/anatase crystalline phase ratio, surface morphological features, surface groups' composition, and defects in the crystal bulk. However, in many cases, there is no unambiguous explanation for the high or low activity of such coatings. In view of this, a detailed study of characteristics of PEO layers is necessary for understanding and explaining their photocatalytic properties.

Coatings containing the anatase modification of titanium dioxide are known to form as a result of plasma electrolytic oxidation of titanium in the phosphate electrolyte [19, 20, 24, 30]. Coatings containing, aside from the anatase modification of titanium dioxide, silicon oxide, which can serve as a support for the photoactive material, are formed in the silicate electrolyte [22]. To obtain iron-containing coatings, the base electrolytes have different iron compounds added to them, for example, K_3 [Fe(CN)₆] [21, 23].

The objective of the present work was to obtain data on the structure, composition, and optoelectronic properties of PEO layers on titanium formed in phosphate or silicate electrolytes with addition of K_3 [Fe(CN)₆] and to study their photocatalytic activity in a model reaction of phenol decomposition.

MATERIALS AND METHODS

Electrodes for plasma electrolytic oxidation were made of sheet titanium of VT1-0 grade in the form of plates of a size of $2.0 \times 2.0 \times 0.1$ cm. Samples were chemically polished in a mixture of concentrated acids HF : HNO₃ = 1 : 3 at 60-80°C for 2-3 s and then rinsed in distilled water.

Oxide layers were formed in the galvanostatic mode on anode-polarized titanium in aqueous electrolytes containing 0.1 M Na₂SiO₃ or 0.1 M Na₃PO₄ with addition of 0.5–8.0 g/L K₃[Fe(CN)₆]. For electrolyte preparation, distilled water and commercial reagents were used: Na₃PO₄ \cdot 10H₂O, Na₂SiO₃ \cdot 5H₂O, and K₃[Fe(CN)₆].

In electrolytes based on sodium silicate, oxide coatings were obtained at an effective current density of $i = 0.08 \text{ A/cm}^2$ for 10 min. In electrolytes based on sodium phosphate, it was at $i = 0.1 \text{ A/cm}^2$ for 5 min.

A TER4-63/460R-2-2-UKhL4 thyristor device with a unipolar current waveform was used as a current source. The process was carried out in a vessel made of heat-resistant glass of a volume of 500 or 1000 mL. The cathode comprised a hollow coil made of stainless steel of the Kh18N9T grade cooled with tap water. Oxidized samples were rinsed with distilled water and dried in air.

The samples' phase compositions were determined by the method of X-ray diffraction analysis (XRD) using a D8 ADVANCE diffractometer (Germany) in CuK_{α} radiation according to the standard technique. Identification of the compounds present in the samples under study was performed in the automatic EVA search mode using the PDF-2 database.

The coatings sections were obtained by etching in argon plasma.

The surface morphology was studied using a Hitachi S-3400 scanning electron microscope (SEM) (Japan) with an UltraDry energy-dispersive spectrometer (Thermo Scientific, United States) and a SUPERPROBE JXA-8100 microprobe X-ray spectral analyzer (JEOL, Japan).

To determine the element composition of the oxide coating surfaces the method of X-ray photoelectron spectroscopy (XPS) was used. The XPS spectra were measured using a Specs superhigh vacuum device (Germany) using a 150-mm electrostatic hemispheric analyzer. Mg K_{α} radiation was used for ionization. The depth of the analyzed surface layer was 2–3 nm. Spectra were calibrated on C1s lines of hydrocarbons, the energy of which was assumed to be equal to 285.0 eV.

Diffuse reflection spectra were recorded in the range of 200–800 nm using a Cary Varian 5000 spectrophotometer (Agilent Technologies, United States) with the spectral resolution of 1 nm. Halogen and deuterium lamps were used as radiation sources.

The band gap (BG) (E_g) was determined by the position of the fundamental absorption edge according to the Tauc equation:

$$(hv F(r))^{1/n} = A(hv - E_g),$$

where E_g —band gap, h—Planck constant, v—oscillation frequency of electromagnetic waves, $F(r) = (1 - r_{\infty})^2/2r_{\infty}$ —Kubelka—Munk's function, and A—constant. The exponent n is determined by the nature of interband electronic transitions. Both direct allowed (n = 1/2) and indirect allowed (n = 2) electron transitions between the valence band (VB) and the conduction band (CB) are known to be possible in the anatase crystalline modification of TiO₂ [35, 36]. The BG value was determined by extrapolating of the linear part of the Tauc curve decline to the abscissa axis (energy of falling photons – hv).

The coatings' photocatalytic activity was determined by phenol photodegradation in an aqueous solution (50 mg/L, pH 3) containing 10 mmol/L H_2O_2 under ultraviolet radiation. Total phenol content in the solutions under study was determined by spectrophotometry according to the Folin–Ciocalteu method [37].

A UV-mini 1240 spectrophotometer (Shimadzu, Japan) was used to measure concentration changes based on the Bouguer–Lambert–Beer equations $A = \epsilon lC$, where A, ϵ , l, and C are the absopbance, the molar absorption coefficient, the path length, and the solution concentration, respectively. Since ϵ and l are constants, while the parameter C is directly proportional to the absorbance, it can be obtained by measuring the A parameter.

To perform photocatalytic studies, 100 mL of a phenol solution with hydrogen peroxide and a sample of a size of 20 × 20 mm used as a catalyst were placed into a quartz cell. A UV lamp (SB-100P, radiation maximum at 365 nm) was used as a radiation source. In each experiment, prior to irradiation, the solution with the sample inside was left in darkness for 30 min to establish adsorption/desorption equilibrium, after which the absorbance was measured, with its value being used as a starting point (A_0). Then, the sample in the solution was irradiated by UV light for 2 h.

To determine the phenol content, 50 mL of tenfold diluted solution under study was added with 1 mL of the Folin–Ciocalteu reagent and 1.5 mL of 20% solution of Na₂CO₃. The obtained mixture was stirred for 30 min to develop the color. The absorbance was measured at $\lambda = 700$ nm. The phenol degradation degree (X) was calculated as

$$X = (A_0 - A)/A_0 \times 100\%$$
,

where A is the solution absorbance upon irradiation and A_0 is the absorbance prior to irradiation upon holding in darkness with the sample for 30 min.

RESULTS AND DISCUSSION

According to X-ray diffraction analysis, coatings formed by the PEO method in the studied electrolytes contain predominantly the TiO_2 anatase form.

Figures 1a and 1b show SEM images of the crosssection and element distribution maps over the thickness of the coating formed in an aqueous electrolyte containing 0.1 M Na₃PO₄. The coating is heterogeneous over the thickness ($\sim 8-10$ µm, see Figs. 1a, 1b). A layer of a thickness of less than 1 µm containing numerous nanopores is adjacent to the metal surface. The main coating part contains hollow microsized caverns. The question on embedding of carbon into the coating during the PEO process and its presence is under discussion in the literature [38, 39]. Comparison of Figs. 1b and 1c enabled one to determine the carbon location in coatings. One can see that carbon is distributed heterogeneously and is present as in the coating bulk as on its surface. However, a major carbon part is concentrated predominantly in the oxide layer surface part (Fig. 1c), which is indicated by the presence of light regions in the coating upper part.

Phosphorus, titanium, and oxygen are distributed rather homogeneously over the coating thickness (Figs. 1d-1f), excluding caverns, in which they are absent.

Figure 2 shows SEM images of the cross section and element-distribution maps over the thickness of the coating formed in the electrolyte containing 0.1 M Na_3PO_4 and 2.6 g/L K₃[Fe(CN)₆]. The general view of the cross section of such coating (Fig. 2a), as well as the distribution of oxygen, phosphorus, and titanium (Figs. 2b, 2c, and 2e) is similar for the coating formed in the phosphate electrolyte without addition of $K_3[Fe(CN)_6]$ (see Fig. 1). In addition, these coatings contain iron (see Fig. 2d). Iron is contained over the whole thickness and is concentrated on the coating surface, which is indicated by strengthening of the surface heterogeneous contrast from internal to external layers; i.e., the area occupied by light areas increases (see Fig. 2d). This fact is also corroborated by SEM images of the coating cross section, in which one can see that the surface contains fine particles of 1 µm in size and smaller (Fig. 3a) and a larger number (as compared to the bulk) of dark particles containing iron (Fig. 3b).

As can be concluded from the data of Fig. 4, iron is distributed over the coating surface heterogeneously as well. According to SEM images, areas characterizing increased iron content are located in caverns in spaces between pores.

Figure 5 shows SEM images of the cross section of coating formed in an aqueous electrolyte containing 0.1 M Na₂SiO₃ and 0.5 g/L K₃[Fe(CN)₆]. The coating thickness is larger than 25 µm (see Fig. 5a). Here, the boundary between the metal and the coating is uneven and rather diffused. As seen from Figs. 5a and 5b, just as in the case of the phosphate electrolyte, carbon is contained predominantly in surface layers of the oxide layer as compact areas, which is indicated by light contrast spots in Fig. 5b. Oxygen, iron, and silicon are distributed rather homogeneously over the coating thickness (Figs. 5c, 5d, 5f), whereas the titanium content decreases upon transition from the boundary between titanium and the coating to upper layers including clearly expressed areas depleted with titanium (Fig. 5e) and enriched with silicon (Fig. 5f). In other words, in accordance with earlier-reported data [40], areas of coatings enriched with silicon and titanium alternate on the surface.

Figure 6 shows SEM images of the coating surfaces formed in the silicate electrolyte containing different quantities concentration of $K_3[Fe(CN)_6]$. The surface of the coating formed in the silicate electrolyte with addition of 0.5 g/L $K_3[Fe(CN)_6]$ (see Fig. 6a) is strongly heterogeneous with high apparent roughness and the presence of a large number of coral-like structures, which characterizes in general the coatings formed in the silicate electrolyte [22]. Along with the increase of the $K_3[Fe(CN)_6]$ concentration in the



Fig. 1. SEM image of the cross section (a, b) and maps of element distribution over the thickness (c–f) of coatings formed in the electrolyte containing $0.1 \text{ M Na}_3\text{PO}_4$.

electrolyte up to 8.0 g/L, the surface relief becomes smoother, coral-like structures are not observed, and broad, but shallow, caverns emerge on the surface (see Fig. 6b). As can be seen on SEM images with high magnification (Figs. 6c, 6d), the surface of such coatings comprises a solid glasslike mass with numerous nanopores.

As was found in juxtaposition of SEM images of the coating surface (Fig. 7a) and the map of iron distribution in it (Fig. 7b), iron is located within caverns occupying a rather large part of the external coating. Thus, on the surface of coatings formed in electrolytes based on sodium phosphate (Fig. 4) or silicate (Fig. 7) with $K_3[Fe(CN)_6]$ addition, iron is concentrated in cavities

and pits, i.e., in defect surface areas formed because breakdown phenomena.

Figure 8a shows Fe2p X-ray photoelectron spectra of oxide layers formed in the silicate electrolyte with addition of 0.5 and 8.0 g/L K₃[Fe(CN)₆]. Binding energy $E_{\rm b}$ Fe (2p_{3/2}) (711.7 eV) indicates that iron is present on the surafce as Fe₂O₃. X-ray photoelectron studies of coatings formed in the phosphate electrolyte with addition of K₃[Fe(CN)₆] addition that iron was also present as Fe₂O₃ on the surface of these samples (see Fig. 8b).

Figure 9 shows the diffuse reflection spectra of oxide layers on titanium formed in the electrolytes under study in the range of 200–800 nm. In both



Fig. 2. SEM image of the cross section and maps of element distribution over the thickness of the coating formed in the electrolyte containing 0.1 M Na₃PO₄ and 2.6 g/L K₃[Fe(CN)₆].



Fig. 3. SEM images of the cross section and element distribution over the thickness of the coating formed in the electrolyte containing 0.1 M Na_3PO_4 and 2.6 g/L $K_3[Fe(CN)_6]$.

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Fig. 4. SEM images of the iron distribution over the surface of the coating formed in 0.1 M Na₃PO₄ + 2.6 g/L K₃[Fe(CN)₆]: (a) amplitude representation, iron particles are localized in cavities located around prominences with pores; (b) phase representation, areas with iron correspond to light parts.

cases, the increase of the $K_3[Fe(CN)_6]$ concentration in the electrolyte yields a substantial "red—shift" of the material fundamental absorption edge. The unstructured band in the range of 200–400 nm is associated with electron transitions between split O-2*p* levels and the top of the TiO₂ conduction band [41, 42]. The presence and position of absorption bands depend significantly on defects in the crystal structure and the particle size in the material.

Extrapolation of the linear decline of the $(F(r)hv)^{1/n}$ curve on the abscissa axis (hv) revealed that the E_g values for the indirect allowed transition were equal to 2.47 and 0.96 eV for the samples obtained in 0.1 M Na₃PO₄ with and without addition



Fig. 5. SEM image of the cross section and maps of element distribution over the thickness of the coating formed in the electrolyte containing 0.1 M Na₂SiO₃ and 0.5 g/L K₃[Fe(CN)₆].



Fig. 6. SEM images of the surface of coatings formed in the electrolyte containing 0.1 M Na_2SiO_3 and $K_3[Fe(CN)_6]$, g/L: (a) 0.5 and (b–d) 8.0.

of K_3 [Fe(CN)₆] (Fig. 10a) and to 2.6 and 1.4 eV for the samples obtained in the silicate electrolyte with addition of 0.5 and 8.0 g/L K_3 [Fe(CN)₆], respectively (Fig. 10c). The obtained values appeared to be significantly lower than those known for the nondoped anatase ($\sim 2.9 \text{ eV}$) [43]. At the same time, the BG value for the direct transition is larger for the coating formed in the silicate electrolyte with addition of 0.5 g/L K_3 [Fe(CN)₆] as well. This value is close to that for the nondoped anatase (\sim 3.3 eV) [44]. However, the increase of the Fe concentration results in diffusing of the energy bands structure and substantial decrease of the BG of the direct allowed transition (Figs. 10b, 10d). More detailed information on the phase composition, structure, and E_g values is shown in Table 1. A substantial decrease of E_g promotes the absorption of photons from not only the UV, but also from the visible, range and, as will be shown below, increases the efficiency of the photocatalytic reaction.

The performed photocatalytic studies demonstrated that phenol degradation under UV radiation did not occur in the absence of PEO coatings and on oxide layers formed in the silicate and phosphate electrolytes without $K_3[Fe(CN)_6]$ addition (see Table 1). A noticeable phenol degradation occurs at using ironcontaining oxide layers and increases along with the increase of the $K_3[Fe(CN)_6]$ concentration in the electrolytes under study (see table). As seen from the table, the degree of phenol degradation on iron-containing oxide coatings formed in the electrolyte based on sodium silicate is substantially higher than that on coatings formed in the electrolytes based on sodium phosphate. Analysis of the table data showed that the coatings formed in the silicate electrolyte with addition of 8.0 g/L K₃[Fe(CN)₆] contain 1.7 at % Fe, which is about half what was found in coatings formed in the phosphate electrolyte with addition of 2.6 g/L $K_3[Fe(CN)_6]$. Moreover, the BG for the coatings formed in the electrolyte based on sodium phosphate is smaller than that for the coatings formed in the sodium silicate-based electrolytes. Thus, the lower photocatalytic activity of the coatings formed in the sodium phosphate-based electrolytes containing larger amounts of iron and characterized by smaller BG is, probably, the result of high rate of recombination of photo-generated electrons and holes. It is worth mentioning that silicon-containing coatings are characterized by higher water absorption [45], specific surface area, and high adsorption capacity [46], which can also have a positive effect on the photocatalytic activity of such coatings.

The fact that phenol decomposition occurs only on coatings containing iron oxide (Fe_2O_3) enabled us to suppose that the photocatalytic reaction took place on Fe-containing surface areas as a result of the photo-



Fig. 7. SEM images of the surface of the coating and the map of iron distribution on the coating surface formed in the electrolyte containing 0.1 M Na₂SiO₃ and 8.0 g/L K₃[Fe(CN)₆].



Fig. 8. XPS spectra of the coatings formed in the electrolytes containing (a) 0.1 M Na₂SiO₃ and K₃[Fe(CN)₆], g/L: (1) 0.5 and (2) 8.0; (b) 0.1 M Na₃PO₄ + 2.6 g/L K₃[Fe(CN)₆].



Fig. 9. Diffuse reflection spectra of the samples obtained in the electrolyte containing (a) 0.1 M Na₃PO₄ with addition of (1) 0.0, (2) 1.6, and (3) 2.6 g/L K₃[Fe(CN)₆]; (b) 0.1 M Na₂SiO₃ with addition of (1) 0.5 and (2) 8.0 g/L K₃[Fe(CN)₆].



Fig. 10. Determination of the fundamental absorption edge for different electron transitions in the samples obtained in electrolytes: (a) and (b) 0.1 M Na₃PO₄ with addition of (1) 0.0, (2) 1.6, and (3) 2.6 g/L K₃[Fe(CN)₆]; (c) and (d) 0.1 M Na₂SiO₃ with addition of (1) 0.5 and (2) 8.0 g/L K₃[Fe(CN)₆].

Fenton process, which can be represented by the following reactions [47]:

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe(OOH)^{2+} + H^+,$$
 (1)

$$Fe(OOH)^{2+} \leftrightarrow Fe^{2+} + HOO^{-},$$
 (2)

$$\operatorname{Fe}^{2+} + \operatorname{H}_2O_2 \leftrightarrow \operatorname{Fe}^{3+} + \operatorname{HO}^- + \operatorname{HO}^{\bullet},$$
 (3)

$$Fe^{3+} + HOO^{\bullet} \leftrightarrow Fe^{2+} + H^+ + O_2,$$
 (4)

$$Fe(OOH)^{2+} + hv \rightarrow Fe^{2+} + HO^{\bullet}.$$
 (5)

Decomposition of photoactive Fe(OOH)²⁺ particles promotes additional formation of HO[•] radicals in solution; i.e., the initial Fenton process accelerates

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Electrolyte composition	Phase composition	Element composition (XPS), at %	Band gap, eV (Tauc method)		X, %
			<i>n</i> = 2	<i>n</i> = 1/2	
0.1 M Na ₂ SiO ₃	TiO ₂ (anatase)	n/d	n/a	n/a	0
$0.1 \text{ M Na}_2\text{SiO}_3 + 0.5 \text{ g/L K}_3[\text{Fe}(\text{CN})_6]$	TiO ₂ (anatase)	Fe 0.6; O 31.4; Ti 0.5; N 2.6; C 47.4; Si 17.5	2.6	3.2	30
$0.1 \text{ M Na}_2\text{SiO}_3 + 8.0 \text{ g/L K}_3[\text{Fe}(\text{CN})_6]$	TiO ₂ (anatase)	Fe 1.7; O 37.9; N 2.2; C 37.4; Si 20.8	1.4	2.6	80
0.1 M Na ₃ PO ₄	TiO ₂ (anatase)	n/d	2.5	3.1	0
$0.1 \text{ M Na}_3\text{PO}_4 + 1.6 \text{ g/L K}_3[\text{Fe}(\text{CN})_6]$	TiO ₂ (anatase)	n/d	1.0	1.8	43
$0.1 \text{ M Na}_3\text{PO}_4 + 2.6 \text{ g/L K}_3[\text{Fe}(\text{CN})_6]$	TiO ₂ (anatase)	Na 0.8; Fe 3.2; O 39.6; Ti 5.8; N 2.5; C 42.7; P 5.5	1.0	1.8	55

Table 1. Data on the element composition (XPS) and the values of band gap (E_g) of the studied samples and the degree of phenol degradation (X, %)

n/d-no determined.

under the light effect, which increases the degree of mineralization of organic substances [48].

CONCLUSIONS

To sum up, the composition, optoelectronic properties, and surface morphology and cross section of coatings formed in electrolytes containing sodium phosphate or silicate with addition of $K_3[Fe(CN)_6]$ have been investigated. The results of X-ray photoelectron spectroscopy revealed that iron was present on the coating surface in the form of Fe₂O₃. The band gap of composite coatings decreases along with the increase of the iron content in oxide layers.

The obtained iron-containing composite coatings are active in photocatalytic degradation of phenol in the presence of hydrogen peroxide. More active photocatalytic coatings formed in the silicate electrolyte with addition of 8.0 g/L K₃[Fe(CN)₆] are characterized by a higher value of band gap in comparison to that of less active coatings formed in the phosphate electrolyte with addition of 2.6 g/L K₃[Fe(CN)₆]. It is evident that the iron-containing oxide coatings formed on titanium are promising for water decontamination from organic contaminants, such as Fenton-like heterogeneous photocatalysts.

The obtained results demonstrate the high potential of using planar photoactive structures based on titanium dioxide modified with transition metals oxides in solution of photocatalytic problems. On the other hand, the approach to creating similar structures used in the present work makes it possible to obtain a material with new optical characteristics, which in some cases [49, 50] may depend on the nature and/or concentration of the present contaminant [51]. In view of the above, further development of these works will be concerned, among other problems, with finding conditions of formation of composite coatings and methods of their photoresponse registration focused on fabrication of hybrid structures combining the properties of a photocatalyst and an optic sensor.

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