Electrodeposition of Zn-Al-GO Nano Composite Coatings on Stainless Steel from Chloride Bath and Its Surface Morphological and Corrosion Protection Studies

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ABSTRACT

Thin films of Zn-Al-GO nanocomposites were prepared by electrodeposition in chloride bath solution with different concentration of dispersed graphite oxide (GO) colloid and Aluminum silicate. The various bath parameters were optimized to get the required morphology of the deposit and their effect on the morphology were studied. The micro morphologies of film were captured by scanning electron microscopy and EDAX, to get information about metal lattice parameters, texture and phase composition of the coatings which dramatically changed from to nanocrystal sheets owing to the addition of GO. The corrosion resistance properties of Zn-Al-GO composite coatings in HCl solution were investigated by the electrochemical methods. Using Stern method the corrosion potential - E_{corr}, corrosion current density - i_{corr}, and polarization resistance - R_p, have been determined as a measure of corrosion resistance. The nanocomposite coatings obtained from optimized bath parameters, showed better corrosion protective ability and surface properties.

Keywords: Corrosion protection; Electrodeposition; Graphite oxide; Micro morphology; Nanocomposites; Scanning electron microscopy

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INTRODUCTION

Electroplating of zinc is a widely used industrial process to coat on steel for enhancing its service life because of its sacrificial nature. As zinc is electrochemically more active than steel and hence it sacrificially protect the steel from corrosion. The life span of the zinc coating and to avoid the white rust formation the alternative methods like surface modification using chromate is adopted. But the chromium salts and other organic agents which are used in surface modification process are toxic in nature and therefore their use is restricted [1]. The steel materials can also be protected by generating good zinc composite coating on its surface from plating bath. The generally used particles for zinc composite coatings are ceramics, polymers, metal oxides or metal carbides etc. In recent years nanoparticles instead of micro particles are employed largely in composite coating because of their advantageous properties along with their easy availability [2]. In metal-nanoparticle composites coating the second phase particles are oxides, carbides or nitrides of different metals.

The zinc and its alloys have been used extensively in industry due to their excellent fluidity, castability, cost effectiveness and good mechanical properties [3-7]. In situations where zinc plating is required to prevent atmospheric corrosion of cast iron, direct substitution of zinc foundry alloy may be possible [8,9]. Aluminium additions have been made to improve the luster or reflectivity of coating, reduce oxidation of the zinc bath and to obtain ductile coating by suppressing the formation of brittle Fe–Zn phases [10]. By the addition of high melting elements such as silicon to zinc-aluminum alloy to produce zinc-matrix composites with improved mechanical properties, wear resistance, fluidity and good thermal stability are achievable [11]. Very few data is available in the literature showing the effect of the alloying elements such as silicon on zinc-aluminum alloys corrosion resistance. Hence the present work has a scope in this area.

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Graphene and graphite oxides are is arguably the most intensively studied materials in recent times, as the graphene is a support material for metal nanoparticles to obtain catalytic, optoelectronic and magnetic properties, etc [12,13]. Graphene is often combined with other materials to form composites in which graphene adds conductivity while the co-material adds specific chemical or electrochemical activity. Graphene composites can either be mechanically blended together or covalently linked by carrying out specific chemical reactions involving the chemical functional groups of the polymer and of graphene oxide, also metal–graphene composites have been prepared [14,15]. These however usually include novel metals such as gold, platinum, palladium or silver, while graphene composites incorporating more reactive base metals have not yet been reported. This would be of great interest since such composites are of significant importance for energy storage/conversion applications and for electrocatalysis.

Metal/graphene composite films have been previously prepared using simultaneous co-deposition from one-pot aqueous reaction mixture [16,17]. These however involved anionic metal complexes such as $[PdCl_4]^{2-}$ or $[PtCl_6]^{2-}$. To the best of our knowledge, no effort was paid on using GO sheets as an additive to obtain nanocrystalline zinc, aluminium silicate sheets and the composites are expected to exhibit more excellent nano properties.

Thus the aim of this study is to study the electrodeposition of aluminium silicate, graphite oxide and cationic Zn^{2+} precursors and then co-deposit in an aqueous one-pot mixture both species simultaneously, resulting in the formation of composite films consisting of GO with active zinc metal.

EXPERIMENTAL SECTION

Chemicals and reagents
Natural graphite flakes, $ZnCl_2$, NaCl, $AlSiO_3$, HCl, CTAB, H_2O_2 (30%), $KMnO_4$ and cetyl trimethyl ammonium bromide are obtained for SD Fine chemicals, India. All the chemicals were of analytical reagent grades and used as received, without further purifications. The aqueous solutions were prepared in double distilled water. Natural graphite flakes were subjected to ultrasonication (Loba Life, India) in acetone for 1 hr. The graphite flakes were dried well and further oxidation was carried out by Hummers method [18].

Hull cell experiments
The standard Hull cell of 267-ml capacity was used to optimize the bath constituents and bath variables [19]. The bath parameters were optimized using a standard Hull cell. The electrodeposition process was carried out under galvanostatic condition using a regulated DC power source (Model: Acceptable Electronics, India). The cathode was mild steel panel and anode was pure zinc, Copper, Aluminum (99.99%). The pH of bath solution was measured using a digital pH meter (Equipetronix, model: 7020) and adjusted with 10% sulphuric acid or sodium bicarbonate solution. Mild steel (AISI-1079, composition C 0.5%, Mn 0.6%, P and S 0.05% and rest Fe) plates of standard Hull cell size were mechanically polished using emery paper (320-800 grit size) to obtain a smooth surface and degreased by dipping in boiling trichloroethylene in degreaser plant followed by water wash. Before each experiment, the aluminum anode surface was activated by dipping in 10% HCl for few seconds followed by washing with water. The same surface area of anode and cathode was used for electrodeposition process. The bath temperature and pH were varied. The cathodic current density was controlled at 1-2 A/dm^2. Various metal nano composites were obtained by optimizing bath parameters so that a uniform, thin, film obtained on a large surface area. After electrodeposition the plates were subjected to bright dip in 1% nitric acid for 2-3 s followed by water wash and drying. The nature and appearance of zinc deposit was carefully observed and recorded through Hull cell codes (Table 1).

Galvanostatic polarization studies
The corrosion studies were carried out under galvanostatic conditions using a conventional three-electrode electrochemical cell was used for polarization studies with SCE reference electrode, Pt counter electrode and the electrodeposited surface as working electrode.

Microhardness test
The Vickers microhardness of the deposit was determined by an indentation technique with a weight of 50g for 10 seconds using Clemex microhardness tester, made in Japan. The average of five replicated values was recorded.

Scanning Electron Microscopic studies
The surface morphologies of the composite samples were examined by scanning electron microscopy, using a ZEISS Supra 40 scanning electron microscope (SEM).

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Table 1: Bath parameters for electrodeposition of Zn-Al-GO nano composite

Basic bath composition		Optimized bath composition	
ZnCl2	160 g/L	ZnCl2	160 g/L
NaCl	200 g/L	NaCl	160 g/L
AlSiO3	24 g/L	AlSiO3	20 g/L
CTAB	1.75 g/L	CTAB	1.5 g/L
Current	1.7 A	Current	1.5 A
---	---	Graphite oxide	0.3 g/L
Voltage	2.7 V	Voltage	2.5V
Time	15 min	Time	10 min
pH	5	pH	6
Anode	Aluminium	Anode	Aluminium
Cathode	Steel	Cathode	Steel

EDAX analysis
The weight percentage of elements in the metal nano-composite coatings were verified by using energy dispersive X-ray analysis using FEI ESEM Quanta (EDAX) machine.

RESULTS AND DISCUSSION

Effect of various bath parameters and optimization of Bath Constituents
The Hull cell experiments with basic chloride bath solution gave coarse dull deposit with pores in the current density range 1-2 Adm^{-2} at 1.7A cell current in the basic bath, where as in the optimized bath it is improved to be closely packed and fine deposit. Basic bath constituents' concentrations were selected based on the appearance and uniform deposition covering maximum surface coating and to improve the nature of the deposit, which is obtained at different concentrations of all the constituents in the bath. The effect of addition agents were studied and optimized by generating composite coating from the bath solution containing different amount of GO as addition agent to the basic bath. The effects of various Hull cell parameters are represented as shown in the Figure 1. The bath parameters are is given in the table 1. At this concentration, cell current and pH the deposit was uniform and almost near to a bright deposit.

Effect of zinc chloride
Zinc chloride is the main salt of zinc ions in electroplating operation. There is a close relation between the concentration of zinc chloride and appearance of plating layer in Hull cell experiment. In order to get highly corrosion resistant composite deposit it is essential to strike a balance between amount of zinc chloride in the bath solution. To find out the effect of zinc chloride concentration on the deposit nature, zinc chloride concentration was varied from 80-200 g/l. According to the Hull cell experiment, the appropriate quantity of zinc chloride in plating solution was 160 g/l. At this concentration the deposit was uniform and large surface area covered in the current density range 0.5-2.0 Adm^{-2}. The effect of zinc chloride on deposit nature is shown in Figure 1.

Effect of sodium chloride
Sodium chloride was added to increase the conductance of the bath solution. The concentration of sodium sulphate was varied from 20-160 gL^{-1}. At low concentrations, the Hull cell panels suffered brittle and uncoated areas at low current density region. The deposit was nearly bright and large area covered over the current density range of 0.2-6 Adm^{-2}. Further increase in the concentration ($>160\ gL^{-1}$) the deposit became burnt at high current density region. The concentration of sodium chloride was fixed at 160 gL^{-1} in the bath solution.

Effect of Cetyl trimethyl ammonium bromide (CTAB)
The concentration of CTAB was varied from 0.5 - 2 gL^{-1}. At low concentration, the Hull cell panels suffered burnt deposit at high current density region and uncoated at lower current density region. There was a uniform, large

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surface area covered and a nearly bright deposit was obtained at a concentration of 1.75 gL^{-1}. The concentration of CTAB was fixed at 1.75 gL^{-1} in the bath solution.
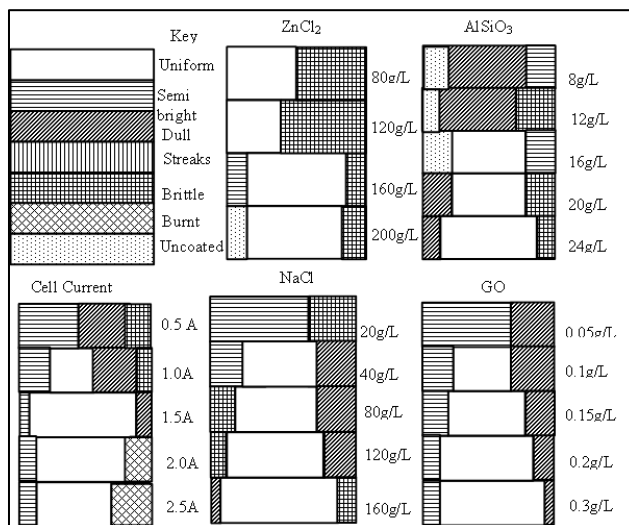

Figure 1: Variation of Hull cell parameters for electrodeposition of Zn-Al-GO nano composite

Effect of pH and temperature

The *p*H of the bath solution was varied from 1-7. At lower *p*H the specimens had uncoated areas at low current density region and burnt deposit at high current density region. At a *p*H 6 satisfactory deposit was obtained. At higher pH (>6) the Hull cell panels showed burnt deposit in the high current density region. From the above observations the pH of the bath solution was kept at 6 as optimum.

Hull cell experiments showed that the optimum temperature range to get bright deposit was 293-303 K. At higher temperature (> 303 K) the supply of ions to the cathode is fastened so that bad quality of deposit is obtained. And also rate of growth of nuclei is increased, leading to coarse grained, thick deposit. Hence from the above observations the optimum deposition temperature was kept at 303K.

Effect of cell current

The Hull cell experiments were carried out at different cell currents (1-3A) for 10 min using optimum bath solution. It was found that at a cell current of 1.5A the satisfactory deposit was uniform, large surface area covered and a nearly bright deposit in the current density range of 0.2-6 Adm^{-2}.

Effect of AlSiO$_3$

The large degree of codeposition of hydrophilic particles confirms that elimination of the hydration force achieved can significantly enhance the codeposition of such particles and can avoid the agglomeration that takes place in aqueous electrolytes. An almost semi bright and uniform deposit of composite was obtained at a concentration of 24g/L of AlSiO$_3$. [20-22].

Effect of graphite oxide (GO)

The concentration of GO was varied from 0.05-0.4 gL^{-1}. Graphite oxide was not uniformly distributed within aluminum because the agglomerates of graphite oxide can be found in the microstructure. It has also been suggested that GO is an amorphous state and can be easily dispersed in the aqueous medium. There are a large number of hydroxyl, carboxyl and other oxygen consisting groups in the GO structure. Hence with a small quantity of GO is incorporated in the composite coating. The expected deposit was obtained at 0.3 gL^{-1} of GO.

Zn ions are proposed to adsorb on the surface of GO sheets. Therefore, nucleation sites will easily form on the surface of GO sheets and the GO sheets will migrate to adsorb on matrix owing to the effect of adsorption and mixing. Moreover, there must be nucleation sites on the surface of matrix due to the applied electric field. Combining the two nucleation factors, the introduction of GO sheets leads to a rising in nucleation sites number which will accelerate the growth of zinc and changes the preferred orientation of the electrodeposited Zn [23].

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Micro hardness measurements

Microhardness values of composite-coated and basic bath coated samples were 175 and 130HV, respectively. It indicates that grain size of composite- coated sample was smaller than alloy-coated sample. The higher hardness of the coating was due to the fine-grained structure of the deposit. During hardness measurements, the dispersed particles in the fine-grained matrix may obstruct the easy movement of dislocations, which was shown by higher hardness values of composite-coated samples. The $AlSiO_3$ particles were codeposited in the Zn-GO matrix and restrained the growth of the alloy grains. Thus the microhardness of the composite coatings were significantly higher in presence of $AlSiO_3$ and GO. Because of higher mechanical properties the coating surface behavior changes and poses certain degree of resistance to corrosion and surface deterioration.

Surface morphology by SEM and EDX analysis

In Figure 2(A) and (B) are shown some SEM images of composite coatings on stainless steel from basic bath and optimized bath respectively.

Zn-Al-GO composite coating is deposited on the SS surface with the variable bath parameters. Aluminium silicate and GO were added to basic bath along with sonication to ensure a smart dispersion of graphene particles inside the aluminium on SS. The morphological characterization of as prepared samples was done using a scanning electron microscope as shown in Figure 2. In Figure 2 (A), it can be seen that, porous, net like structures are observed for the composite deposition from basic bath. This may be due to the less interfacial binding between SS surface and aluminium matrices solidification of porous different spots [24].
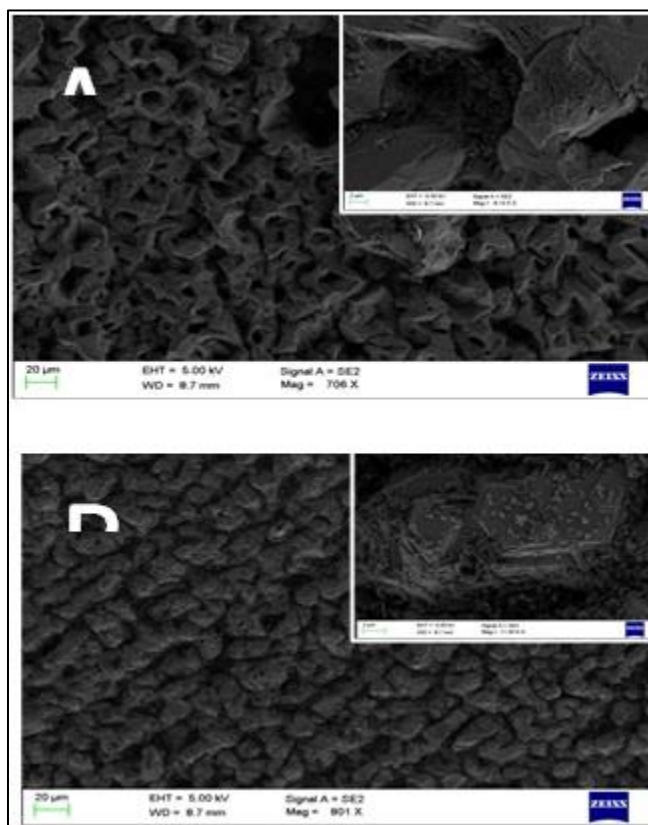

Figure 2: SEM images of (A) Zn-Al (B) Zn-Al-GO nano composite coatings on stainless steel from basic bath and optimized bath respectively. The insets are the corresponding high-resolution images

Although the graphite is a non-load bearing constituent, a strong particle/matrix interface helps graphite particles embed themselves into the matrix properly, improving the fracture resistance. An improvement in interfacial bonding between the graphite and aluminum matrix has been reported [25,26] as shown in Figure 2(B). In this investigation, good bonding between the graphite oxide particle and the matrix is evident as shown flake like structure in the inset picture of Figure 2(B). Hence there is no sign of void formation or extensive separation at the

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particle-matrix interface. The particles are well embedded in the matrix and the fracture shows ductile behavior as river patterns are quite prominent. Scanning electron microscopy of the composite also supports the fact that the interface is clean and sharp without any evidence for the formation of open pores on the substrate.

Figure 3 and Table 2 show the EDS spectra and the quantitative elementary analysis of Zn-Al-GO composite coating obtained from the optimized bath respectively. The EDS spectrum indicates that a strong particle/matrix interface helps graphite oxide particles embed themselves into the matrix properly in the composites because of the presence of nearly 30% C and 65% O, and 5% Al by atomic percentage as shown in the table 2. Hence there is an improvement in interfacial bonding between the graphite and aluminum on steel substrate [27,28].
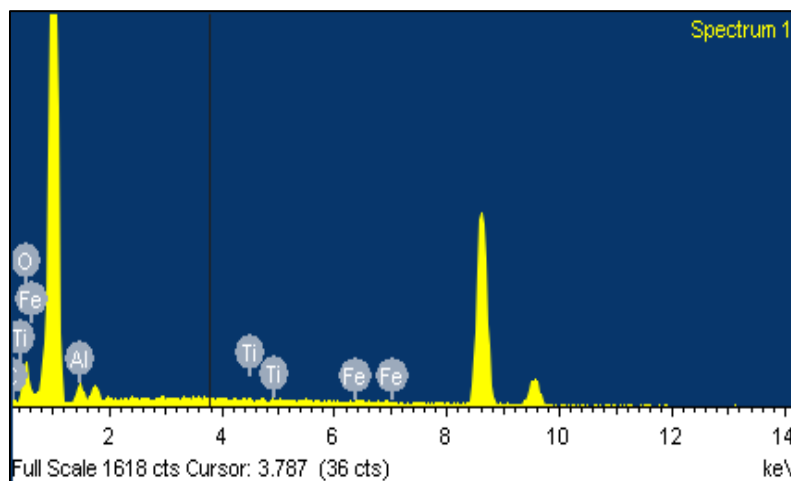

Figure 3: EDS spectrum of Zn-Al- GO nano composite coatings on stainless steel from optimized bath

Table 2: Quantitative Elementary Analysis (EDAX) of Zn-Al-GO nano composite coatings

Element	Weight %	Atomic %
C K	23.17	29.65
O K	68.03	65.34
Al K	8.79	5.01
Ti K	0	0
Fe K	0	0

Electrochemical corrosion studies

The electrochemical polarization measurements out under galvanostatic conditions were carried out in 0.05, 0.1 and 0.2 HCl solution to study the corrosion behavior of the surface nano composite coatings coating which were generated on SS from the basic optimized bath. The galvanostatic polarization curves obtained from 0.2N HCl for the steel samples coated with nano composites from basic bath and optimized bath are shown in Figure 4.

In order to study the effect of GO content and Al on the corrosion behavior of SS, galvanostatic polarization was carried out electrode immersion in 0.05, 0.1 and 0.2N HCl solution. The extent of corrosion protection by this composite coating was obtained from Tafel plots. The polarization curves were not much shifted towards either positive or negative potentials in case of composite-coated samples from the optimized bath when compared to that of basic bath as shown in the Figure 4. The values of E_{corr} and I_{corr}, were obtained from Tafel plots for electrochemical polarization in 0.2N HCl is as given in Figure. It is generally agreed that the cathodic reaction for Al in aerated near neutral pH solutions is the oxygen reduction followed by its adsorption [29,30].

The value of I_{corr} reduced to 1.9 mAcm^{-2} from 0.4 mAcm^{-2} for optimized bath. This shows the corrosion resistance of the composite coating incorporated with GO is increased and there is a formation of passive film on the surface [31].
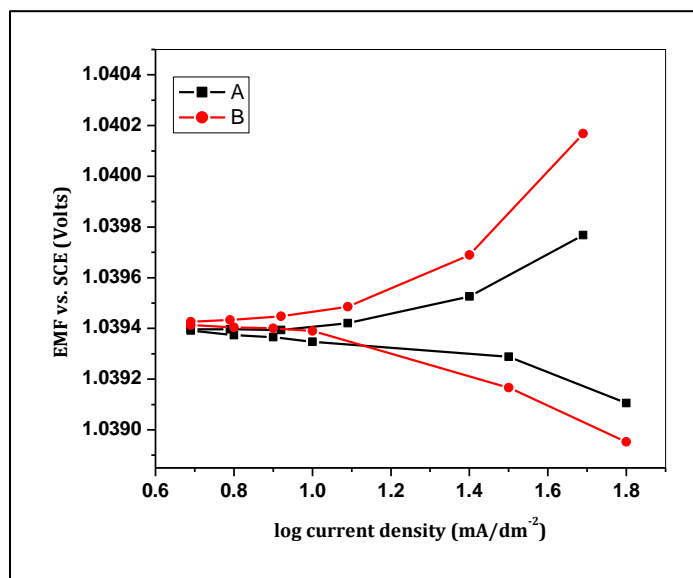
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Figure 4: Galvanostatic polarization curves in 0.2N HCl for Zn-Al-GO nano composite coatings on stainless steel from A) basic bath and B) optimized bath

With increase in acid concentration the corrosion resistance is little decreased, may be due to the insertion of the acid into the pores of the coating. The corrosion parameters are given in the Table 3.

Table 3: Corrosion parameters for of Zn-Al-GO nano composite coatings in HCl of different concentrations

Electroplating bath	Corrosion medium					
	0.05N HCl		0.1N HCl		0.2N HCl	
	Ecorr (V)	Icorr (mAcm-2)	Ecorr (V)	Icorr (mAcm-2)	Ecorr (V)	Icorr (mAcm-2)
Basic	1.0392	1.1	1.0392	1.5	1.0392	1.9
Optimized	1.0392	0.2	1.0392	0.4	1.0394	0.4

The improved corrosion protection in the presence of GO can be explained by two mechanisms of the nanocomposite coatings. First, the GO nanoparticles act as inert physical barriers by occupying very small pores in the metal matrix, which modifies the Zn layer microstructure and provides a superior corrosion resistance of the composite coating in comparison with the pure alloy coating.
Also surface passivation can occur due to formation of firmly bonded, hard and non-porous layer. The degree of passivation will depend on the acidity of the environment. The passivation of the surface of the coating will also affect its ability to provide cathodic protec tion. Hence aluminium will be transformed into aluminium oxide, thereby creating a barrier that is non-porous, except in saline atmospheres [32,33]. The composite coating form protective films of Aluminium compounds according to the nature of the metal being protected, providing anodic and cathodic protection. This is due to the dissolution of silica restricts the pH increase at cathode [34].

CONCLUSION

A nanocrystalline Zn-Al-GO was electrodeposited on mild steel from simple chloride bath. The technique adopted to obtain the Zn-Al-GO composite is a versatile technique and is a technologically and economically viable production route to metals, alloys and metal matrix composites, both in bulk form and as coatings. The obtained composite coatings by varying the bath parameters, shown better and improved surface mechanical properties. The deposits obtained from optimum bath are highly corrosion resistant, as it was evident by SEM, EDAX and electrochemical studies. The higher corrosion resistance could be attributed to the presence of GO in the composite matrix.

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