Effect of Nano-Zinc Oxide Particles on the Performance Behavior of Waterborne Polyurethane Composite Coatings

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Abstract- **A nano-composite coating was formed by incorporating nano-ZnO pigments in a waterborne polyurethane dispersion (WPUD) to different loading levels (0.1% and 1.0% by weight). Corrosion performance of the nano-composite coatings were evaluated by applying these nano-composites coatings on mild steel substrate and exposing them to salt-spray, humidity and accelerated UV-weathering. Mechanical properties like scratch resistance, abrasion resistance and pencil hardness were also studied. The electrochemical performance and mechanical properties of the composite coatings were evaluated using various analytical techniques. FTIR technique was used to investigate the interaction between nano-ZnO particles and the polymer functionalities. SEM and AFM were used to investigate dispersion of nano-ZnO particles and the changes in the surface behavior of the modified coatings before and after exposure to the test environment. The optical property of the coating was evaluated using UV-Visible spectrophotometer. The results showed an improvement in the corrosion, UV and mechanical properties of the coatings at lower concentration (0.1% by wt), indicating the positive effect of addition of nano-ZnO particles in the coatings. It was found that the optical transparency of the coating was not altered at lower loading level of nano-ZnO particles.**

Key Words- Waterborne; Polyurethane; Nano-Zno; Corrosion Resistance; UV Resistance

I. INTRODUCTION

An aqueous polyurethane dispersion is a binary colloid system in which polyurethane particles are dispersed in a continuous aqueous medium [1, 2].The basic building blocks of solvent borne polyurethanes like diisocyanates, polyols, amines catalysts and additives are common to aqueous based system as well [3]. Though, the development of aqueous polyurethane dispersions was motivated primarily by environmental considerations, one technical advantage of aqueous polyurethane dispersion is that the viscosity of dispersion is independent of the molecular weight of polymer. Thus, polyurethane dispersion can be prepared at a high solid content with a molecular weight high enough to form films with excellent performance solely by physical drying [2]. Economical aspect is another reason as they do not contain the expensive solvents [3]. Compared to their solvent counterparts, polyurethane dispersions can offer the following advantages: viscosity and flow properties independent of molecular weight, the absence of external emulsifiers, environmental safety, good adhesion, and rheology characteristics [4]. Other advantages which make them attractive as waterborne coatings are the outstanding properties of solvent, stain, chemical resistance, toughness with flexibility [5].

With the quest for new developed coating systems with better performance, aqueous based polyurethane coatings are modified with various nano-particles [6-13]. Nanotechnology presents a wide range of opportunities to improve performance of coatings and promises to deliver breakthrough performance specifically with respect to scratch and mar resistance, barrier properties including corrosion resistance and mechanical properties [14, 15]. Optical clarity is one of the many features of nano-particles, extremely important in expanding nano-particle applications in coatings. They can be added to a clear coating formulation with little or no adverse impact on visual characteristics. Nano-particles most commonly used in coatings are SiO2 [7, 11, 12, 13], TiO2 [16], ZnO [6, 8, 9, 17], Al2O3 [18.19], Fe2O3 [20] and CaCO3 [21]. Use of nano-particles are most commonly based on the inherent properties they posses. For example nano-titania and nano-zinc oxide are most commonly used as UV blocking agents, whereas nano-alumina and nano-silica are used to improve scratch and abrasion resistance of the coating. The enhanced properties are result of the much greater surface to volume ratio of the nano-pigment that is often characterized by very high aspect ratios [23].

Present study refers to the effect of addition of nano-zinc oxide on water-borne polyurethane coating system at two different loading levels (0.1% and 1.0% by weight). The nano-modified coatings were applied on pretreated mild steel panels by dip coating techniques. Dip coating techniques can be described as a process where the substrate to be coated is immersed in a liquid and then withdrawn with a well-defined withdrawal speed under controlled temperature and atmospheric conditions. The coating thickness is mainly defined by the withdrawal speed, by the solid content and the viscosity of the liquid. Dip coating was used keeping into view the industrial viability of the coating. Using this technique uniform film can be applied onto flat and cylindrical substrates with ease and high production rates and high transfer efficiency. The process is cost effective and requires low labor as compared to other application process. The performance behavior of the nano-particle modified coating systems with respect electrochemical, UV resistance and mechanical properties was investigated.

II. EXPERIMENTAL

A. Material Used

Nano-ZnO with a mean size of 35 -40 nm and specific area of 29 m2g-1 was procured from Horsehead Corporation Company (USA). A one pack water-borne polyurethane dispersion (WPUD) based on aliphatic urethane was procured from Dooall Corporation Pvt. Ltd, India.

B. Preparation of Nano-Particle Modified Polyurethane Waterborne Coating

Waterborne polyurethane dispersion (WPUD) was stabilized with nano-zinc oxide pigments in different concentrations by Ultrasonic probe dispersion equipment for about 45 minutes until a clear coat was obtained. The nano-modified coating system thus formed was applied on pretreated cold roll milled steel panels by dip-coating. Pre-treated mild steel substrates were immersed in the solution of the coating material at a constant speed and held in coating bath for a while. The substrate was pulled up from the bath while the thin layer of the coating deposits itself on the substrate. The excess coating dripping from the substrate was wiped off and the coating was allowed for oxidative curing at room temperature for 24 hours. The coating thickness was found to be 10 µm. The coated panels were used for electrochemical and mechanical characterizations.

III. RESULTS AND DISCUSSION

A. Characterization of Nano-Composite Coating

The interaction of nano-particles with base matrix was investigated using Fourier transform infra-red spectroscopic (FTIR, Nicolet Magna 550 FT-IR spectrometer). Electrochemical behavior of the coating was investigated by exposing the test panels to Salt Spray (ASTM B117), Humidity (ASTM D2247) and UV weathering (ASTM G53). Mechanical properties were studied by Scratch (BS.3900), Taber abrasion (ASTM D4060) and pencil hardness (ASTM D-3363-05) methods. Optical property was studied using UV-Vis spectrophotometer (Shimadzu UV-160A) surface morphological studies were carried out using Scanning Electron Microscopy (SEM, Model no.S3400, Hitachi) and Atomic force microscopy (AFM, Digital Instrument Nanoscope IV).
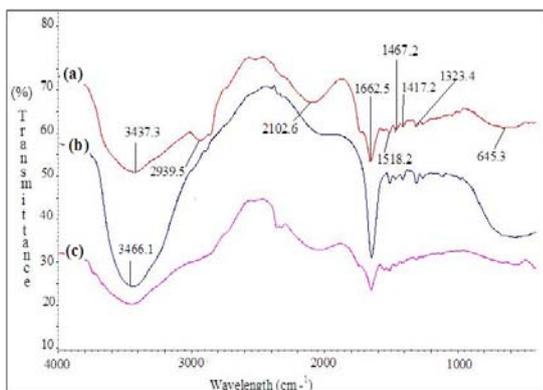

Fig. 1 Shows the FT-IR spectra of (a) Neat-WPUD and WPUD modified with (b) 0.1% nano-ZnO and (c) 1.0 % nano-ZnO.

B. Fourier Transform Infra-Red Spectroscopic (FTIR) Analysis

Fig. 1 shows the overlay FTIR spectra of neat-WPUD coating and nano-ZnO modified composite coatings. The functional groups corresponding to the particular frequencies are given in Table I and Table II respectively. From (Fig. 1a) N-H stretching in neat WPUD is observed at 3437.3 cm-1, while in WPUD modified with 0.1 % nano-ZnO, the N-H stretching peak lies at slightly higher value of 3466.1 cm-1(Fig. 1b). The probable reason for this shift is attributed to hydrogen bonding between N-H and free NCO groups in neat-WPUD. After adsorption of WPUD on nano-ZnO surface,

the hydroxyl groups on nano-ZnO gets hydrogen bonded with NCO groups on WPUD. Thus, N-H groups are constrained by nano-ZnO surface and thus cannot form hydrogen bonds. Therefore, N-H stretching appears at a higher frequency in IR spectrum and on other hand, N-H group can easily find a carbonyl group to form hydrogen bonds to stabilize the system. It thus suggests a strong interaction between polymer and nano-ZnO particle [8]. Similar results were obtained for WPUD modified with 1.0% nano-ZnO. (Fig. 2c). Also, reduction of peek intensity at 2939.5 cm-1 (C-H stretching in neat-WPUD) in modified coating indicates the interaction of nano-particle surface with the polymer functionality.

TABLE I BAND ASSIGNMENT FOR NEAT-WPUD

Band (cm^{-1})	Assignments
2939.5	C-H Stretching
3437.3	N-H Stretching Due to Hydrogen Bonding
1662.5	C=O Stretching
1323.4	C-N Stretching

TABLE II BAND ASSIGNMENT FOR NEAT-WPUD MODIFIED WITH NANO-ZNO PARTICLES IN DIFFERENT CONCENTRATIONS

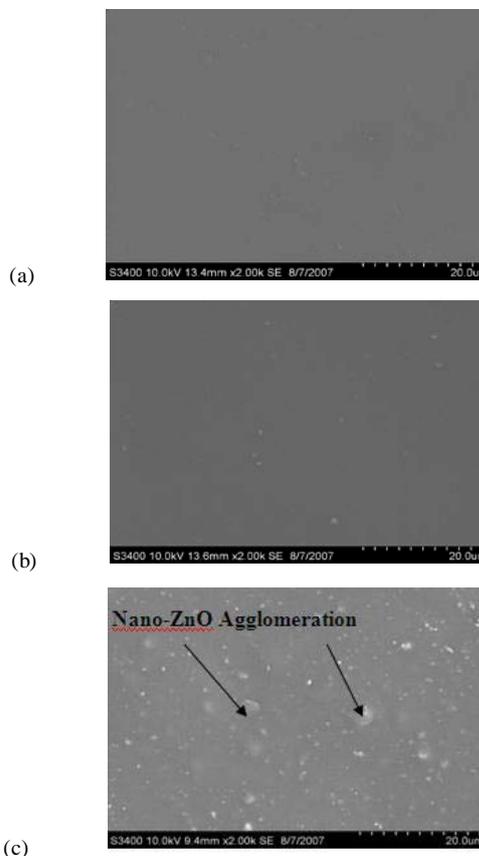| Band (cm-1)	Assignments
3466.1	N-H Stretching (Free) i.e. without Hydrogen Bonding
1662.5	C=O Stretching
1316.2	C-N Stretching

Fig. 2 SEM surface micrographs of unexposed samples: (a) Neat-WPUD,

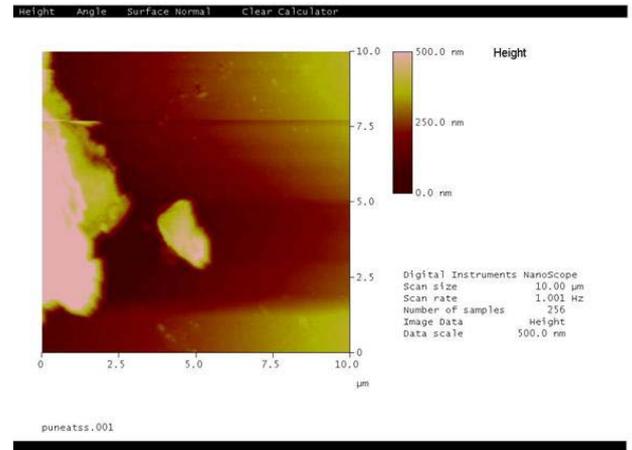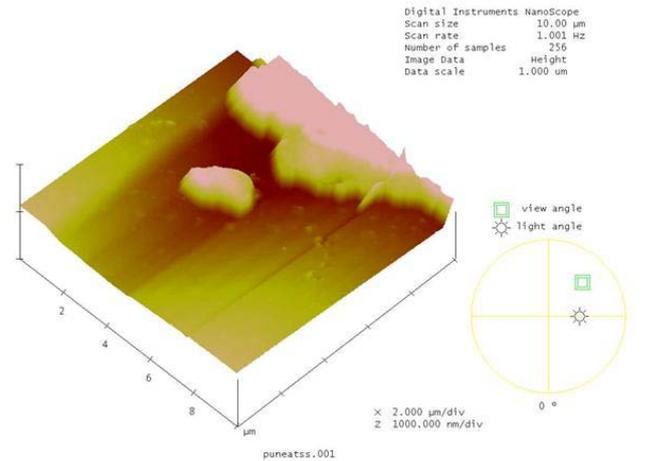(b) WPUD + 0.1% nano-ZnO and (c) WPUD + 1.0 % nano-ZnO

IV. ELECTROCHEMICAL ANALYSIS

Fig. 2 shows the SEM micrographs of neat-WPUD coating and coating modified with nano-ZnO particles in different loading levels, before exposure to the test environments. From Fig. 2a, it can be clearly seen that the coating formed is uniform and free from heterogeneity on the surface. After modifying WPUD with nano-ZnO particles, the coating modified with 0.1% nano-ZnO particles (Fig. 2b) show uniform surface morphology indicating proper dispersion of nano-particles, while the surface micrograph of coating modified with 1.0 % nano-ZnO particles (Fig. 2c) show white spots all over the surface indicating agglomeration of the nano-particles.
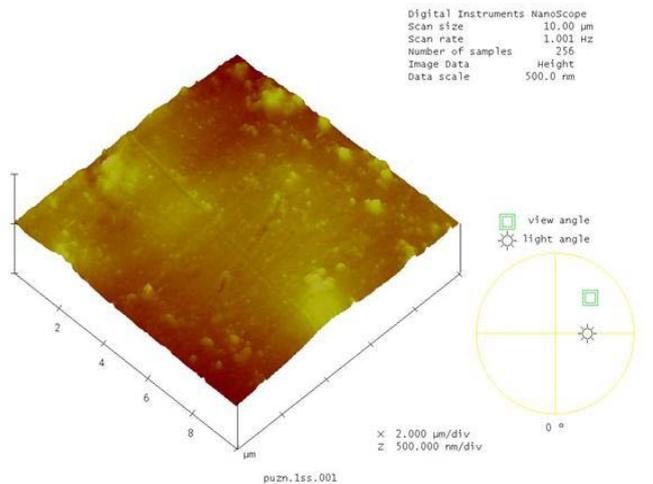
Fig. 3 shows the surface micrographs of the neat WPUD and nano-composite coatings after 800 hours of exposure in salt spray chamber. From Fig. 3a, it can be seen that the coating degradation after exposure to salt spray is more distinct in neat sample than those modified with nano-ZnO particles, indicating that the neat WPUD coating has undergone chemical changes during exposure. However, the performance was better for the coating modified with 0.1% nano-ZnO (Fig. 3b) than for coating modified with 1.0 % nano-ZnO (Fig. 3c). At lower loading level, the concentration of nano-ZnO particle is so small that the well-disperse particles in the coating restricts the diffusion of the corrosive electrolyte through the coating film acting as an effective barrier. It may be attributed that for lower loading level of nano-ZnO, the well-dispersed particle having large surface area and small size absorb more resin on its surface which enhances the density of the coatings thereby reducing the transport paths for the corrosive electrolyte to pass through the coating and consequently reducing the corrosion process [9, 24, 25]. At higher loading level the increase in the number of particles form agglomerates because of their high surface activity introducing defect in coatings. These defects act as site for electrochemical reaction affecting the coating performance. AFM topographic images for salt-spray exposed samples for 800 hours also provide the same information (Fig. 4). As can be seen from Fig.4a, the surface of neat sample is completely heterogeneous as compared the surface of coatings modified with nano-ZnO particles (Fig. 4b and Fig. 4c), which show a little change on the surface appearance, indicating better protection.
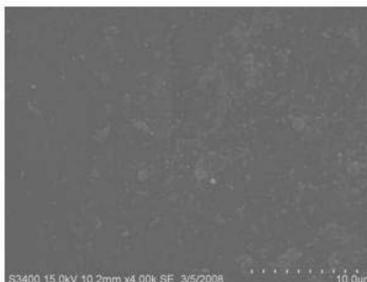

(a)

(b)
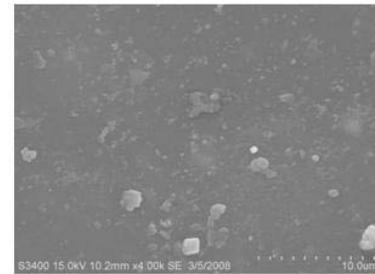
(c)

Fig. 3 SEM micrographs of salt-spray exposed samples: (a) Neat-WPUD, (b) WPUD + 0.1% nano-ZnO and (c) WPUD + 1.0 % nano-ZnO
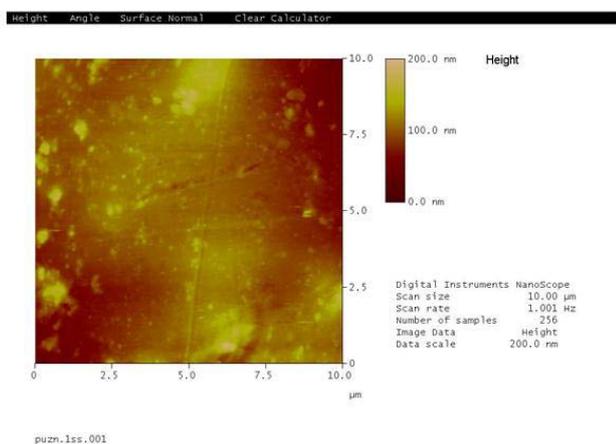

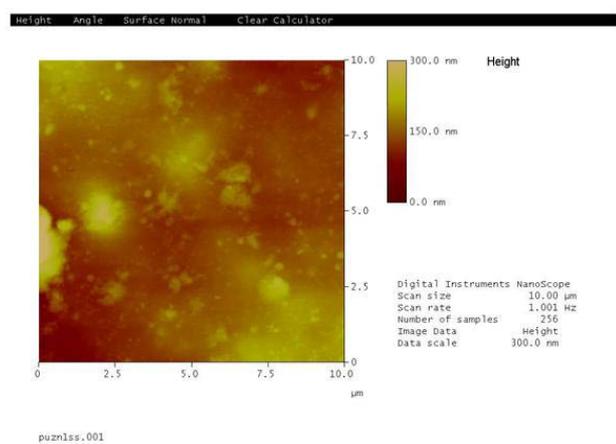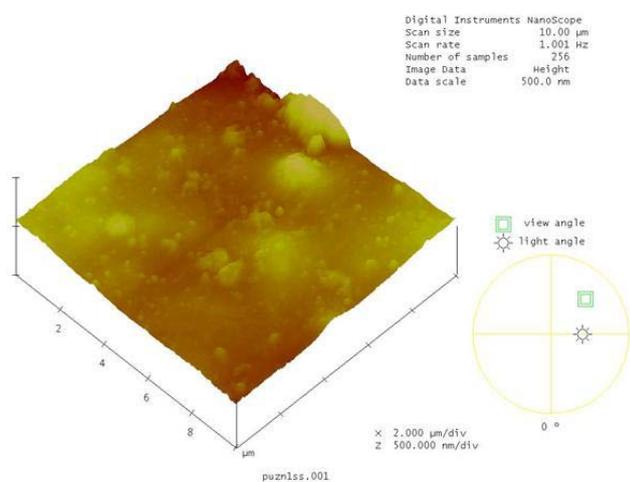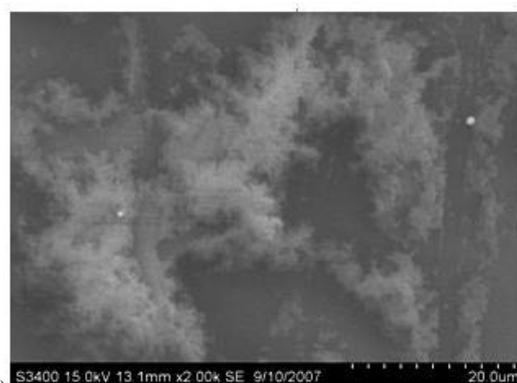(a)
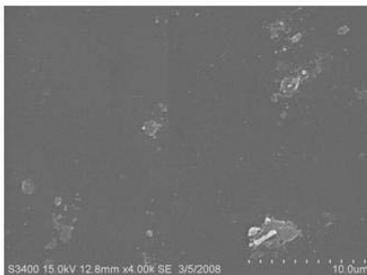
(b)

(c)

Fig. 4 AFM topographic height images of Salt-spray exposed coating surface at a scan size of 10μm x 10μm (a) Neat-WPUD, (b) WPUD + 0.1% nano-ZnO and
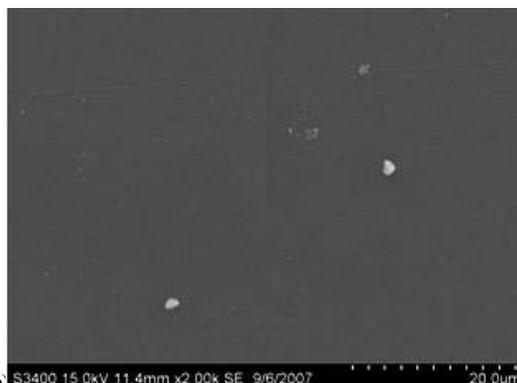
(c) WPUD + 1.0 % nano-ZnO

Fig. 5 shows the SEM micrographs of humidity exposed samples for 1000 hrs. The surface micrograph of the neat sample (Fig. 5a) shows presence of blisters all over the surface. This indicates that the coating has undergone drastic changes during exposure leading to the failure. With the incorporation of nano-ZnO pigment in the coating system, no such defects were observed. Fig. 5b and Fig. 5c represent the SEM surface micrographs of the coating modified with nano-ZnO particles at different concentrations respectively. As can

be seen from the SEM micrographs (Fig. 5b) coating at lower loading level (0.1%) appears more uniform and devoid of areas of delamination, degradation and blisters. This again can be attributed to proper pigment concentration and dispersion in the polymer matrix. Also, the interaction of the nano-ZnO with the polymer is strong, whereby the strongly bounded interface does not allow the permeation of water. However, at higher loading level some pinholes and other heterogeneities are clearly observed at the agglomerated sight (Fig. 5c). AFM topographic height images (Fig. 6) for humidity exposed samples also provide the parallel observations. Fig. 6a represents AFM image of neat samples showing completely distorted surface, indicating changes in the surface roughness and microstructure of the coating. Coating system with lower concentration of nano-ZnO particles (0.1% by wt) show little change in the surface roughness and microstructure of the coating (Fig. 6b) as compared to the coating system (Fig. 6c) with higher loading level (1.0 % by wt), suggesting the improvement in the humidity resistance of the coating.

(a)

(b)
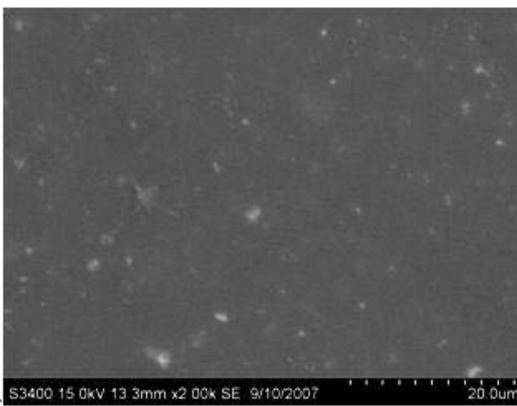
(c)

Fig. 5 SEM micrographs of humidity exposed samples: (a) Neat-WPUD,

(a) WPUD + 0.1% nano-ZnO and (c) WPUD + 1.0 % nano-ZnO
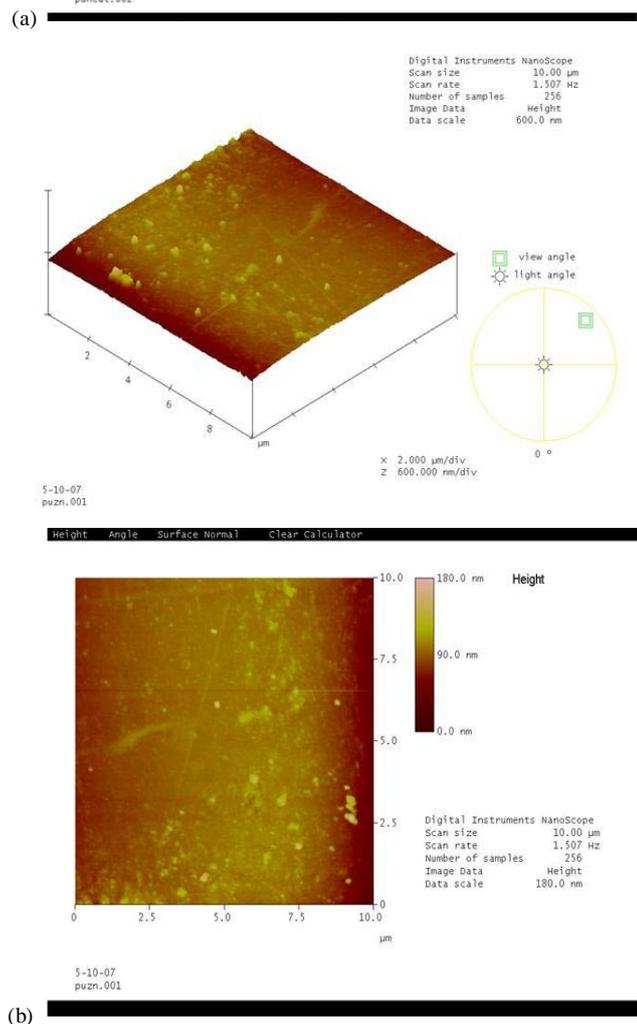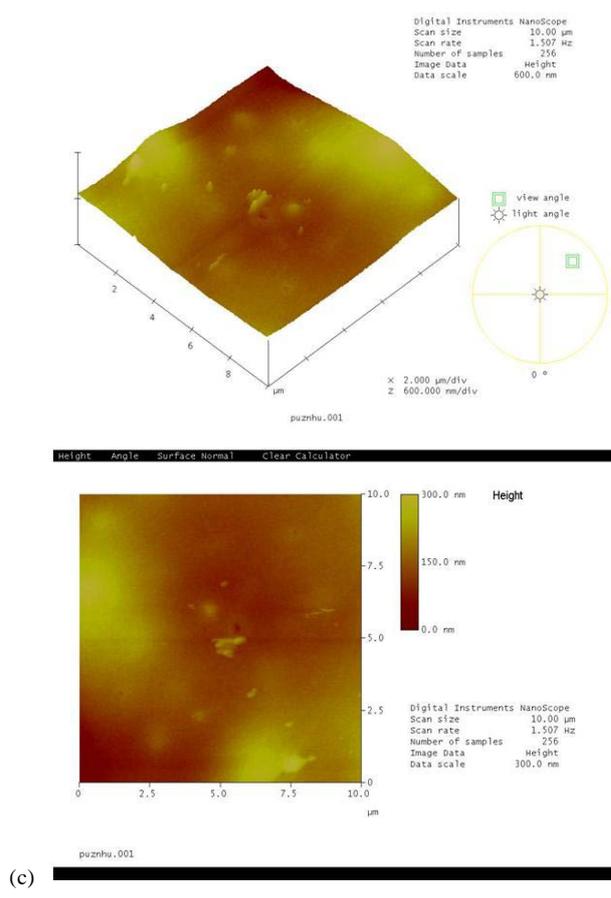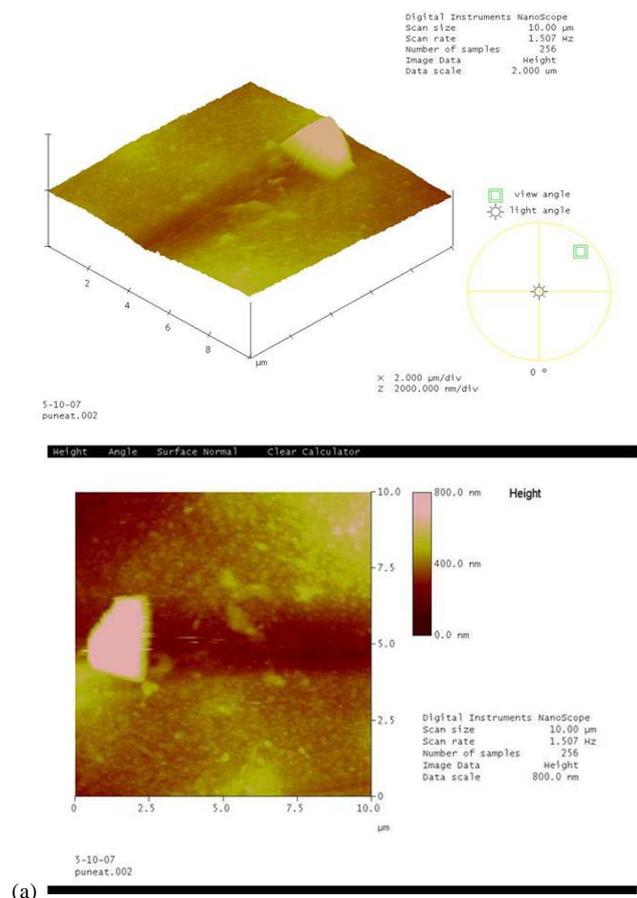
(a)

(c)

Fig. 6 AFM topographic height images of humidity exposed coating surface at a scan size of 10μm x 10μm: (a) Neat-WPUD, (b) WPUD + 0.1% nano-ZnO and

(c) WPUD + 1.0 % nano-ZnO

Fig. 7 shows the surface micrographs of UV exposed samples after 1000 hours, where the source of irradiation used was UV-B lamp which emits wavelength of 313 nm. The degradation of coating due to photo-chemical interaction is distinctly observed in neat- WPUD coated sample. The presence of surface heterogeneity clearly indicates the degradation of coating due to long term exposure to UV radiation (Fig. 7a). The coating modified with nano-ZnO showed an improvement in the UV resistance. No changes were observed for the coating modified with 0.1% of nano-ZnO (Fig. 7b). However, for coating modified with 1.0 % of nano-ZnO (Fig. 7c) appearance of pin-holes are clearly observed. This suggests that, though the induction time for surface degradation is delayed, the performance of the coating was inferior as compared to the coating modified with lower concentration of nano-ZnO. The improvement of UV resistance of the modified coating can be attributed to the fact that, nano-ZnO has a wide band gap (3.37 eV) and large excitation binding energy of 60 meV, therefore it can absorb light that matches or exceeds their band gap energy and which lies in the UV range of the solar spectrum [26, 27] . Thus, a well dispersed nano-ZnO particles attenuate UV radiations and protects the polymer matrix from degradation. Fig. 8 shows the AFM topographic height image of UV exposed samples. For Neat-WPUD coating the surface appears to be more heterogeneous with increased roughness, indicating surface degradation (Fig. 8a). Coating with 0.1% nano-ZnO shows effective improvement in UV blocking properties (Fig. 8b). It can be attributed that the small surface area per unit mass and volume increases the effectiveness of the blocking

(b)

UV radiation and prevent photo-degradation of base polymer matrix. Also, nano-ZnO due to their ceramic nature are inherently stable [28] and at this dimension posses lower photochemical activity [29] thereby providing good UV blocking property to the coating system without interacting with the UV radiation. However, the performance of nano-ZnO at higher loading level is not satisfactory, as presence of pinholes and cracks are clearly seen (Fig. 8c) due to formation of agglomeration in the coating matrix.
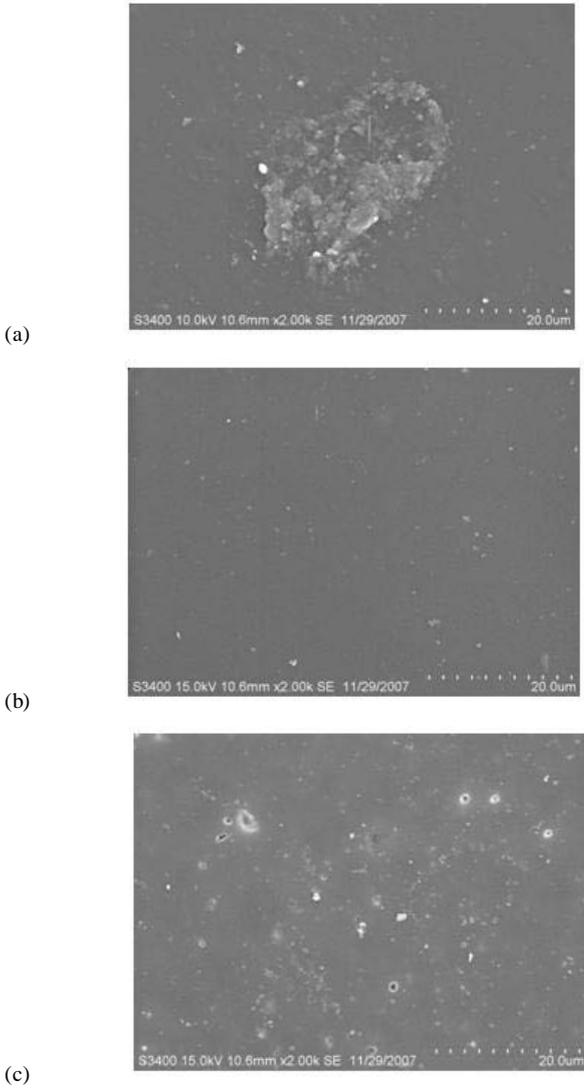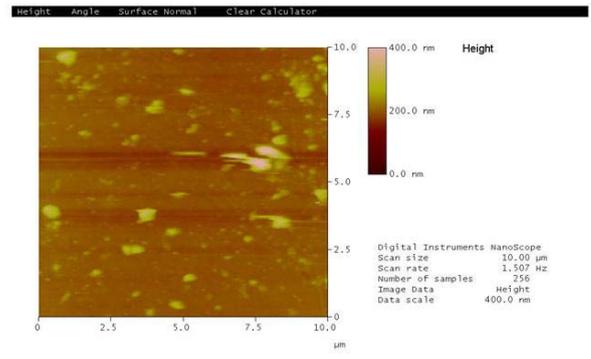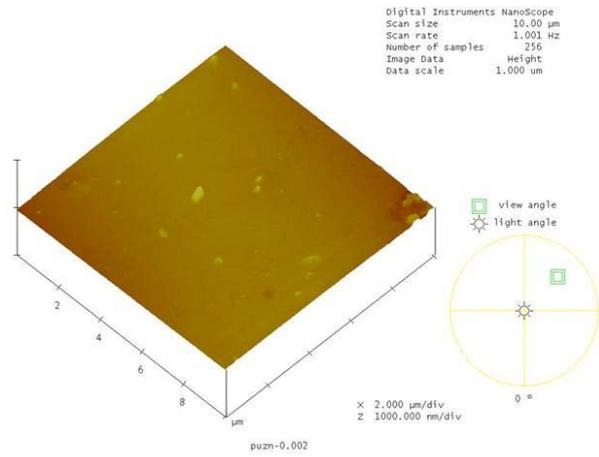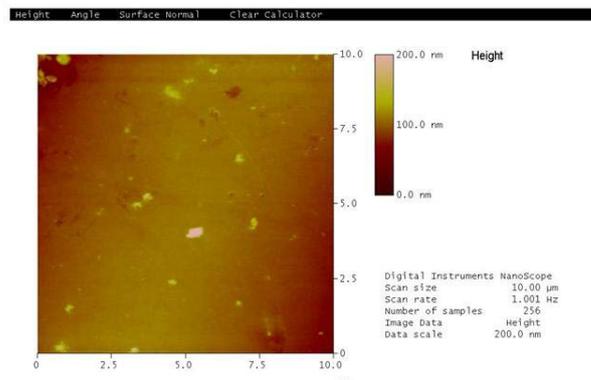
(a)

(b)

(c)

Fig. 7 SEM micrographs of UV exposed samples: (a) Neat-WPUD, (b) WPUD + 0.1% nano-ZnO and (c) WPUD + 1.0 % nano-ZnO

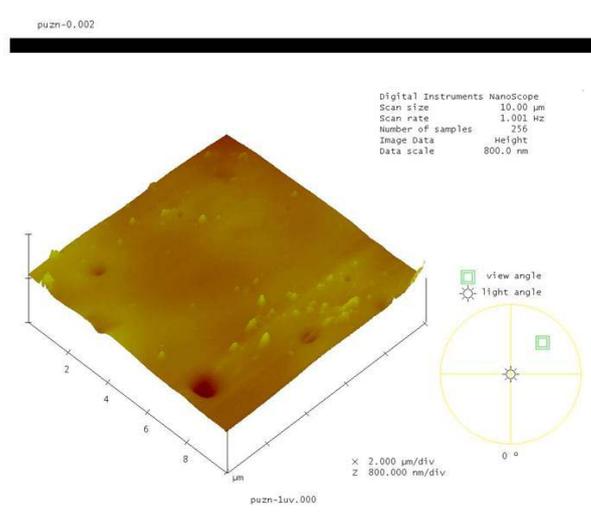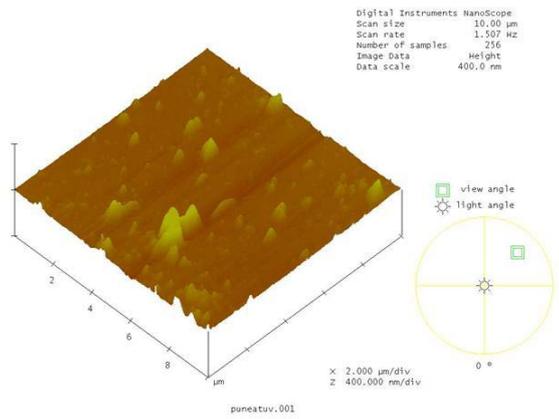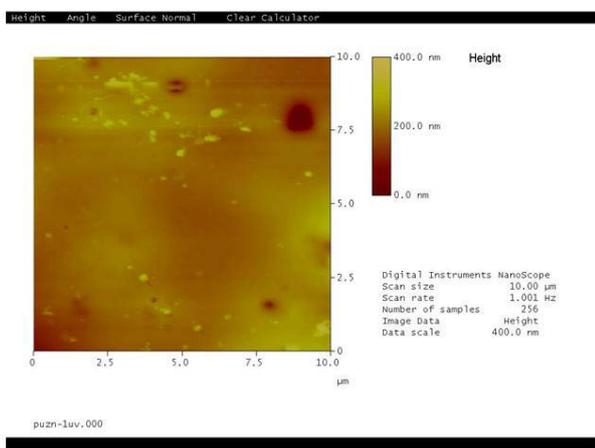(a)

(b)

(c)

Fig. 8 AFM topographic height images of UV exposed coating surface at a scan size of 10μm x 10μm: (a) Neat-WPUD, (b) WPUD + 0.1% nano-ZnO and (c) WPUD + 1.0 % nano-ZnO

V. AFM SURFACE ROUGHNESS ANALYSIS

Table Ⅲ represents the surface roughness values for neat-WPUD and nano-ZnO modified WPUD coating system before and after exposure to the test environment. After exposure to various test environments it was found that the surface roughness of neat sample is higher due to breakdown of polymer matrix as compared to the surface roughness of nano-particle modified coating. This suggests the improvement in the properties of the coating after modification. However, the surface roughness of coating modified with 0.1% nano-ZnO was relatively less then the coating modified with 1.0 % nano-ZnO, suggesting that for a higher loading level of nano-particles the resin available is not sufficient to fill all inter-pigmentary interstice leading to porous film with inferior corrosion resistance.

TABLE Ⅲ AFM SURFACE ROUGHNESS VALUES (NM) MEASURED FOR COATINGS EXPOSED TO SALT SPRAY, HUMIDITY AND UV RADIATION

Test	Neat-WPUD	WPUD + 0.1% Nano-Zno	WPUD + 1.0% Nano-Zno
Salt Spray	128.66 nm	22.00 nm	34.04 nm
Humidity	132.71 nm	14.55 nm	46.24 nm
UV-Weathering	20.54 nm	13.00 nm	23.00 nm

VI. OPTICAL STUDY

Fig. 9 shows the transmittance spectra of neat-WPUD and nano-ZnO modified WPUD. From the graphs it can be seen that the transmission values for the neat-WPUD and WPUD modified with 0.1 % nano-ZnO particles are ranged between 80%-95%. This indicates that the transparency of the coating system is not much affected on addition of nano particles, supporting the fact that nano-particles do not affect the clarity of the coatings. This may be because of the fact that, particles in nano-dimension are smaller than the wavelength of visible light and so no scattering and reflecting occurs in the visible light range leading to transparent nano-composite [30]. However, the transmittance value for WPUD modified with 1.0% nano-ZnO particles is ranged between 50-60 %. This is due to formation of agglomerates of nano-ZnO particles that protrude out on the film increasing the surface roughness of

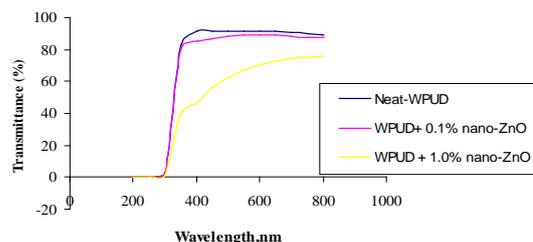the coating resulting into reduced optical transparency of the coating.

Fig. 9 Transmittance spectra of neat-WPUD and nano-ZnO modified WPUD in different concentrations as labeled

VII. MECHANICAL CHARACTERIZATION

A. Scratch Resistance

Fig. 10 shows the variation of load (weight in grams) with different concentartion of ZnO nano-particles during scratch test. From the graph it can be seen that the neat-WPUD coating is resistant to scratch at a load of 700 gm, while nano-ZnO modified WPUD coated sample showed resistance to scratch at loads of 1100 gm and 900 gm for 0.1% and 1.0% loading levels, respectively. The improvement in the scratch resistance of the coating at lower level (0.1 % by wt) can be attributed to the strong bonding network between functionalities of polyurethane and nano-ZnO particles along with their propre dispersion, which provides more resistance to scratch causing less deformation in the sample [31]. The decrease in the scratch resistance at higher loading (1.0 % by wt) may be attributed to the heterogeneities in the coating system due to aggregate formation that remained poorly dispersed in the matrix, causing inferior bulk properties at higher loadings.
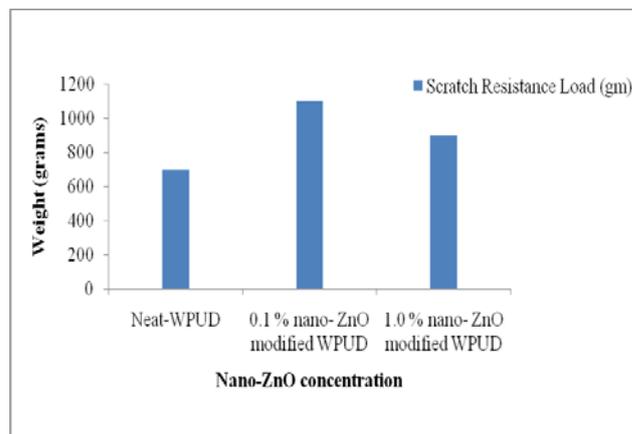
Fig. 10 Effect of the nano-ZnO concentration on the scratch resistance of WPUD

B. Abrasion Resistance

Taber Abrasion test was carried out to determine the abrasion resistance of coating. Depending upon the thickness of the coating, a specified number of revolutions was performed (1000 cycles) with all coated samples. Fig. 11 shows the SEM micrographs of taber abraded coatings. It can be seen from Fig. 11a, that the coating systems without nano-ZnO are completely wearied with more distorted surface morphology indicating poor response to abrasive action. With

incorporation of nano-ZnO particles, the improvement in abrasion resistance of the coating was observed. Coating modified with 0.1% nano-ZnO (Fig. 11b) showed better abrasion resistance then the coating modified with 1.0 % nano-ZnO (Fig. 11c). The differences in the coating performance are related to the dispersion state of the nano-particles and the volume fraction of the polymer surrounding the particles. For coating modified with 0.1% of nano-ZnO, it may be attributed that strong surface interaction between the dispersed nano-ZnO surface and polymer matrix results into compact coating providing strength against abrasive action. However, for coating with 1.0 % loading of nano-ZnO, the formation of aggregates decreases the effective surface area of the particle, which in turn decreases the volume fraction of the interphase region. Agglomerate formation in coating introduces defects which act as preferential sites for crack initiation leading to abraded surface morphology indicating poor abrasion resistance [31].
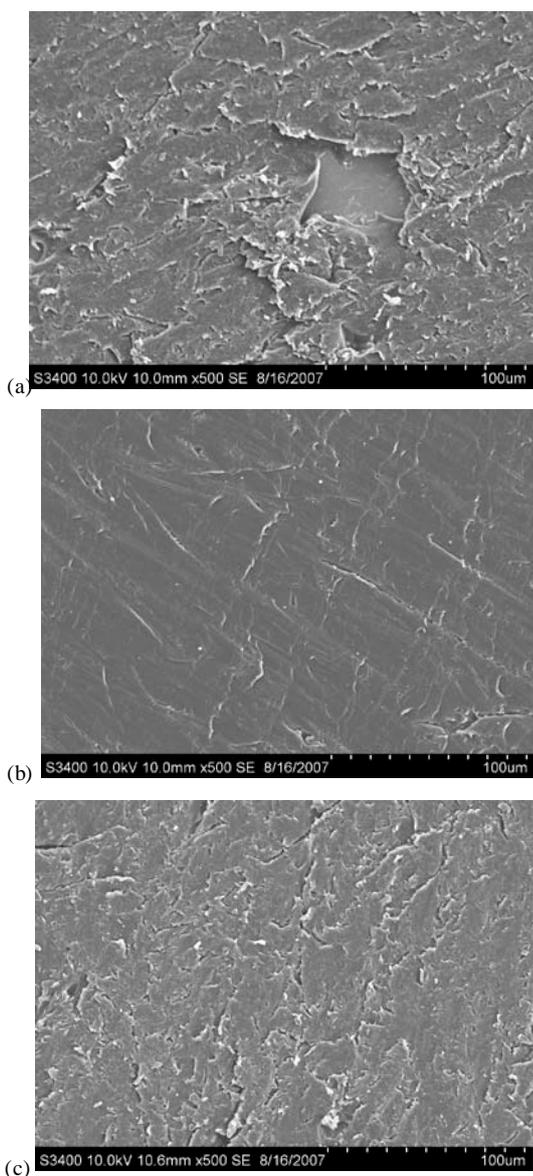

(a)

(b)

(c)

Fig. 11 SEM micrographs of abraded coating (a) Neat-WPUD and modified with (b) 0.1% nano-ZnO and (c) 1.0 % nano-ZnO

C. Pencil Hardness

Pencil hardness test was carried out for neat-WPUD and nano-ZnO modified WPUD (Fig. 12). Pencil hardness for the neat-WPUD coated sample was found to be 3H. With addition of nano-ZnO particle, the hardness of the coating was enhanced, the grade being 5H at the lower loading level (0.1%) and 4H at higher loading level (1.0%).
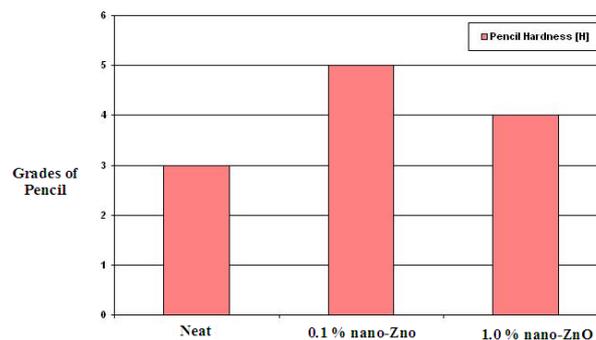

Fig. 12 Pencil hardness test

VIII. CONCLUSION

The effect of nano-ZnO particles on waterborne polyurethane dispersion (WPUD) was studied. The nano-composite coating modified with 0.1% nano-ZnO enhanced corrosion resistance, UV resistance and mechanical properties maintaining its optical transpernacy, as compared to the coating modified with 1.0 % nano-ZnO. Nano-ZnO can serve as a good barrier pigment and UV blocking agent in WPUD, however optimizing their concetration and improved dispersion in polymer matrix can further improve the performance properties of the coating.

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