Advances in High Performance Polymer Nano Composite Coatings for Better Resistance to Corrosion and Ultraviolet Rays

Shambhu Sharan Kumar

Abstract— In this industrial extensive research work in the fields of corrosion protection and surface coatings, conventional micron sized rutile TiO_2 pigment based automobile grade polyester-amino (butylated melamine formaldehyde resin-BMF) stoving paint was formulated. In subsequent approach, nano TiO_2 and nano ZnO alongwith nano SiO_2 particles modified super white stoving industrial paints were formulated for the purpose of comparative study and to improve overall performances of surface coatings with respect to the best possible protection of automobile grade steel surfaces. With reference to the improvement of erosion and corrosion resistance, weathering and ultraviolet (UV-rays) resistance, water repellence and chemical resistance, dispersion stability and aging resistance, surface covering and adhesion property, film smoothness and gloss retention alongwith other mechanical properties; nano materials adapted paints have shown great potential in several industrial applications. The nano pigment particles were characterized by SEM and XRD. Performance evaluation of surface coatings was done as per ASTM/BIS test procedures. After rigorous test observations, excellent performance results have been found i.e. 100% adhesion, 100% gloss, appreciable results in aging test, 4000 hours passed in salt spray test and 3600 hours passed in quick ultraviolet weathering resistance test due to surprising synergistic effects of dispersed different nano materials in crosslinked polyester-amino resins media. It has experimentally been proven that the proper application and dispersion of suitable nano materials in paint formulations, improved overall performances of surface coatings for the purpose of better surface-protection.

Index Terms— Corrosion resistance, nano engineered paint, nano particles, weathering resistance.

I. INTRODUCTION

It is well known fact that corrosion is a natural oxidation process by which a material degrades drastically due to chemical or electrochemical reaction with its environment, and it is also scientific fact that corrosion cannot be completely stopped but it can be reduced by applying proper technology and management. In this perspective, it has also been acknowledged that among all the methods of corrosion protection, protective coatings have become the most commonly used methods for corrosion-control [1, 2, 7]. In this evolution, it is to state that paints have been fabricated at micron level for a long but in recent years nano technology has been introduced in the field of surface coatings to improve overall quality of industrial paints and coatings. Proper addition and optimum dispersion of required nanoparticles in

Shambhu Sharan Kumar, Assistant Professor, Chemistry Dept., Birla Institute of Technology, Mesra, Ranchi, Extension Centre, Allahabad- 211 010, India, Mobile No. +91 9451731437.

high quality of resin media can upgrade several properties of surface coatings by producing multipurpose reinforced composite coating with a little cost difference [2, 8, 9]. That's why in present work, nano TiO_2, nano ZnO alongwith nano SiO_2 particles were incorporated with designed compositions in polyester-amino resins media to explore the best possible performances of nano coatings.

Nano coatings are polymer-nano composite materials made of resin, solvents, pigments and additives, produced by dispersing nano pigments in resin media at the nano scale (approx 1-100 nm) to form a denser product, which give a solid film on substrate surface after application alongwith curing for the purpose of better surface protection and aesthetic looks as well [2, 13].

The applications of suitable nanoparticles within compatible ratio in paint formulations carry many advantages and opportunities to paint and coating industries. Coating industry is one of the first among all to utilize the potential of nanotechnology [2, 7, 9]. Nano coatings, sometimes made of self-assembling mono layers, are applicable in many ways e.g., from scratch resistant coating to super hydrophobic self-cleaning surfaces and also to weathering and corrosion resistant coatings [3,4,13]. Further, due to unique composition of nano materials, pigment, binder, solvents and additives in paint formulation; better adhesion, flexibility, durability along with excellent gloss as well as transparency make nano-coatings even more effective. Many of the nanoparticles like nano TiO_2 and ZnO are non-toxic in nature and thus add an extra advantage to coating industries [2, 9, 12].

II. MATERIALS AND METHODS

Paint formulations were carried out in several steps: theoretical formulation, ball-mill charging, grinding, dispersion examination, let down stage, make up stage, testing and packing etc. Composition-percentage of micron sized TiO_2 and other nano pigments were designed maintaining pigment-binder ratio to get optimum dispersion of pigment particles in polyester-amino resins media shown in Table 1. Compatibility of amino resin with polyester resin was checked and determined (as per ratio 2:8, 3:7 & 5:5) w.r.t. consistency, transparency and adhesion of clear-film of each coating system. Several types of paints were formulated in which resin, solvent & additives were kept constant, only micron & nano pigments were manipulated for comparative study as per following approaches:

- Conventional micron sized rutile TiO_2 based polyester-amino stoving paint,
- Nano pigment particles modified polyester-amino super white stoving top coats.

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Table 1. Composition-design of micron & nano pigment particles (by weight % ratio) in different paint formulations

Coating Sample No.	Micron sized TiO$_2$ Wt.% Ratio	Nano TiO$_2$ Wt.% Ratio	Nano ZnO Wt.% Ratio	Total Wt.% Ratio of Pigment
1.	22.0	-	-	22.0
2.	21.0	1.0	-	22.0
3.	20.5	1.5	-	22.0
4.	20.0	2.0	-	22.0
5.	21.0	-	1.0	22.0
6.	20.5	-	1.5	22.0
7.	20.0	-	2.0	22.0
8.	20.0	0.5	1.5	22.0
9.	20.0	1.0	1.0	22.0
10.	20.0	1.5	0.5	22.0

Table 2. Ball-mill charging with designed pigment compositions (as referred in Table-1) and supplementary ingredients for formulation of different mill bases

Composition	Wt. % ratio (in gram) × 20	Total weight
Rutile micron TiO$_2$ + Nano TiO$_2$ + Nano ZnO	22.0 (as per Table-3)	440 gm
BMF resin	12.0	240 gm
Disperbyk additive	1.0	20.0 gm
Butanol	2.5	50.0 gm
Butyl cellosolve	1.0	20.0 gm
Xylene	2.3	46.0 gm
Solvent C-IX	2.0	40.0 gm
Nano byk (nano silica) additive	0.2	4.0 gm
Total	43.0%	860 gm

Table 3. Make up stage for polyester-amino paint preparation by above mill-bases shown in Table 2 alongwith following calculated ingredients

Composition	Polyester-amino Paint	Total weight in gm.
Mill-base (micron + nano pigment)	43.0%	860
Polyester resin	43.0%	860
Xylene	3.7%	74.0
Butanol	2.0%	40.0
Butyl cellosolve	1.0%	20.0
Solvent C-IX	4.8%	96.0
Methoxy Propyl acetate	2.0%	40.0
Slip additive	- -	- -
Dispersion additive	0.2%	4.0
Thixotropic additive	0.3%	6.0
	Total 100%	2000gm
Paint samples	1, 2, 3, ….., 10	

All formulated paints have been characterized by pot life testing (there should be no pigment settlement, sedimentation, skinning and vehicle separation), viscosity, thinning ratio, non volatile contents, tack free time, curing schedule etc. Paints were applied by way of three coating-layers (i.e.

cathodic electrodeposition primer (CED), intermediate coat and then top-coat) on surface treated (alongwith tricationic phosphating) standard mild steel panels (150mm X 75mm X 1 mm) and cured each coated layer at 133±2°C for 30 minutes. After curing, coated dry film testing was carried out as per ASTM/BIS quality test methods, e.g. dry film thickness (DFT), opacity, gloss, adhesion, aging test, hardness, impact test (cupping value test), immersion test, corrosion test, and weathering resistance test etc [3, 4]. Ten types of prepared polyester-amino stoving super white top coat samples (1-10) have been characterized and reported.

Synthesis of nano TiO$_2$: The sol-gel method is a versatile process, used in making various ceramic materials. In a typical sol-gel process, a colloidal suspension or a sol is formed from the hydrolysis and polymerization reactions of the precursors, which are usually inorganic metal salts or metal organic compounds such as metal alkoxides. TiO$_2$ nano materials have been synthesized by the sol-gel method from hydrolysis of a titanium precursor. This process normally proceeds via an acid-catalyzed hydrolysis step of titanium (IV) alkoxide followed by condensation. The development of Ti-O-Ti chains is favored with low content of water, low hydrolysis rates and excess of titanium alkoxide in the reaction mixture. The formation of Ti(OH)$_4$ is favored with high hydrolysis rates for a medium amount of water [1, 8].

In addition to this a typical colloidal synthesis of TiO$_2$ nanoparticles has been followed: Titanium tetra chloride reacts with butanol to give the product titanium butoxide.

$$TiCl_4 + 4\ C_4H_9OH = Ti\ (C_4H_9O)_4 + 4\ HCl$$

18 ml of 0.1M HNO$_3$ is added to the 3.0 ml titanium butoxide dropwise at room temperature under vigorous stirring. A white precipitate forms instantaneously after the hydrolysis; the slurry is heated at ≈70^{0}C for 10 hours under vigorous stirring to achieve peptization. The solution is then filtered on glass pot to remove nonpeptized agglomerates and the final filtrate concentrate ~ 5 wt%. The growth of particle size achieved under hydrothermal condition in stainless steel hydrothermal bomb in temperature range of 200° C-250° C in oven for 12 hours. The particle size are temperature dependent and after autoclaving the particle are re-dispersed using ultrasonic horn (400W,15*2s pulses), after sonication the colloidal suspension is introduced in a rotary evaporator at 35^{0}C to get a final TiO$_2$ concentration of 11 wt% which used for the preparation of thin film of TiO$_2$. The final solution was used to prepare different samples of TiO$_2$ film by a general procedure in which the conducting glass plate was slowly immersed into TiO$_2$ colloidal solution using a programmable dip coater.

Sample 1: one repetition of dipping in TiO$_2$ paste (SEM image: Figure 3):
Dipping speed: 2 mm/min.
Drying time at each repetition: 3 min.
Lifting speed: 2 mm/min.
Rest time in dipping: 1 min.
Sample 2: two repetitions of dipping in TiO$_2$ paste (SEM image: Figure 4):
Dipping speed: 2 mm/min.
Dry time at each repetition: 3 min.

Lifting speed: 2 mm/min.
Rest time in dipping: 1 min.
Dipping length: 10 mm.

III. RESULTS AND DISCUSSION

XRD patterns of nano TiO_2 and micron sized TiO_2 in rutile and anatase phases have been shown in Figure- 1 and Figure-2 respectively. In Figure-1, XRD patterns exhibited strong diffraction peaks at 27°, 36° and 55° indicating TiO_2 in the rutile phase. On the other hand, in Figure-2, XRD patterns exhibited strong diffraction peaks at 25° and 48° indicating
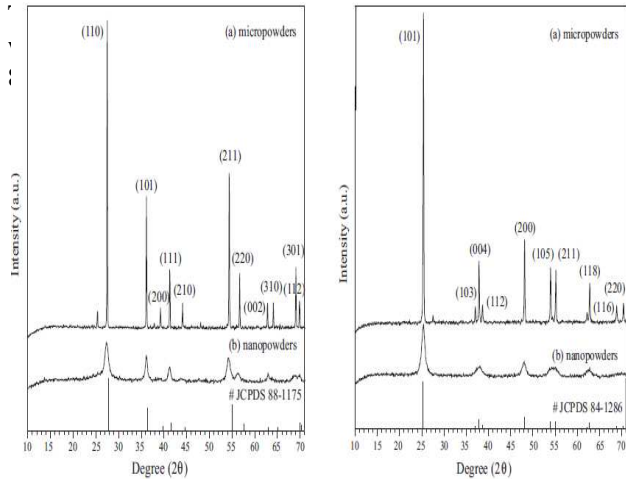

Figure 1 X-ray diffraction of rutile TiO_2 (a) micropowders and (b) nanopowders.

Figure 2 X-ray diffraction of anatase TiO_2 (a) micropowders and (b) nanopowders.

From figure-1 and figure-2, it is clear that the diffraction pattern peak intensity of the TiO_2 increases with increasing particles size. These results refer that the nano TiO_2 powder is composed of irregular polycrystalline materials. Amorphous compound revealed a broad pattern with low intensity; however, the effect of the amorphous materials on the broadening of the XRD patterns of nano-sized TiO_2 is negligible. TiO_2 was dried by azeotropic distillation with *n*-butanol; subsequently calcined at 700 °C for one hour. However, rutile is a high temperature stable phase and has an optical energy band gap of 3.0 eV [1, 8, 10]. As it can be observed from SEM figure-3 & 4 that nano TiO_2 exists mostly as rutile and anatase phases and both of them have the tetragonal structures. However, rutile is a high-temperature stable phase.
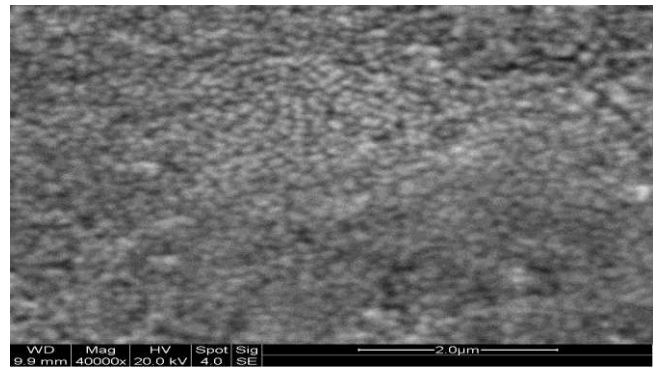

Figure 3. SEM image of TiO_2 thin film

Figure 4. SEM image of TiO_2 thin film

Table 4. Performance test observations of surface coatings (sample 1-10) with reference to respective compositions of micron & nano pigments in different paint formulations

| Coating sample no.	Cross cut Adhesion Test	Gloss at 60^0 angle	Aging Test at 80°C for 48 hours	O.U.V. weathering Test: Passed Hours	Salt spray Test: Passed hours
1	100/100 (100%)	96%	gloss reduced by 5%	650 hours	800 hours
2	100/100	98%	No appreciable change (NC)	1300	1600
3	100/100	99%	NC	1700	2000
4	100/100	100%	NC	2100	2400
5	100/100	97%	NC	1300	1600
6	100/100	97%	NC	1700	2000
7	100/100	97%	NC	2100	2400
8	100/100	98%	NC	2700	3150
9	100/100	99%	NC	3150	3600
10	100/100	100%	NC	3600	4000
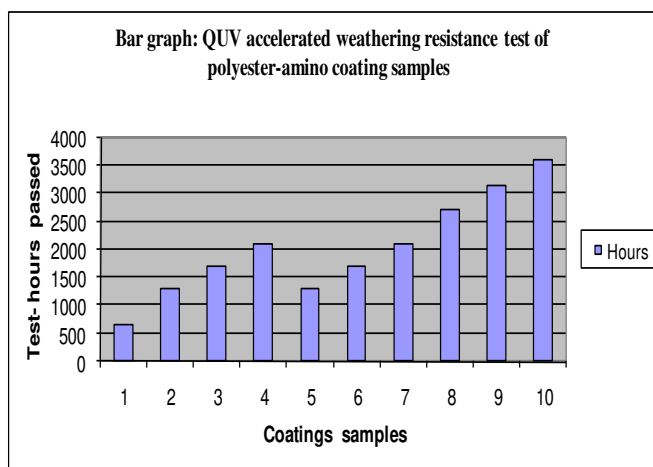
Figure 5. Quick ultraviolet (QUV) weathering resistance test of polyester-amino coating samples (passed in hours)

Coating-film characterization reported in Table 4 [3,4,11].

- ASTM- B 487, 499; Dry film thickness of coating-film: 80-90 micron.

- ASTM- D 3359; Adhesion test: 100/100, (i.e. 100% adhesion; in cross cut adhesion test).

- ASTM- D 523-89; Gloss test (at 60^0 angle): 96 at micron-sized paint coated surface,
  97-100 at nano-pigment modified paint coated surface.

- ASTM- B 117-94; Salt spray test: 800 hours passed by micron paint surface,
  1600-4000 hours passed by nano pigment modified paint surface.

- ASTM- G 154; Aging test (at 80^0C for 48 hours in diesel and engine oil): No appreciable change in gloss, shade and hardness and adhesion of nano-pigment modified paint surface.

- ASTM- D 3912; Immersion test: 800 hours passed by micron sized particles surface,
  4000 hours passed by nano-pigment modified paint surface.

- ASTM- D 4587 & 4329 & ISO 4892; QUV accelerated weathering resistance test: the effect is measured by exposing test-samples to varying conditions: 650 hours passed by micron sized painted surface,
  1300-3600 hours passed by nano-pigment modified paint surface.
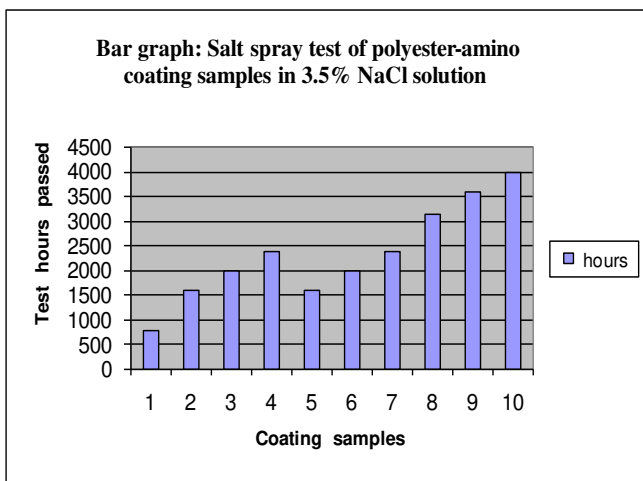
Bar graph: Salt spray test of polyester-amino coating samples in 3.5% NaCl solution

Figure 6. Salt spray test (corrosion resistance test) of polyester-amino coating samples (passed in hours)

These results refer that with the increase in the concentration of nano TiO_2 in cross-linked polyester-amino resins media, there was a continuous improvement in gloss due to high refractive index of rutile nano TiO_2 and with the increase in concentration of nano TiO_2 and nano ZnO alongwith lower percentage of nano SiO_2, there was a continuous improvement in almost all the properties of surface coatings [5, 6, 13].

Since micron sized bulky particles are used as pigment for conventional coatings, where water, dirt and other foreign particles can permeate into the voids and pin-holes and due to such activity blistering, erosion as well as corrosion take place on the substrate surface [6, 8, 11]. On the other hand, nano engineered paint and surface coatings are densely packed with robust molecules of nano ZnO, nano TiO_2 and nano SiO_2 that act as an impermeable and functional barrier to foreign environment for the purpose of overall protection [2, 9, 13]. Appreciable improvement was observed in corrosion resistance (i.e. no evidence of blistering and rust during salt spray test), QUV weathering resistance (i.e. no appreciable evidence of chalking, paint peel-off or gloss-reduction) and also in other mechanical properties of surface coatings. Thus positive impact has been found due to impermeability as well as synergistic effect of compactly interstitial packing of nano materials (e.g., nano ZnO, nano TiO_2 and nano SiO_2) with high surface energy in voids between microns sized pigment particles [3, 4, 6].

It is also to be noted that nano particles below 20 nm are optically transparent and they change color with changing of their sizes, that's why size of pigment is more important. Chemical reactivity increases with decreasing size also [1, 9]. Efficiency w.r.t. particle size can be observed from Fig. 7.
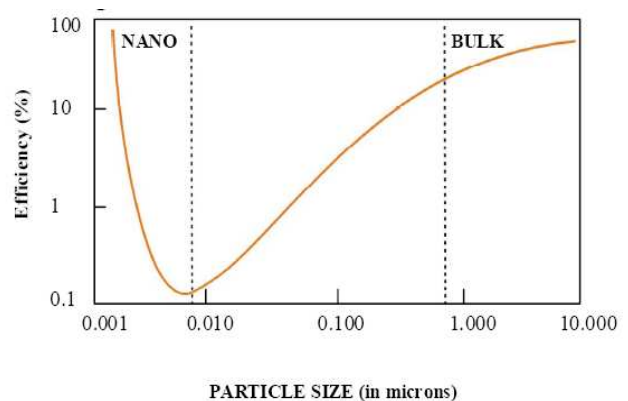
Figure 7. Efficiency of Nano material increases non-linearly as the particle-size decreases below 20 nm.

Self-cleaning action by nano paint film

With reference to the self-cleaning action, nano engineered paint performs super hydrophobic properties having contact angle >150^0, which causes water droplets to bead off of a fully cured surface picking up dirt and other surface contaminant along the way. This self-cleaning action helps to clean and maintain the coating-surfaces, and to accelerate drying, leaving the surface with minimal spotting, long term painted-surface protection against water-stains, dirt, grime, corrosion, chipping, scratches and weathering etc [6, 9].
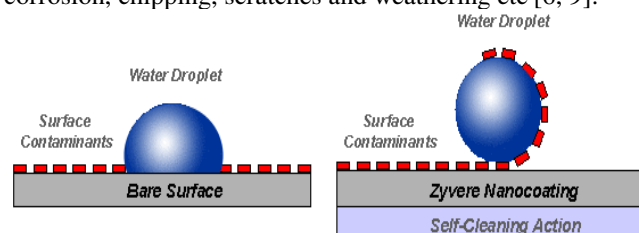
It is observed that only optimum amount of nanoparticles should be added to the coating system to get maximum benefits. Excess nanoparticles should not be used as the amount of resin may not be enough to wet all the nano-pigments, which may result in the formation of discontinuous film and in turn give rise to defects in the coating systems [1, 2, 9].

IV. CONCLUSION

Appropriate applications and optimum dispersion of rutile micron TiO_2 pigment alongwith nano TiO_2, nano ZnO and nano SiO_2 particles in varying compositions in high quality of resin media upgrade overall coating-performances. Nanomaterials have shown to improve the mechanical properties even at low pigment-binder ratio due to the synergistic effect of their small particle sizes and high surface energy. Nano composite coating has many properties in a single coat system as well as in hybrid coatings system and hence can give excellent corrosion & UV protection without affecting its gloss and appearance.

There are some limitations of nano coatings. Main problem occurs during the use of nano particles for coating purpose is dispersion and stability. Agglomeration may take place because of high surface energy possessed by nanoparticles due to their large surface area. Ultrafine pigments may lose their color on reducing their size to nano level and hence lose their opacity and hardness. However, benefits of nano coatings outweigh its drawbacks; therefore, our aim for future work should be to overcome these drawbacks and to make even more effective coating-system using stable binders with nano ZnO, nano CdS and nano TiO_2 particles.

ACKNOWLEDGEMENTS

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Shambhu Sharan Kumar, Assistant Professor, Chemistry Dept., Birla Institute of Technology, Mesra, Ranchi, Extension Centre, Allahabad- 211 010, India; M.Sc. Chemistry, M. Tech. (Surface Sc. & Engineering: N.I.T. Jamshedpur), Ph. D. (pursuing), M.I.I.Ch.E. (Life Member- Indian Institute of Chemical Engineers), M.I.S.T.E. (Life Member - Indian Society for Technical Education), M.I.A.Eng. (Member - International Association of Engineers, Hong Kong). His research area: synthesis of nano-pigment particles and their applications in high performance polymer nano composite coatings w.r.t. corrosion protection and weathering resistance.