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Design and Synthesis of Polymer Nano Composite Enamel for Improvement in Weathering and Corrosion Resistance

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ABSTRACT

In the scenario of universal corrosion occurrences, counteractive measures are being performed for the purpose of protection of metallic surfaces fulfilling the decorative and super aesthetic demands of end-users. That's why extensive research and development work on protective coatings have been carried out in the areas of industrial paints and surface coatings. In present work, long established conventional micron sized rutile titanium dioxide pigment based thermosetting acrylic (TSA), polyurethane and amino resins based stoving enamel has been formulated. Further, in the viewpoint of continuing industrial extensive research work, rutile nano titanium dioxide (TiO_2), nano zinc oxide (ZnO) and nano silica (SiO_2) particles incorporated several types of TSA-polyurethane-amino stoving super white top coats have been formulated to improve the quality of industrial stoving paints for the purpose of getting best viable protection of automobile grade metallic surfaces. Previously characterized micron and nano pigment particles have been used in these paint formulations. On the basis of detailed experimentations, it has been proven that the appropriate applications of well-suited nano particles in paint formulations augment the overall performances of paints and render the improved coating surfaces.

KEYWORDS: *Nano-TiO_2 particles, nano-ZnO, nano engineered paint, corrosion protection and weathering resistance*

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INTRODUCTION

Corrosion is a natural oxidation process by which a metal mortifies tremendously due to chemical or electrochemical reaction with its aggressive surroundings[1]. Concurrently it has also been recognized as the universal fact that corrosion cannot absolutely be stopped but it can be minimized by applying corrosion control techniques and protection management[1,2]. In the perspective of protection, it has been accredited that among all the protective methods, surface coatings have become the most universally practiced and cost effective methods for the purpose of corrosion protection[3,4]. In the evolution of paints and surface coatings, it is considered that paints might have been manufactured at micron level from ancient time, but since last few decades, appropriate nano materials are being incorporated in paint formulations to get superior quality and performances of paint coatings[5-8]. Proper incorporation and best possible dispersion of suitable nano particles in paint media can improve many properties of paints and surface coatings and can produce multipurpose reinforced composite coatings with a slight technological modification[7,8,9].

In the perspective of present industrial demand, conventional rutile titanium dioxide pigment based TSA-polyurethane-amino stoving top coat and rutile nano-TiO_2, nano-ZnO and nano-SiO_2 particles incorporated stoving super white top coats have been formulated to get better quality of industrial stoving paints for the purpose of best possible protection of industrial grade metallic components. The incorporation of suitable nanoparticles in TSA-polyurethane-amino resins based paint formulations brought a lot of prospects, improvement and effectiveness to paints and coatings. It is the reason for selection of TSA-polyurethane-amino resins composition for formulation of industrial stoving paints to attain the goal for making good synthetic enamel to get durable coatings with extra gloss-retention, better aesthetic looks, better weathering resistance and excellent corrosion protection to metallic surfaces[10-12].

Experimental

In this work, previously synthesized rutile nano-TiO_2 was taken whereas nano-SiO_2 and nano-ZnO particles have been procured from Byk Additives and Instruments Company Limited. Micron sized rutile TiO_2 pigment, TSA resin, polyurethane, amino resin and other ingredients were provided by Berger Paints Company Limited Kolkata. These nano pigment particles were previously characterized by TEM, SEM and X-Ray diffraction techniques in our continuing research and development work.

Paint formulations have been executed in several steps: in 1st step, composition of micron sized TiO_2 and other nano pigments were designed (Table - 1) keeping the outlook of pigment-binder ratio for optimum dispersion of pigments in acrylic-amino resins media. In first approach, conventional micron sized rutile TiO_2 based TSA-polyurethane-amino (butylated melamine formaldehyde resin) stoving paint was formulated as sample no. 1. In further approach, nano pigment particles modified TSA-amino super white stoving top coats were formulated as sample no. 2-12. Resins, solvents and additives were kept constant, only ratio of micron and nano pigment compositions were manipulated in paint-formulations for comparative study. Prepared paints were evaluated as per specified standard, applied with specific methods on surface treated standard steel panels (150.0 mm X 75.0 mm X 1.0 mm) and cured at 133±2°C for 30 minutes. Performance evaluations of all cured panels were carried out as per ASTM/BIS quality test methods.

Table 1: Composition design (by weight % ratio) of nano and micron pigments for different paint formulations

Coating Sample No.	Micron TiO_2; Wt. % ratio	Nano-TiO_2; Wt. % Ratio	Nano-ZnO; Wt. % Ratio	Nano-SiO_2; Wt. % Ratio	Total % of pigment
1	22.5	-	-	-	22.5
2	21.5	1.0	-	-	22.5
3	21.0	1.5	-	-	22.5
4	20.5	2.0	-	-	22.5
5	21.5	-	1.0	-	22.5
6	21.0	-	1.5	-	22.5
7	20.5	-	2.0	-	22.5
8	20.5	0.5	1.5	-	22.5
9	20.5	1.0	1.0	-	22.5
10	20.5	1.5	0.5	-	22.5
11	20.0	1.0	0.5	1.0	22.5
12	20.0	1.0	1.0	0.5	22.5

For the purpose of proper blending & grinding of mill base raw materials, the ball mill was run for 24 hours with above designed ingredients to get particle size ≤ 1µm. Dispersion was being checked using Hageman's fine-gauge until particles-sizes were found less than 1 micron. Then mill base was dropped in a pot. Thus table-2 shows different types of mill base raw materials having 44% by weight for further use, i.e. make-up stage for required paint samples. By using above mill-bases, required paints were prepared (Table - 3).

In present study, twelve types of prepared TSA-amino paints (sample no. 1-12) have been characterized by pot life testing (there should be no pigment settlement, sedimentation, skinning and vehicle separation), viscosity testing, thinning ratio, non-volatile contents, sagging, tack free time, drying time, settling property, curing schedule, wrinkling test, dry film thickness (DFT), opacity test, shade matching, gloss test, impact test/cupping value test, aging test, salt spray test (corrosion test), and QUV weathering resistance test were done as per ASTM test methods for automotive paints[7,8].

Table 2: Preparation of mill bases by different nano & micron pigment compositions

Composition	Wt. % ratio (in gram)
Rutile TiO_2, nano-TiO_2, & nano-ZnO	22.5
MF resin	12.0
Disperbyk-103	1.0
Byk-310	0.1
Butanol	2.8

Butyl cellosolve	1.0
Xylene	2.0
Solvent C-IX	2.4
Nano-byk additive (silica)	0.2
Total wt. % of mill base	44.0 %

Table 3: Make up stage for TSA-amino paint preparations

Composition	Wt. % ratio
Mill-base	44.0
Polyurethane resin	10.00
TSA resin	33.0
Xylene	8.5
Butanol	1.0
Butyl cellosolve	1.0
Solvent C-IX	2.0
Methoxy Propyl acetate	- -
Slip additive	0.2
Dispersion additive	- -
Thixotropic additive	0.3
Total	**100.0 %**
Enamel samples	**1, 2, 3, …., 12**

For proper application and excellent adhesion of paint film, surface treatments (i.e. degreasing, water-rinse, de-rusting, water-rinse, activation, phosphating, water-rinse, passivation and drying) on standard mild steel panels have been done as per high quality automotive specifications[7-8]. Tri-coat system (i.e. electrode position primer, intermediate coat and top coat) have been applied on surface treated mild steel panels and cured at 133±2°C for 30 minutes (i.e., optimum curing schedule of synthesized stoving paints).

Results and discussion

Dry film thickness (DFT: ASTM- B 487, 499; measured by Elcometer) of paint films has been kept in the most advantageous range of DFT, i.e. 80-95 micron. More or less than this DFT-range, paint film may not provide excellent protection to the substrate surfaces as per our practical experiences and reported literature as well[2,7,8].

Table 4: Performance test results of paint coatings w.r.t. different compositions (by weight % ratio) of micron and nano pigments in different paint formulations

Coating Test Sample No.	Micron sized TiO_2 Wt. % Ratio	Nano TiO_2 Wt. % Ratio	Nano ZnO Wt. % Ratio	Nano SiO_2 Wt. % Ratio	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	22.0	-	-	-	100%	94	No change (NC)	650 hours passed	800 hours passed
2	21.0	1.0	-	-	100%	97	NC	1300	1600
3	20.5	1.5	-	-	100%	98	NC	1700	2000
4	20.0	2.0	-	-	100%	99	NC	2100	2400
5	21.0	-	1.0	-	100%	97	NC	1300	1600
6	20.5	-	1.5	-	100%	97	NC	1700	2000
7	20.0	-	2.0	-	100%	97	NC	2100	2400
8	20.0	0.5	1.5	-	100%	97	NC	2700	3200
9	20.0	1.0	1.0	-	100%	98	NC	3150	3600
10	20.0	1.5	0.5	-	100%	99	NC	3600	4000
11	19.5	1.0	0.5	1.0	100%	90	NC	3600	4000
12	19.5	1.0	1.0	0.5	100%	92	NC	3600	4000

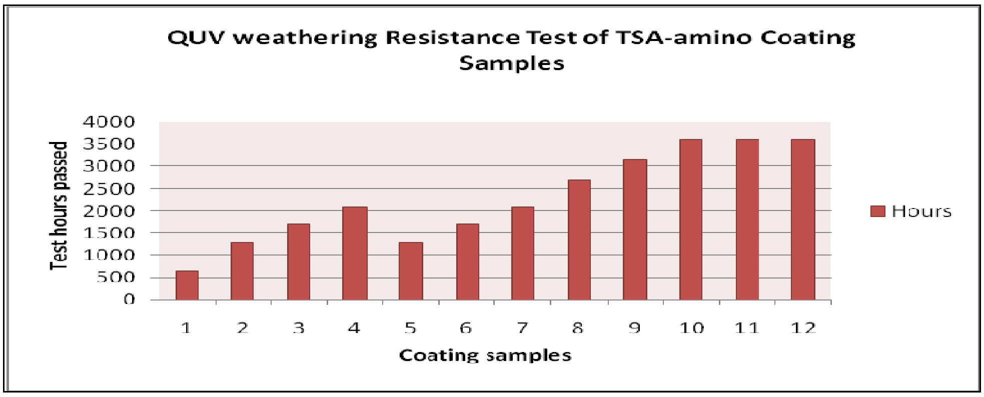

Figure 1: Bar graph of coated samples performed in QUV accelerated weathering Resistance test

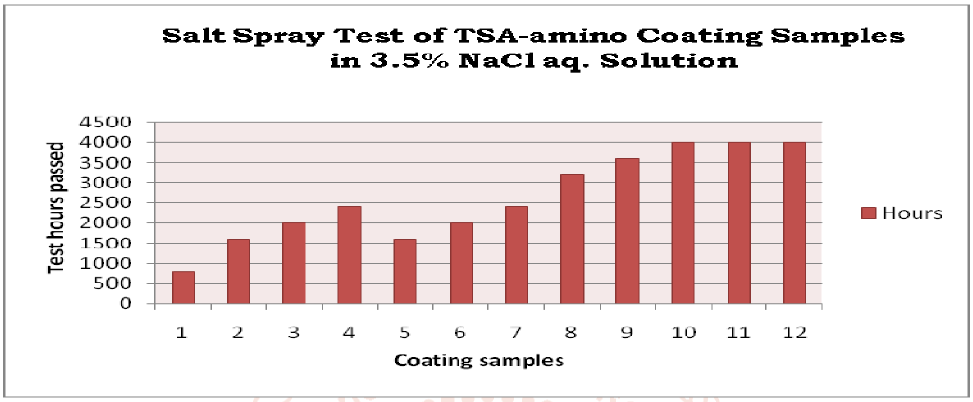

Figure 2: Bar graph of coated panels passed in salt spray test

At first scratch resistance of coated film was improved by using micron sized inorganic fillers, but they caused matt and semi-matt appearance at the coated surface by scattering visible light. However, by using nano pigment particles, scattering of light was reduced significantly. Nano powders with particles size around 40-60 nm are effective fillers. Even a small amount of added nano particles can retain the better appearance of surface gloss. All materials are made from atoms and their properties depend on the arrangement of atoms[10-12].

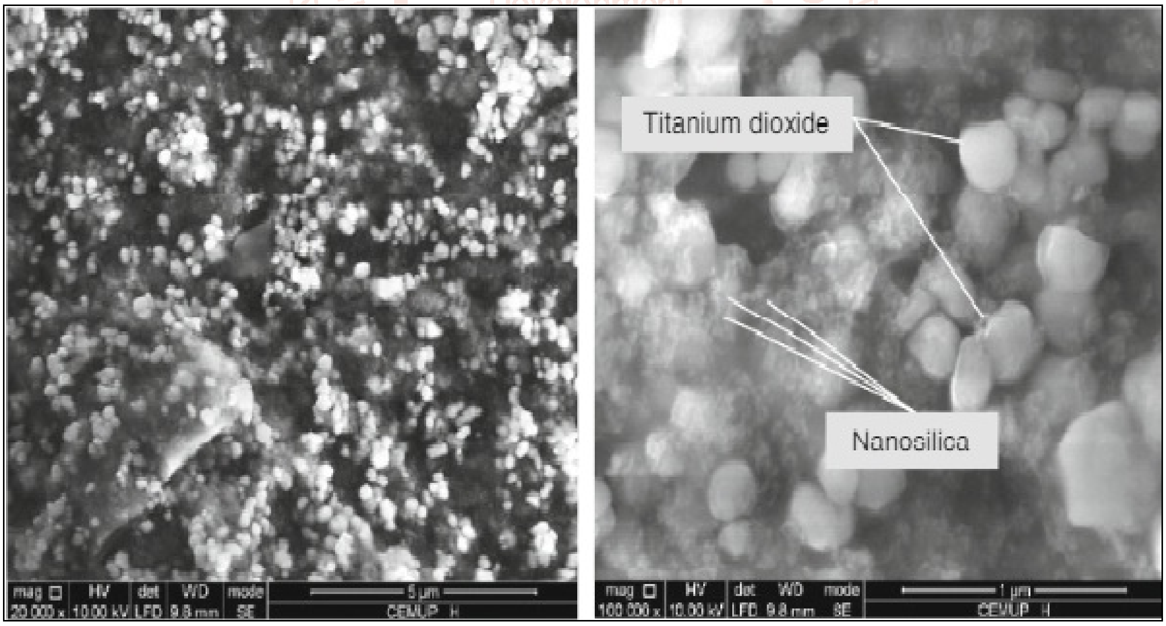

Figure 4: SEM images of nano-composite paint surface. The silica nanoparticles are visible on the right image, being apparently well dispersed throughout the polymer matrix. The larger particles are titanium dioxide pigment

Conclusion

Optimum incorporation and dispersion of suitable nano particles (TiO_2, ZnO and SiO_2) along with rutile micron TiO_2 pigment performed synergistic effects in TSA-polyurethane-amino resins media resulted profound improvement in the quality of industrial grade stoving paints and coatings. Properties like adhesion, gloss retention, corrosion resistance and resistance to ultraviolet radiations, anti-aging property, chemical resistance and other mechanical properties, i.e. 3600 hours passed by nano-coatings in QUV test in comparison to 650 passing hours by micron-paint coated sample. 4000 hours passed in salt spray test by nano-paint coated panels whereas 800 hours passed by micron coating. 100% adhesion, 99% gloss & appreciable aging resistance have been improved significantly using suitable nanoparticles along with micron sized rutile TiO_2 pigment. Nanoparticles have shown to improve the mechanical properties even at low pigment-binder ratio due to their small particles-size and strong inter-molecular force.

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