Progress in Paint Formulations by Nano-Silica Dispersion in a Blend of Alkyd-Polyester-Melamine Formaldehyde Resins Media

Shambhu Sharan Kumar

Abstract— **Regular improvement in any system is a natural phenomenon that is why advancement in corrosion protection, paint formulations and surface coatings are being taken place since ancient time to modern era. In the horizon of industrial paints and coatings, it has been acknowledged that the modern paints are being manufactured to comprise the particles-shape, size, and arrangement, pigment-dispersion consistency, film smoothness, better looks, improved quality and robustness to both exterior and interior paint coatings by the incorporation and blending of appropriate ingredients i.e., resins, pigments, solvents, additives and now nano-particles also for surface protection of industrial components. In this work, five types of automotive grade stoving top coats have been formulated. In first phase, industrial grade micron sized rutile TiO_2 (21 % total pigment by weight) based alkyd-butylated melamine formaldehyde stoving paint was formulated. In second phase, nano particles modified (i.e. nano SiO_2 particles: 0.5 weight %, 1.0 wt %, 1.5 wt. %, and 2.0 wt. % alongwith rutile micron TiO_2; i.e. total 21% pigment having nano-particles size range 30-60 nm) alkyd-polyester-amino resins based stoving paints were formulated for evaluating the overall properties. Appropriate applications of nano-particles in these resins media based stoving paint formulations offer surety to perform better in diversified field applications as observed by ASTM/BIS quality test methods for requirements of automotive top coats such as gloss (measured as 87-91 % at 60^0 angle), improved adhesion (performed 100%), quick ultraviolet accelerated weathering resistance (QUV) test (passed 400-1416 hours), salt spray test (passed 600-2424 hours) and attained better mechanical properties.**

Index Terms— **Alkyd-polyester ratio, amino resin, nano coatings, corrosion protection, weathering resistance.**

I. Introduction

Worldwide advancement in paint formulations and surface coatings are needed on large-scale basis for better protection and decoration. Automobile industry is one of the most significant consumers of recent advancement in surface coatings and nano technology [1,2]. Paint and coating industries are growing with innovation day by day on global basis. These days, coating not only provides the purpose of beautification but also used as the means of protection of valuable metals, materials, vehicles, ships, structures and buildings from corrosion and weathering which almost accounts for approx 4% of world's gross national product [2,3,4].

In our normal life, general travelling and communications take place by automobile vehicles, trains, aerospace vehicles and ships etc; so very good aesthetic appearance alongwith surface protection should be continued mainly through their coated surfaces. Surface coating technology has been introduced as the surface science and engineering, corrosion protection technology or paint technology in industrial sectors [3,4]. Paint preparations have been improved gradually as per regular development of civilization by applying innovative science, techniques and technology to get better quality of paints and surface coatings [5,6].

Formulations and applications of paints have been very wide-ranging i.e., from micron to nano level materials and from extraordinarily hard materials to soft polymeric coatings [4-7]. In ancient era, paint was prepared from plant-extracts, natural gums and natural resins, animal's fat etc as binder whereas grinded rock powder and minerals as pigments and water had been a common solvent [7-9].

In ancient time, surface polishing, wiping and water rinsing were done as surface treatment before painting [8,9]. In this context, it is to say that surface treatments are done to remove dust, dirt, rusting, oil, grease etc from metallic to modify the surfaces for applying further steps of surface coatings on materials and components. To design for a suitable surface treatment process before coating is a tough but essential job for a given combination of different corrosive metallic materials [8-10]. Apart from removing contamination from the surface, pre-treatments activate the active centers at the substrate-surface and therefore substantially improve the bonds between coating-film and substrate-surface, and to activate surface molecules for tri-cationic phosphate applications [10,11].

Modern surface treatment processes are being designed as per ASTM/BIS standard requirements of automobile industry following these steps: degreasing, water rinsing, derusting, water rinsing, activation, phosphating, mineralized water rinse, and passivation (if required). There are mainly three phases of surface coatings after surface-treatment: primer coat application (by dip coating process/spray coating/electrodeposition coating), intermediate coat and top coats [10-12].

Manuscript received: Aug. 19, 2014.
Shambhu Sharan Kumar, Assistant Professor, Department of Chemistry, Birla Institute of Technology, Extension Centre Allahabad, India, Tel. 09451731437. (E-mail: shambhu66bit@rediffmail.com).

Although, many new formulations of paints and coatings have been developed in recent years, but none is able to carry out all the requirements in a single paint-formulation [13,14]. Nano-composite-coatings are the materials produced by reducing the particles' size of paint-materials at the nano meter level or molecular level to form a polymeric viscous fluid product for the purpose of coatings [15,16].

The incorporation and effectiveness of nanoparticles carry many advantages and opportunities to paint and coating industries. Coating industry is the first among all to gain the potential of nanotechnology. Proper addition of nanoparticles to paints and coatings can upgrade a lot of properties of coating system and can produce multipurpose coatings with a little cost difference; from scratch resistant coatings to self-cleaning surface coatings, corrosion resistant coatings to weathering resistance coating. Further, unique composition, better strength and flexibility along with excellent gloss and transparency make nano-coatings even more effective. Many of the nanoparticles like nano TiO_2, nano SiO_2 nano ZnO are non-toxic in nature and thus add an additional advantage to coating industries [17,18].

Scratch resistance of coating can be improved by using micron sized inorganic fillers, but they cause matt or semi-matt appearance to coating by scattering visible light. However, by using nanoparticles, scattering of light can be reduced significantly. Nano powders of particle size around 30 to 70 nm are effective fillers. Nanoparticles such as SiO_2 have been embedded in ultraviolet (UV) curable lacquers, resulting in improved abrasion resistance. Nanoparticles have been shown to improve the mechanical properties even at low pigment loading, and due to their small particles size (less than 30 nm); they do not affect the transparency of clear coats. Scratch resistance has also been improved further due to homogeneous distribution of nano particles in polymer matrix. Even a small amount can retain the good appearance of surfaces without any negative impact on coating and its gloss [10-12].

High performance coatings are being formulated by using nano materials. It is possible to produce better pigments, additives and coating systems that can provide better corrosion resistance, UV resistance and transparency to visible light according to the need along with different colors. Nano-coating is a great demand of automobile industry. Arrangement of nano pigments can be changed in paints by altering electrical field. Thus, paints can change its color as a function of voltage. This concept can be highly applicable for automobile sector. Nano-sized pigments particle having narrow particle size distribution packed well at the surface of the film resulting in a uniform surface finish. This uniform surface complemented by high scattering power of nanoparticles gives excellent gloss properties to coating systems [3,13,18].

II. Materials and Methods

Paint materials and characterization facilities have been made available by Berger Paints Limited, Kolkata. Nano-silica has been procured by BYK Additives and Instruments Company Ltd.

In this work five types of paints have been formulated. In 1st approach, micron sized rutile TiO_2 pigment based alkyd-amino paint has been formulated. In 2nd approach, nano-pigment particles modified (i.e. nano SiO_2 particles: 0%, 0.5%, 1.0%, 1.5%, and 2.0% by weight alongwith required rutile micron TiO_2 pigment, i.e. total pigment concentration was kept 21% by wt.) alkyd-polyester amino (butylated melamine formaldehyde) resins based paints were formulated . In paint formulations, resins, solvents and additives were kept constant, only compositions of pigments were manipulated for comparative study.

Keeping the view of systematic coating process of mild steel panels; surface treatment, phosphating, cathodic electrodeposition primer coat (CED), intermediate coat and then formulated top coats were applied properly. All five types of paints were characterized as per specified standard and then these were applied on different standard mild steel panels (15o mm X 75 mm; thickness: 1mm) and cured in an oven at temperature 130^0C for 30 minutes. After cooling at room temperature, testing was done.

III. Results and Discussion

1. Meticulous performance evaluation of surface coatings was carried out as per following ASTM/BIS quality test [10- 12]:

- DFT: ASTM- B 487.
- Gloss: ASTM- D 523.
- Adhesion test: ASTM- D 3359.
- Salt spray test: ASTM- B 117.
- Aging test: ASTM- G 154.
- QUV Test:- ASTM- D 4587,

To get effective dry film thickness (DFT measured by Elcometer), the paint-DFT was kept as 5-8 micron for tri-cationic phosphate coating, 20-30 micron for CED primer, 25 - 35 micron for intermediate coat, and 30 - 40 micron for top coat.

Gloss test was done by Glossometer (at 60^0 angle) and reported in Table-1: 91 % at micron sized particles surfaces and 87- 90% at nano-silica modified surfaces.

Gloss could not be enhanced by incorporating silica nano-particles in paint formulations. Silica nano-particles have lesser refractive index than the refractive index of rutile TiO_2, that's why gloss was decreased as ratio of silica nano particles increased. Gloss directly depends upon refractive index of incorporated pigment particles.

In adhesion test, all coated samples passed with 100% adhesion capability in cross-cut adhesion test (Table-1). After detail comparative test of surface coatings, satisfactory results were found (given in Tables 1 & 2). Test results have been demonstrated that applications of nano materials in paint formulations promise to fulfill the objective of required smart coating.

Table 1: Adhesion and gloss test of formulated paint coatings:

Pigments- composition in paints (% by weight)	**Cross cut adhesion (%)**	**Gloss at 60^0 angle (%)**
Micron TiO_2 21 % (Nano-silica 0%)	100/100	91
Micron TiO_2 20.5 % + Nano-silica 0.5 %	100/100	90
Micron TiO_2 20 % + Nano silica 1.0 %	100/100	89
Micron TiO_2 19.5 % + Nano silica 1.5 %	100/100	88
Micron TiO_2 19 % + Nano silica 2.0 %	100/100	87

These results show that with the increase in concentration of nano SiO_2 in cross-linked alkyd-polyester-amino resins media, there was a continuous decrease in gloss due to lesser refractive index of silica nano particles with respect to that of rutile TiO_2. Except gloss, there was a continuous improvement in almost all the properties of surface coatings [5, 6, 13].

Corrosion resistance of coated samples was also examined by a salt spray test according to ASTM B-117 specifications. In salt spray test, standard coated steel panels were kept in a closed salt spray chamber in which spray was continuously generated by 3.5% sodium chloride aqueous solution. Observation was done at regular interval (Table 2) of time: 400 hours passed by micron sized coating on bare steel panels. 600 hours passed by micron sized particles-surfaces, with primer coat. 1200-2424 hours passed by nano pigment modified paint coated surfaces (with primer coating).

Salt spray test provides information about the nature of failures like blisters, rusting or cracking and de-lamination of coating films. Corrosion protection properties of the coated mild steel substrates were evaluated by exposing the substrates to a salt fog chamber having 3.5 weight % aqueous NaCl solutions at 27^0C environment. The salt spray tested samples (Fig. 2) indicated that after 1200 hours the 1.0 wt. %, 1.5 wt. % nano & 2.0 wt. % nano paint formulations do not corrode while the other formulation corrodes severely. This may be due to higher contact angle and lower corrosion rate of 1.0 %, 1.5% & 2.0 wt% nano pigmented paints compared to that of others.

Table 2: Salt spray test and QUV weathering test of formulated paint coatings:

Pigments- composition in paints (% by weight)	**Salt spray test passed (in hours)**	**QUV weathering test passed (in hours)**
Micron TiO_2 21 % (Nano- silica 0%)	**600.** 400 (bare steel panel)	**400.** 300 (bare steel panel)
Micron TiO_2 20.5 % + Nano-silica 0.5 %	1200	800
Micron TiO_2 20% + Nano silica 1.0 %	1600	1000
Micron TiO_2 19.5% + Nano silica 1.5 %	2000	1200
Micron TiO_2 19% + Nano silica 2.0 %	2424	1416

It is significant to point out that the bare structural surfaces are very much aggressive to corrosive environment and also does not fulfill the purpose of good aesthetic appearance. That's why proper surface coatings are required to improve surface properties of existing materials and products [3-5]. Following Figure-1 shows the functional coatings on panels for the purpose of corrosion protection.

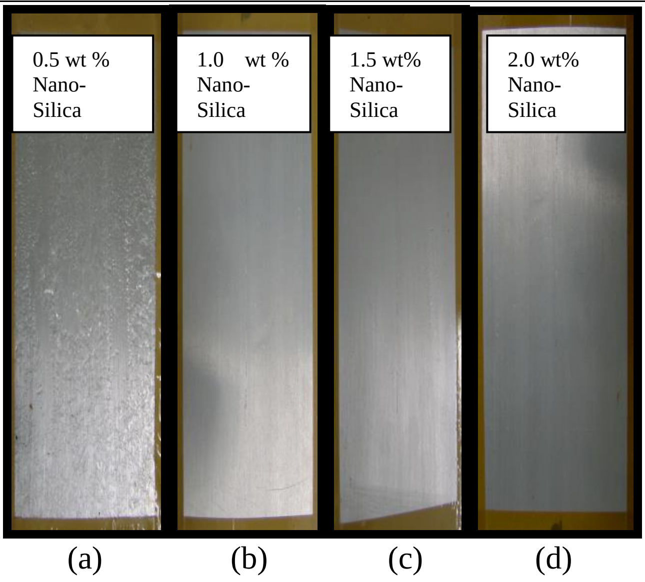

Figure 1: Image of characteristic applications of functional coatings for the purpose of corrosion protection of metallic surfaces.

In aging test, properly paint coated samples (immersed in automobile grade diesel/engine oil) were kept in an oven at 80^0C for 48 hours; there was no appreciable change on coated steel panels.

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 SiO_2 that act as an impermeable and functional barrier to foreign environment for the purpose of overall protection of surfaces [2, 9, 13].

A robust molecular bond in the contact zone remains most favorable, provided that internal stresses within the coating are not too high and no long-term degradation occurs within the coating-substrate composite [13-15].

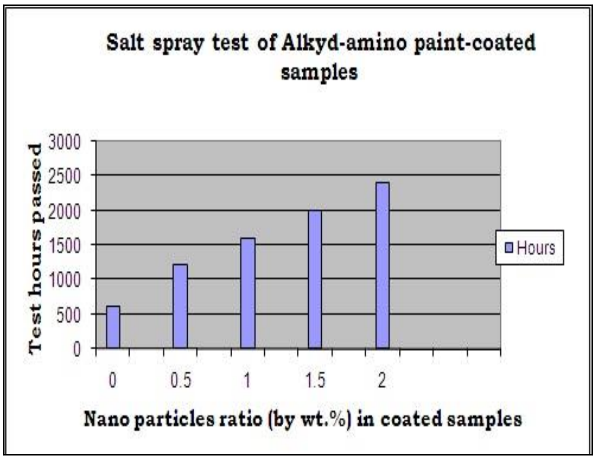

Figure 2: Salt spray test of coated panels having weight % ratio (0, 0.5, 1.0, 1.5, 2.0) of nano-SiO_2 particles.

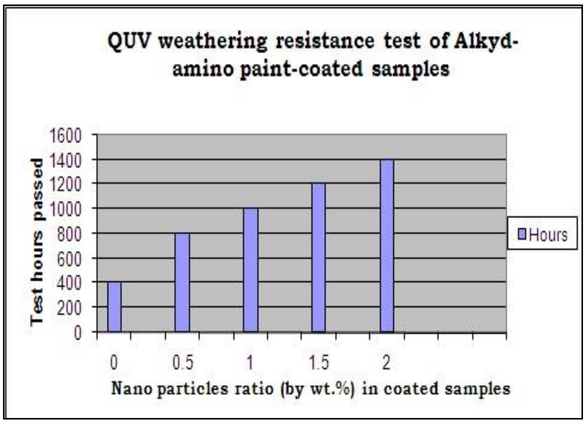

Figure 3. QUV weathering resistance test of paint coated mild steel panels having weight % ratio (0, 0.5, 1.0, 1.5, 2.0) of nano-SiO_2 particles.

In Q.U.V. accelerated weathering resistance test, the weathering effect has been measured by exposing coating-samples in varying conditions (Table 2); 300 hours passed by micron sized particles based paint coated film (on bare mild steel panels). 400 hours passed by micron sized paint coated surface, and 800-1416 hours passed by nano pigment modified paint surface. In this test, we see that using nanoparticles like titanium dioxide or zinc oxide or silica nano particles improve the UV resistance property by reflecting dangerous rays. Also, they are not easily destroyed by UV radiations and hence can increase the life of paint films [11-13].

Photochemical degradation caused by UV rays is a common way of paint failures of most of the coating systems. It causes the oxidation and decomposition of polymer films along with inorganic or organic pigments. Organic UV stabilizers also undergo deterioration process after certain periods of time.

Bond strength between paint film and substrate surface primarily depends upon the quality of a paint ingredients and coating techniques. This macroscopic property is controlled by proper combination of materials, treatment done at interface, microstructure, process conditions, and types of substrates.

Hydrophobic and oil repellent property: Addition of nanoparticles to coating systems increases its surface area and pore volume, which in turn increases the surface roughness. Increase in roughness increases the contact angle of water and other solvents significantly and hence decreasing the surface tensions of a surface. Self-cleaning property is admired in nano-coatings. It checks even very fine dirt or droplets to be accumulated on coated surfaces. If nano-coating is applied to glass surface, nanoparticles will interact with ultraviolet rays, loose down the dirt particles and than using water, dirt is removed from the surface. So, on such glass, dirt can easily be washed off. Main advantages of nano-coatings are:

- ❖ Very good adherence on different type of materials
- ❖ Better surface appearance
- ❖ Better chemical resistance
- ❖ Better retention of gloss and other mechanical properties like scratch resistance.
- ❖ Anti-reflective in nature,
- ❖ Self-cleaning property, and
- ❖ Decrease in permeability results resistance to corrosive environment and hence better corrosion protection.

IV. Conclusion

By using nano materials in paint formulations, properties of surface coatings have been improved by which life span of existing materials and products have been improved. Surface engineering designs and improves physical, mechanical and chemical properties of surface coatings for the purpose of surface protection even in the aggressive environment. Incorporation of nano silica particles improves the overall surface properties of surface coatings. Nano coatings strike on the several coating troubles particularly for automobile components.

Acknowledgment

Author is thankful to Prof. N.D. Pandey, S.S. Narvi; M.N.N.I.T. Allahabad for valuable suggestions and also grateful to Prof. A.S. Khanna, Corrosion Engg, I.I.T. Bombay, Prof. A.C. Pandey, Nano Technology Application Centre, Allahabad University and Berger Paints Limited

Kolkata for providing their well equipped R&D Laboratories to carry out the extensive research work.

REFERENCES

[1] P.J. Gellings; Introduction to corrosion prevention and control, Delft University Press, 1985.
[2] L.C. Zhou, B. Koltisko, Journal of Coatings Technology, 2005, 2(15), 54–60.
[3] I. P. Parkin, R. G. Palgrave, Journal of Materials Chemistry, 15 (17), P: 1689–1695, (2005),
[4] A.S. Khanna, Nanotechnology in High Performance Paint Coatings, Asian J. Exp. Sci., Vol. 21, Issue- 2, P: 25-32, (2008),
[5] C. Carr, E. Walstom, Progress in Organic Coatings, 28-161, 1996.
[6] J.C. Tiller, C.J. Liao, K. Lewis, A.M.Klibanov, Proc. National Acad. Sci.USA 2001, 98 (11), 5981–5985.
[7] K. Johns, Surface Coatings Int. Part B: Coating Transactions, 2003, 86 (B2), 91–168.
[8] A.R. Di Sarli, Progress in Organic Coatings, 2003, 48, 50–62.
[9] N. Kouloumbi, P. Moundoulas, Pigment Resin Technology, 2002, 31(4), 206–215.
[10] Sargent J.R., Pickett J.E., Accelerated QUV weathering using Xenon Arc with Boro Filters, Important Factors for Testing and Translation to Standard 58 FL Outdoor Test Protocols. ICCG Proceedings 6, P: 215–219, (2006)
[11] American Society for Testing and Materials: ASTM International Standard, *chemical analysis of paints and paint materials*, 2010, D 817-96, P. 10-62.
[12] American Society for Testing and Materials: ASTM Int. Standard, *Standard practice for preparing, cleaning, and evaluating corrosion test specimens*, 2011, G1-03, 9-46.
[13] Haefer R, Journal of Surface Coating Technology; Springer, Berlin, (1987).
[14] Leupolz A, Multifunctional Automotive Glazing—Examples and Trends, Proceedings Glass Processing, P: 475–478, (2003).
[15] Farrington RB, Advanced Automotive Glazing: A Cool Idea for Hot Cars. 45th Annual Technical Conference Proceedings, Society of Vacuum Coaters, P: 209–215, (2002).
[16] Gunji F, Present Status and Future Trend of Coatings on Glass for Automobiles. Proceedings: Glass Processing, P: 502–504, (2001).
[17] Matthai A, Sepeur-Zeitz B, Horstmann F, Schu¨ tz J Intelligent Coatings for Automotive Applications. Proceedings of the ICCG 6, P: 39–42, (2006).
[18] Taga Y, Recent Progress in Coating Technology for Surface Modification of Automotive Glass. Journal of Non-Crystalline Solids 218:335–341. (1997).

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