Nanotech Enabled Anti-Graffiti Clear Coating System

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Abstract

Here is a 'Nanotechnology Approach to High Performance Anti-Graffiti Coatings'. Anti-graffiti is a property of a coating that does not allow dye, permanent markers, stickers, graffiti, paint or any other markings to bond to dry film. It is a special modified Silicone resin based formulation, Poly Urethane and acrylic based non-hazardous coating. Apart from being cost effective, this coating offers numerous benefits over the conventional alkyd enamel paint system and Epoxy cum Poly Urethane based systems. Depending on the substrate and the severity of graffiti, different coatings offer different advantages and disadvantages. Because of its non-sticky characteristic, it does not allow dust particles to stick upon its body. This particular property of Anti-graffiti top coat renders a better aesthetic look during service. Anti-graffiti coating is on trial on the coaches of passenger trains like Shatabdi in India.

Keywords: Anti-graffiti, Polysilazanes, hydrophobic and oleo phobic ligands, nanoparticles, Silicone resin, Nanometal primer, Dry Film Thickness

1. Introduction

Anti-graffiti is a property of a coating that does not allow dye, permanent markers, stickers, graffiti, paint or any other markings to bond to dry film. Anti Graffiti Coating is simple to use. It adheres to most surfaces and can be roll applied, sprayed or painted on. Its unique formulation provides a hard and durable clear gloss finish that also seals the surface and provides easy removal of graffiti. This coating is considered as PERMANENT in nature. This means that the coating itself does not get removed once graffiti has been removed. Removal of graffiti can be done using a pressure washer or graffiti remover.

Anti-graffiti coating is already on trail for the coaches of the passenger trains like shatabdi (See Figure 1), etc in India.

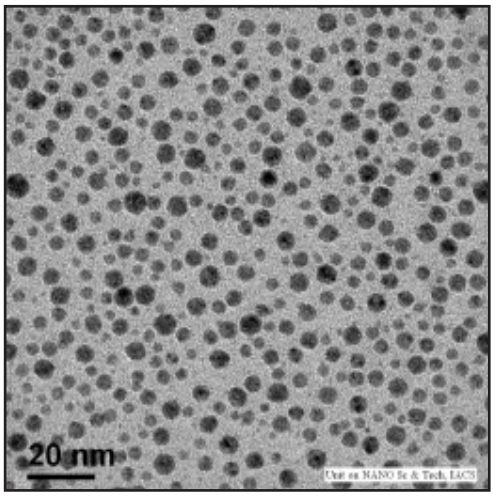
Nanotech Enabled Anti-Graffiti Clear Coating System

Source: Shatabdi Express

Besides anti graffiti properties, this coating has better UV protection, higher gloss retention, better durability and corrosion resistance.

2. Anti –Graffiti Characteristics

Anti-graffiti is a single component product with excellent chemical resistance. It is well suited for high performance applications where hardness, flexibility and abrasion resistance is required. This coating has excellent UV resistance, thereby permitting use in severe exterior applications. It is the perfect coating for applications in areas where there is a high risk of vandalism from graffiti. Anti-graffiti Coating and Anti-graffiti Paint are formulated for effective graffiti protection and exhibit high cross-linked densities, non-stick properties and excellent chemical resistance. Graffiti spray paint, permanent marker and pen sit on the surface of the coating but do not penetrate. Graffiti removal is simple, using water-based, non-toxic graffiti remover. Coatings are permanent, so once graffiti spray paint or permanent marker is removed from the surface, the coating remains ready to protect against the next graffiti attack (See Figure 2).



No Agglomeration at Nano Size Level

Source: Unit on NANO Science & Technology, IACS, Kolkata

Permanent anti-graffiti coatings are usually based on a tough glossy polyurethane or silazane based coating, from which graffiti can easily be removed either with wipes impregnated with solvent or by using a citrus based cleaning agent and washing off with cold or warm water.. This coating can be applied to most substrates and previously coated surfaces. It can also be available in an opaque silazane based anti-graffiti coating which is available in pigmented form also.

The Ultra thin anti-graffiti coating system has been developed using and applying Nanotechnology.

3. Nanotechnology- Fundamental Concepts

The manipulation and control of materials on an extremely small scale offers many benefits to the metal-finishing industry. Nanomaterials have morphological features smaller than a one tenth of a micrometre in at least one dimension. Despite the fact that there is no consensus upon the minimum or maximum size of nanomaterials, a logical definition would situate the nanoscale between microscale (0.1 micrometre) and atomic/molecular scale (about 0.2 nanometers).

An aspect of nanotechnology is the vastly increased ratio of surface area to volume present in many nanoscale materials which makes possible new quantum mechanical effects, for example the "quantum size effect" where the electronic properties of solids are altered with great reductions in particle size.

This effect does not come into play by going from macro to micro dimensions. However, it becomes pronounced when the nanometre size range is reached. A certain number of physical properties also alter with the change from macroscopic systems.

Broadly speaking, nanotechnology is the synthesis and application of ideas from science and engineering towards the understanding and production of novel materials and devices. These products generally make copious use of physical properties associated with small scales.

As mentioned above, materials reduced to the nanoscale can suddenly show very different properties compared to what they exhibit on a macro scale, enabling unique applications. For instance, opaque substances become transparent (copper); inert materials attain catalytic properties (platinum); stable materials turn combustible (aluminium); solids turn into liquids at room temperature (gold); insulators become conductors (silicon). Materials such as gold, which is chemically inert at normal scales, can serve as a potent chemical catalyst at nanoscales. Much of the fascination with nanotechnology stems from these unique quantum and surface phenomena that matter exhibits at the nanoscale.

3.1 Nanotechnology Applications:

Nano-coatings have already been applied to a diverse but specialized array of objects, from parts for nuclear steam generators and barrels of field artillery to surface coating.

In essence, nanotechnology has the ability to bring order to chaos. Under a microscope, even the smoothest crystalline coatings—such as polished chrome—show irregular gaps between the crystals. The irregular gaps can be exploited and made worse by outside forces such as water, temperature, and ultra-violet light from the sun. Air pressure, weight, and g-forces will also stress coatings and can lead to coating failure over time. This causes the coating to weaken, crack and creep. In general, these gaps can be controlled in one of two ways: by reordering the gaps into a uniform pattern, or by reducing crystal size.

With nanotechnology, a large set of materials and improved products rely on a change in the physical properties when the feature sizes are shrunk. Nano particles, for example, take advantage of their increased surface area to volume ratio. Their optical properties, e.g. fluorescence, become a function of the particle diameter. When brought into a bulk material, nano particles can strongly influence the mechanical properties of the material, like stiffness or elasticity. For example, traditional polymers can be reinforced by nano particles resulting in novel materials which can be used as lightweight replacements for metals. Therefore, an increasing societal benefit of such nano particles can be expected.

Such nanotechnologically enhanced materials will enable a weight reduction accompanied by an increase in stability and an improved functionality.

3.2 Need of Nanotechnology in Coatings (See Figure 3)

Mumbai's huge and crowed rail network has been plagued by graffiti:

Need for Anti-graffiti Coating in Indian Coaches

The primary reason for high level of interest of coating technologist in nanotechnology is the promise of this technology to deliver breakthrough coating performance in such areas as, scratch and mar resistance, barrier properties including corrosion resistance, mechanical properties and most importantly, cost effectiveness.

It should be noted that "Smaller is better" is not an entirely new concept to coating technologist and formulators. Several decades ago, coating scientists learned that small particle size latexes (particle size between 100-500 nm) gives better film formation and provide superior pigment binding ability in architectural paints. This lead to introduction of small particle latexes (even lower than 100 nm) by several raw material suppliers. Polyurethane dispersions (PUDs) which are commonly used in coatings provide another example of organic nanoparticles. TiO_2, a key opacifying pigment, with a particle size between 300-400 nm is present in almost every paint. Early use of colloidal silica and fumed silica as thixotropic agent find uses in many paints. As a result, several new nanomaterial technologies are emerging which can reduce the conventional graffiti based costs[5] (See Table 1).

4. Different Types of Anti-graffiti Coatings and how they Work

Annual Graffiti Cleaning Costs:

Location	Overall Cost Involved
Germany	Over US$ 700 million
London	US$ 200 million
UK	US$ 1.5 Billion
Los Angeles	US$ 140 million

Source: Castano, Victor M., and Rogelio Rodriguez, 'A Nanotechnology Approach to High-Performance Anti-Graffiti Coatings', International Journal of Applied Management and Technology, 2, 2004, 53-58.

Anti-graffiti coatings can be invisible to the naked eye making them ideal for preserving historic buildings. There are three different categories of anti-graffiti coatings:

4.1 Sacrificial Coatings: These are applied to a surface and then removed when graffiti is applied. The surface underneath will be left clean and a new sacrificial coating can be applied. Hence a sacrificial coating forms a clear coat barrier over the wall or surface being protected. If the surface is vandalized, the coating can be removed (sacrificed) using a high-pressure washer taking the graffiti with it. The coating then must be reapplied. The materials used to make a sacrificial coating are usually inexpensive optically clear polymers such as acrylates, biopolymers, and waxes. These polymers form weak bonds with the substrate to allow for easy removal.

4.2 Semi Sacrificial Coating: A semi sacrificial coating known as a 'safety shield', acts as a penetrating sealer on the wall or surface protecting the surface pores. If the surface is vandalized, the coating can be particularly removed using a combination of graffiti removal solvent and high-pressure washer. The anti graffiti safety shield is generally reapplied every second attack. While it is possible to use only pressure to remove coating, this will cause additional surface erosion.

4.3 Permanent Coatings: These prevent graffiti from adhering to a surface in the first place. These work by creating a protective surface that spray paint cannot bond to. Some of the types of permanent coatings include those based on polyurethanes, nano-particles, fluorinated hydrocarbons, or siloxanes. Polyurethane coatings are useful because of their barrier properties. High chain stiffness and high crosslinking density reduces the ability of the polymer to swell and absorb graffiti paint. Silicon based coatings are hydrophobic, which means the surface repels water. This reduces the effects of photo-oxidation of surfaces

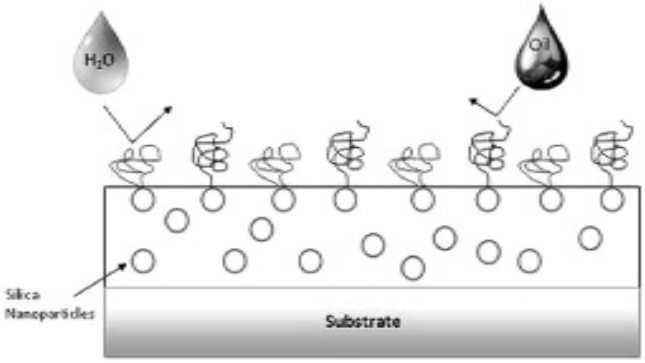
5. A Novel Approach to the Surface Coatings

Polysilazanes resin forms a highly transparent protective layer, which does not affect the surface or the appearance of the substrate material. Due to ultra thin coating, the protective layer is extremely light and economical, particularly when used to cover large surface area. The protective coating will seal the surface and thus will ensure that paints and sprays are unable to adhere strongly to the surface. The colors will run and can be removed very easily and quickly. The scope of this ultra thin protective polysilazane coating can be both on the painted metal & non-metal surfaces.

5.1 Polysilazanes based Anti-graffiti finish coatings: Polysilazanes are the base for the highly stable Silicon-Nitrogen-hydrogen compound forming oxygen metal covalent bonding system. Polysilazanes react under ambient pressure and temperature with the moisture in the air to form a dense and extremely thin $(-Si-N-)_n$ layer, which adheres strongly to the substrate. This advanced material offers protection against weathering, UV radiation from natural systems and also protects the surface against all kinds of dirt, soiling, spit marks and graffiti.

For anti-graffiti coatings, hydrophobic and oleo phobic (oil-fearing) ligands are grafted onto the nanoparticles (See Figure 4).

Hydrophobic ligands are non-polar molecules such as hydrocarbon chains. Oleophobic ligands consist of polar molecules. Normally these two different types of molecules would phase separate in solution, for the same reason that water and oil do not mix. By



Hydrophobic and lipophobic ligands grafted to nanoparticles in coating

Ref- 11) http://en.wikipedia.org/wiki/Anti-graffiti_coating

chemically drafting the ligands onto the nano particles, this effect is counteracted. The effect is a coating that shows an equal dislike for both water-based and oil-based paints.

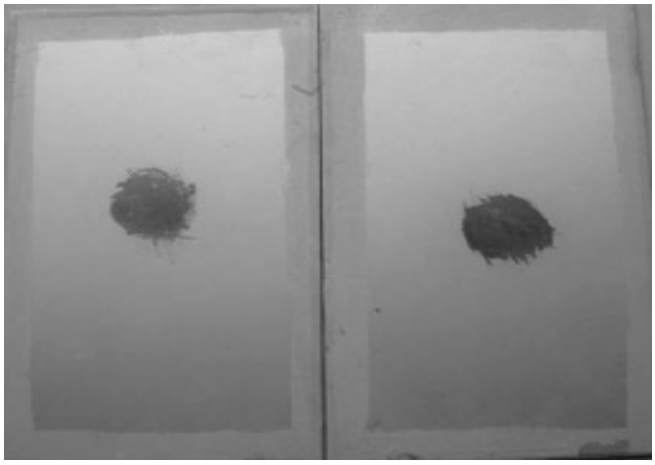
5.2 Silicon Resin based Nano Metal Primer

Silicon based coatings are hydrophobic, which means the surface repels water this reduces the effect of photo-oxidation of surfaces.

One of the newer additions to this ever growing market are nanoparticles based (single pack ready to use coatings) coatings. Silica particles are formed using the sol-gel method. The resulting silica particles have both reactive (Si-OH) and nonreactive (Si=O) groups on the surface. The reactive groups provide locations for further chemical processing, which allow changing the surface properties of the nanoparticles. Using above technology, nanometal primer may be developed with variety of shades and gloss values (for example See Figure 5).

6. Evaluations During Application (In Accordance with Rdso)

- Two coats of Primer and one coat of Ultra thin anti graffiti top coat applied by spraying.
- Nano primer & Ultra thin anti graffiti top coating are nano technology based coatings.
- As a result, a thin coat of 17- 20 micron by air spray gives the same effect of conventional coating of 200 micron.



Resistance to Salt Spray Test

NANO METAL PRIMER (1-COAT) ON 301 SS PANELS

Source: Metallurgical & Chemical Laboratory, Research Designs & Standards Organisation, RDSO, Indian Railways

- Since they are applied in thin layers and particles are in nano form, their drying time & application time is faster.
- The cycle time for application of this paint is around two days compared to that of conventional PU painting of 9 days.
- Paint characteristics like gloss, Dry Film Thickness are recorded.
- Coating quality is preserved.

7. Analysis of Nanotech Enabled Anti-graffiti

- UV resistance and other weather resistance properties emanate from the fact that Polysilazanes are the base for the highly stable Silicon – Nitrogen –hydrogen metal covalent bonding system. This advanced material offers protection against weathering, UV radiation because Silicon – Nitrogen – metal covalent bonding has got better UV resistance in comparison to carbon-carbon bonding.
- Anti-graffiti property -The protective coating will seal the surface and thus will ensure that paints and sprays are unable to adhere strongly to the surface and also protect the surface against all kinds of dirt, soiling, spit marks and graffiti making cleaning easier and time saving.
- It dries fast, because solvent and diluents used have faster evaporation rate and also due to ultra thin coating, the solvent evaporates at much faster rate than thick coating.
- Being a nanotech enabled coating, different level of gloss value can be achieved with different shade by incorporating different type of nano pigment particle.
- Its spreading capacity is much more than conventional because of very low Dry Film Thickness (1-4 micron).
- Its flash point is low due to use of Butyl acetate as a solvent making its use with more care. (See Table 2).

8. Advantages and Disadvantages over Conventional Pu System

8.1 Advantages

- No blasting is required to prepare the surface for paint application.
- Easy-to-clean surface, dirt and soiling hardly adheres

Proposed Tests for Anti-graffiti Coatings

Sr. No	Characteristics	Testing performance required
1.	Drying time at 27 ±2°C i) Surface dry/touch dry ii) Hard dry/recoating time	1 hr. 24 hrs.
2.	Finish	Smooth and glossy
3.	Gloss at 60°	May be supplied at mutually agreed value between purchaser and supplier
4.	Flexibility & adhesion	No crack and detachment be observed
5.	Impact resistance test	Deformed coating shall be free from cracks
6.	Adhesion test	Coating from none of the squares of the lattice shall be removed.
7.	Consistency/Pot time at 27 ±2°C	Smooth & Uniform
8.	Protection against corrosion under condition of condensation.	No sign of corrosion
9.	Salt spray test	No sign of corrosion
10.	Volume solids %	Tentative
11.	Resistance to 10 % v/v citric acid	To pass the test
12.	Resistance to 5 % v/v ammonia	To pass the test
13.	Resistance to hydrocarbon oil	To pass the test
14.	Resistance to solvents: i) Acetone ii) Toluene	To pass the test(No cracking, discoloration, blistering, peeling or softening of film)
15.	Flash point	Not less than 27°C
16.	Wiping property/graffiti	To pass the test
17.	Anti Graffiti test	To pass the test
18.	Identification of base material/resin	To pass the test
19.	Dry film thickness per coat, min. by wet gauge	1-4 micron
20.	Pencil hardness	To pass the test

Source- Metallurgical & Chemical Laboratory, Paint & Corrosion Engineering Division, Research Design & Standards Organisation (RDSO)

- Protects against ''bad inks'', marker inks, spray paints, spit marks, weathering and UV radiation
- Efficient in three ways:
  - o Reduces cleaning time by up to 60 percent
  - o Reduces the out of service times
  - o Reduces the overall costs
- Suitable for use on almost all surface materials
- Easy to apply, fast curing and Durable.
- High covering capacity, almost five times.

- Easy recoatability after proper surface preparation.
- Cost effective in comparison to conventional PU paint (See Table 3).

8.2 Disadvantages

Estimated Cost Comparison per Coach with Reference to Present Pu System

Cost Break up	Conventional PU Paint System	Nano Metal Primer + Ultra Thin Clear Coating system
Cost of Material	Rs. 1,00,000	Rs. 1,25,000
Life	3 Yrs	3 Yrs
Total Life Of Coach	30 Yrs	30 Yrs
Life Cycle	10	10
Total Cost in life	Rs 10,00,000	Rs. 12,50,000
Loss of Revenue in case of Coach Holding for 9 days @ 11000 per day for 10 cycles	Rs. 9,90,000	--
Loss of Revenue in case of Coach Holding for 2 days @ 11000 per day x 10 cycles with Clariants system	--	Rs.2,20,000
Manpower coatings @ 750 Rs per day x 5 man x 9 days = 33750 per cycle x 10 painting cycles for PU paints.	Rs.3,37,500	--
Manpower coatings @ 750 Rs per day x 5 man x 2 days = 7500 per cycle for 10 cycles Clariants system	--	Rs.75,000
Total Spending in life	Rs. 23,27,500	Rs. 15,45,000
Saving Per Coach	=	Rs. 7,82,500

Source- Metallurgical & Chemical Laboratory, Research Designs & Standards Organisation, RDSO, Indian Railways

- The clear top coat does not have good scratch resistance property, although when coated as a system the Anti-graffiti properties are not affected and the film is not destroyed.
- Flash point of the Primer is low, which may lead to storage problem therefore proper care should be taken.

9. CONCLUSION

1. Drying time of the anti-graffiti painting system is higher than other conventional painting system which will result in faster turn out yielding higher productivity.
2. Being only 3 coat system in comparison to other coating system, which has got 4-5 coats, this will reduce the time taken resulting in higher productivity.
3. Different level of gloss value can be achieved as per the requirement of the user without affecting other properties substantially.
4. It provides good corrosion resistance properties almost at par with other conventional painting system.
5. Gloss retention property is inferior to existing PU system.
6. Scratch Hardness of clear top coat is not good but as a full system, it may be considered as satisfactory.
7. The spreading capacity of clear top coat is almost 5 times to PU paint at 1-4 microns Dry Film Thickness resulting in cost effectiveness of system.
8. Due to good anti graffiti properties, cleaning operation is quiet easier than other system which saves the time and labour substantially.
9. Clear coat as well as system shows good resistance towards various solvent, alkali & heat upto 200°C
10. Repainting of top coat is easier & can be over coated on any other painting system with slight rubbing down of existing paint.
11. The flash point of painting system is low; therefore, it should be preserved and used with utmost care.
12. The anti-graffiti clear coat can be used on already painted substrates by conventional PU system for its ease of cleanliness and maintenance of good aesthetic value.

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