

PHOTOCATALYTIC SURFACES: ENVIRONMENTAL BENEFITS

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Abstract

The use of photocatalytic titania nanoparticles in the development of self-cleaning and depolluting paints and microbiological surfaces is demonstrated. In the former case surface erosion and sensitised photooxidation is shown to be controlled by the use of catalytic grades of anatase nanoparticles. For environmental applications in the development of coatings and cementitious materials for destroying atmospheric pollutants such as nitrogen oxides (NO_x) stable substrates are also illustrated with photocatalytic nanoparticles. Here porosity of the coatings through calcium carbonate doping is shown to be crucial in the control of the effective destruction of atmospheric NO_x gases. Good environmental stability of the coatings is also crucial for long term durability and this aspect is examined for a variety of material substrates. For the development of microbiological substrates for the destruction of harmful bacteria/fungi effective nanoparticle anatase titania is shown to be important with hydrated high surface area particles giving the greatest activity. Data from commercial pilot studies is used to signify the important practicalities of this type of new technology.

KEYWORDS: nanoparticles, pigments, titanium dioxide, anatase, rutile, de-pollution, self-cleaning, cementitious, photocatalysis, anti-bacterial, paints, coatings

General instructions

1. Introduction to Photocatalysis: Titanium Dioxide Chemistry and Structure – Activity

For many years, titanium dioxide pigments have been used successfully for conferring opacity and whiteness to a whole host of different materials. Their principal usage is in such applications as paints, plastics, inks and paper but they are also incorporated into a diverse range of products, such as food and pharmaceuticals. The fundamental properties of titanium dioxide have given rise to its supreme position in the field of white pigments. In particular, its high refractive index has enabled the efficient scattering of light. Its absorption of ultraviolet light has conferred durability to products. Its non toxic nature has meant that it can be widely used in almost any

application without risk to health and safety. However, the primary reason for its success is the ability to reflect and refract, or scatter light more efficiently than any other pigment, due to its high refractive index in comparison with extenders, fillers, and early pigments¹⁻⁵.

Titanium dioxide exists in three crystalline modifications, rutile, brookite, and anatase, all of which have been prepared synthetically. In each type, the titanium ion coordinates with six oxygen atoms, which in turn are linked to three titanium atoms, and so on. Anatase and rutile are tetragonal while brookite is orthorhombic. Brookite and anatase are unstable forms. Brookite is not economically significant since there is no abundant supply in nature.

Titanium dioxide has the highest average refractive index known. For anatase, it is 2.55 and for rutile it is 2.76. These high values account for the exceptional light-scattering ability of pigmentary titanium dioxide when dispersed in various media, which in turns yields the high reflectance and hiding power, associated with this pigment. Although single crystal titanium dioxide is transparent, as a finely divided powder it has a very high reflectance and it is intensely white because its high reflectance is substantially uniform throughout the visible spectrum. This white colour is different in tone for both crystal structures due to their different reflectance curves across the visible and near visible spectrum. Although the difference in refractive index gives rutile pigments up to 15% opacity benefit over the anatase pigment, the bluer tone and lower hardness of anatase pigments are beneficial in some applications, especially where low abrasivity may be an issue. Where the highest possible optical efficiency (opacity) and durability are required, rutile pigments are superior.

Refractive index varies with wavelength and for titanium dioxide the refractive index is greater for shorter wavelengths (blue region) and lower for longer wavelengths (red region) of the visible spectrum.

The performance of a pigment in a surface coating is significantly affected by the interaction of the medium with the pigment surface. The consequences are felt at all stages, but are particularly relevant for dispersion, shelf stability and exterior durability. Treated TiO_2 absorbs UV radiation and protects the polymer photochemically; untreated TiO_2 , however, is itself photocatalytic. Although it converts most of the UV energy into heat, the remaining energy creates radicals and other active species which accelerate the breakdown of the polymer. Virtually, almost all titanium dioxide used in plastics applications is surface treated. Treatments are essentially the same, whether the base pigment is produced by the chloride or sulphate route. The level of photocatalytic activity may be reduced by surface treatment of the base pigment with suitable inorganic compounds¹. The most common precipitates are oxyhydrates of aluminium and silicon. Also used are oxides and oxyhydrates of zirconium, tin, zinc, cerium, and boron. The treatment functions by placing a physical barrier between the pigment surface and the polymer matrix, blocking the active sites, and minimizing degradation. The treatment may also aid and reduce the requirements of power and shear when mixing. Many TiO_2 pigments have also a final organic treatment, such as trimethylol propane or pentaerythriol. Other proprietary chemical treatments may also be used. Its primary function is to modify the interfacial region between the hydrated inorganic oxide TiO_2 particle surface and various less-polar organic polymers. Some surface treatments also behave by deactivation of surface active species by entrapment processes.

During the manufacturing process of TiO_2 , the pigment is formed as discreet particles of around 0.2-0.4 microns. The titanium dioxide manufacturers control the operation variables to produce

particles of a uniform size and distribution. These 0.2-0.4 micron particles have been engineered to maximize the scattering of light, resulting in optimum brightness and opacity.

However, as soon as the particles are manufactured, they begin to combine into aggregates, agglomerates, and flocs. *Aggregates* are associations of pigment particles that are fixed together along the crystal faces. Bonds between particles are strong and cannot be broken by conventional grinding devices. *Agglomerates* are associations of pigment particles and aggregates that are weakly bonded together. *Flocs* are associations of crystallites, aggregates, and agglomerates joined across corners or held together by short range attractive forces. These flocs disperse under moderate shear.

Aggregates can only be broken into individual pigment particles with intensive milling. One of the last manufacturing steps performed by the TiO₂ manufacturer is micronization and/or milling to dissociate as many aggregates as possible. Aggregates will not reform unless the pigment is heated to over 500 °C. Agglomerates are also broken up in the milling step. However, agglomerates will easily reform during packing, storage and transportation. The disruption of these inter-particle bonds is generally understood to be the dispersion that needs to be performed by the TiO₂ consumer.

It is possible to manipulate TiO₂ particle size to within a very narrow range around a predetermined optimum. Generally, in paint applications this optimum is approximately 0.2-0.3 microns, for it is within this range that TiO₂'s light scattering ability is at its peak, which in turn maximises the level of gloss finish.

TiO₂ pigment particles are submicroscopic with size distributions narrower than many so-called monodisperse particulates. Appropriately ground, pigment dispersions contain less than five weight percent of particles smaller than 0.10 microns and larger than 1.0 micron. Optical effectiveness, that is, light scattering is controlled by the mass/volume frequency of particles in the size range from 0.1 to 0.5 microns. Gloss is diminished by a relatively small mass/volume fraction of particle larger than about 0.5 microns. Dispersability and film fineness is degraded by a very small mass/volume fraction of particles larger than about 5 microns. Important optical properties like opacity, hiding power, brightness, tone, tinting strength and gloss are all dependent upon the particle size and particle size distribution.

Pure titanium dioxide possesses by nature an internal crystal structure that yields an innately high refractive index. When the particle size and particle size distribution is to be optimised so as to contribute along with its high refractive index to a maximum light scattering, *conventional or pigmentary* titanium dioxide is obtained. It reflects all the wavelength of the visible light to the same degree, producing the effect of whiteness to the human eye. All these attributes, together with its opacity, are achieved for an optimal particle diameter which is approximately 0.2 to 0.4 microns, that is, in the order of half the wavelength of visible light. This fact can also be demonstrated on the basics of Mie theory⁶.

There exists, however, another type of titanium dioxide whose median crystal size has been explicitly reduced up to 0.02 microns. This is the so called *nanoparticles or ultrafine* TiO₂ and will be the subject matter of this article.

The history of nanoparticle titanium dioxide dates back to the late 70's when the first patent on the preparation of these materials was issued in Japan. It is in principle possible to obtain nanoparticle TiO_2 by simple milling of the pigmentary TiO_2 to a finer particle⁴. However, the properties of the fine powders in terms of purity, particle size distribution and particle shape remain highly unsatisfactory.

Several wet-chemical processes were developed during the 80's by TiO_2 pigment manufacturers like Ishihara, Tioxide and Rhone Poulenc - Thann Facility. The first part of the process, the production of the nanoparticles base material uses after-washes titanium hydroxylate as the raw material. After subsequent process steps involving the decomposition of the hydroxylate crystal structure and the re-precipitation of the TiO_2 , the product is calcined to obtain oval-shaped particles with a desired primary crystal size and narrow size distribution. The base crystals are coated in the after-treatment unit according to the requirements of the end-use. One of the primary tasks of the after-treatment is to ensure good dispersability of extremely fine particles in the final application.

TiO_2 nanoparticles are also routinely produced by the gas-to-particle conversion in flame reactors because this method provides good control of particle size, particle crystal structure and purity⁴.

Typically, the crystal size of these products is about a tenth of the size of the normal pigmentary grade. Figure 1 shows typical TEM micrographs for pigmentary and nanoparticulate titanium dioxide at the same magnification.

Figure 1: Typical TEM Micrographs of pigmentary and nanoparticles.

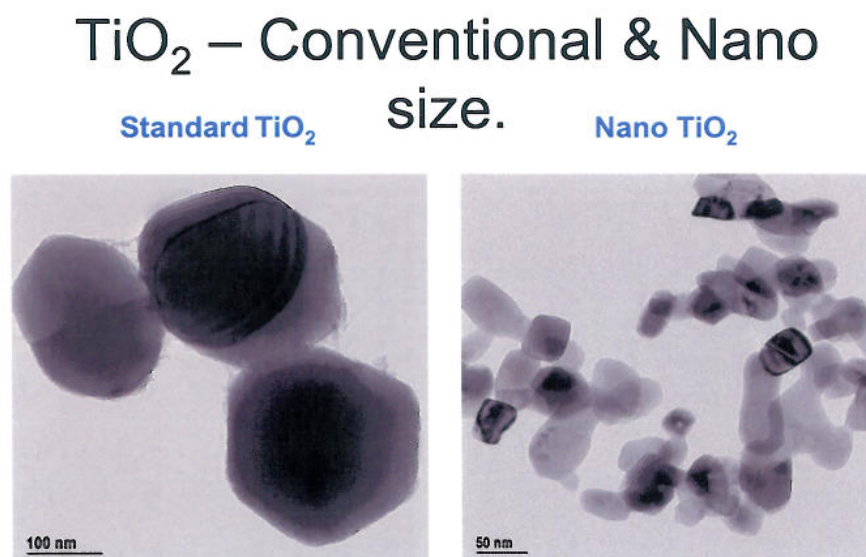


Table 1 shows a comparison of some typical values of physical properties of nanoparticle and conventional titanium dioxide products.

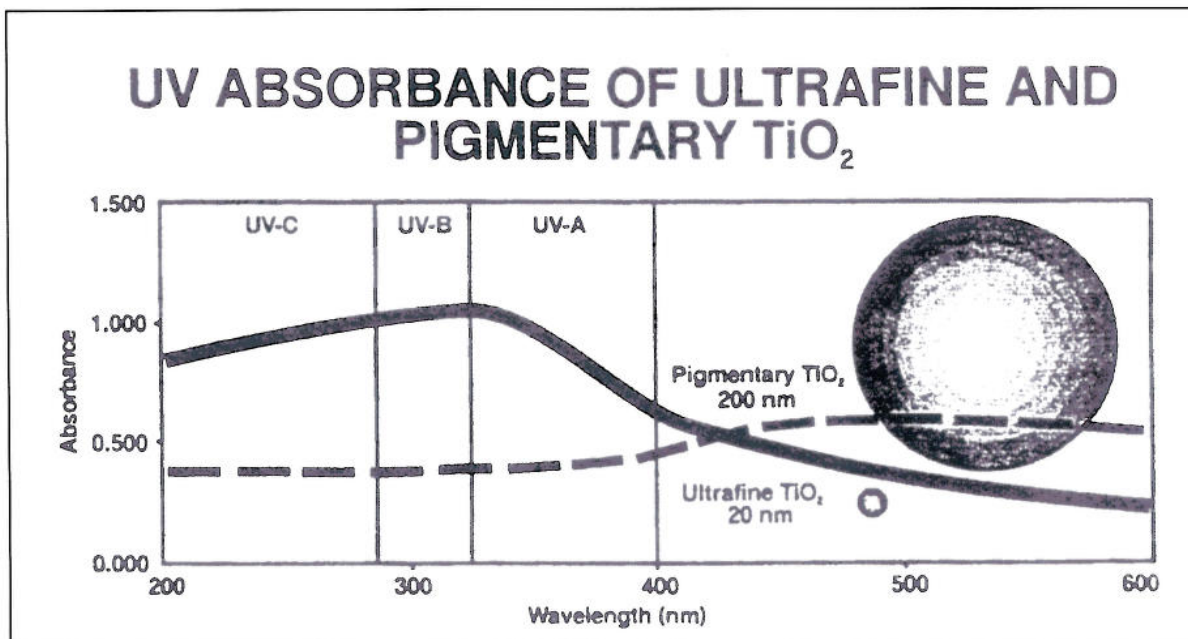
Table 1: Typical properties of conventional and nanoparticle titanium dioxide.

	Nanoparticle	Pigmentary
Appearance	White powder	White powder
Crystal structure	Anatase or Rutile	Anatase or Rutile
Crystal size (microns)	0.005-0.05	0.15-0.3
Specific surface area (m ² /g)	50- >300	15
Bulk density (g/ml)	3.3	4.0
Oil absorption (g/ 100g)	30	16

The smaller crystal size influences various properties and leads to higher values for the surface area and oil absorption. Lower values for specific gravity and bulk density are also achieved. Otherwise, it has many of the properties of conventional TiO₂ pigments: non-toxic, non-migratory, inert, and stable at high temperatures.

The optical behaviour of ultrafine TiO₂ differs dramatically from that of conventional TiO₂ pigment. The optical properties of nanoparticle TiO₂ are governed by the Rayleigh theory of light scattering. A simple interpretation of this theory is that the shorter wavelengths of light are more efficiently scattered by very small particles. The intensity of the scattered light is inversely proportional to the fourth power of the wavelength. In practical terms, reduction in the crystal size of a TiO₂ product leads to an optimum size of TiO₂ of the order of 20-50 nm where the ultraviolet spectrum of light (200-400nm) is effectively scattered from the particles while the visible wavelengths are transmitted through the material. The material thus appears virtually transparent to the naked eye. The behaviour is demonstrated in Fig. 2, which shows the difference between pigmentary and nanoparticle TiO₂.

Fig 2



The complete picture of the optical behaviour of TiO_2 becomes more complete by recognizing that TiO_2 is a semiconductor. TiO_2 exhibits a characteristic energy gap of 3.23 eV or 3.06 eV between the valence band and the conduction band for anatase and rutile, respectively. Wavelengths shorter than 390 nm for anatase and 405 for rutile –corresponding to higher energy than the threshold energy- will excite electrons from the valence to the conduction band. Summarizing, titanium dioxide exhibits various mechanisms under exposure to light depending on the wavelength and the particle size: (see table 2 and Figure 3). Electron-hole pairs are formed giving rise to various sensitisation processes.

Table 2: Optical behaviour of pigmentary and nanoparticle TiO_2 under visible and UV light.

Particle size	Wavelength < 400	Wavelength > 400
Pigmentary TiO_2 .	<ul style="list-style-type: none"> Semiconductor absorption. 	<ul style="list-style-type: none"> Scattering and reflection. (Mie scattering)
Nanoparticle TiO_2 .	<ul style="list-style-type: none"> Semiconductor absorption. Scattering and reflection. (Rayleigh's theory) 	<ul style="list-style-type: none"> Transmission of light. Particle diameter \ll wavelength

Based on the light scattering property described earlier, nanoparticle titanium dioxide can be used to impart excellent UV protection. Compared to the available UV absorbers, ultrafine nano- TiO_2 possesses effective UV filter properties over the entire ultraviolet spectrum (UVC + UVB + AVA). For example, it is gaining a wide acceptance for use in sun creams. Nanoparticle TiO_2 , apart from its effective attenuating characteristics is extremely inert and therefore, safe to use next to the skin⁵. Nanoparticle TiO_2 can also be used in clear plastic films to provide UV protection to foodstuffs. UV radiation from artificial lighting in a grocery store induces autooxidation in e.g meat and cheese, resulting in discoloration. In this regard it also exhibits ant-bacterial behaviour. However one of the most important function is the use of nano particle TiO_2 in paint and concrete for de-pollution. The schematic below shows how the product works.

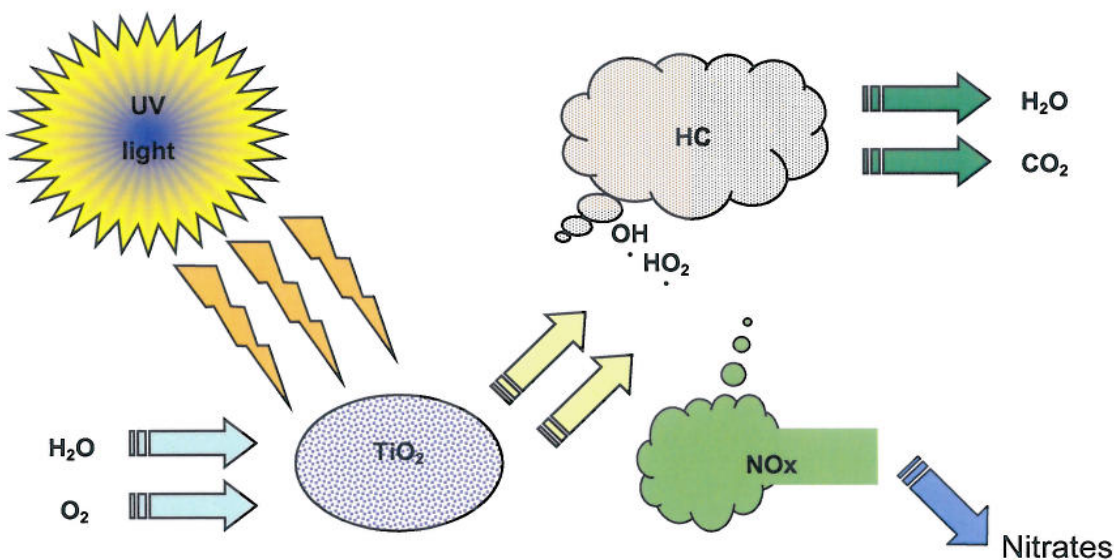


Fig 3.

2. Applications (Manila Trial)

Recent trials in London, Paris and Manila, show how effective paints can be at reducing pollution. For example in Manila we have painted 13 different locations with photocatalytic paints and 5 control areas without the photocatalytic paint. The locations are shown below in Fig. 4. They are all around a very polluted urban highway close to the MRT station in Metro-Manila. The trial was conducted by Connexor a consultancy specialising in pollution monitoring. The paint was produced by Pacific Paints in conjunction with Cristal Global.



Fig.4

The trial sites were monitored for a period of 9 months in total using diffusion monitors. Comparisons between the sites coated with non photocatalytic paint and the photocatalytic paint were made over that period. The fig 5 shows a box plot of the data which shows a 43 unit drop in the NO_x level at location 3 compared to location 18. Locations 3, 4 and 5 are shown below. As you can see they have different degrees of confinement. Locations 3 and 4 are more confined than location 5. Also, each experience different exposure to direct sunlight.



Location 3.



Location 4



Location 5

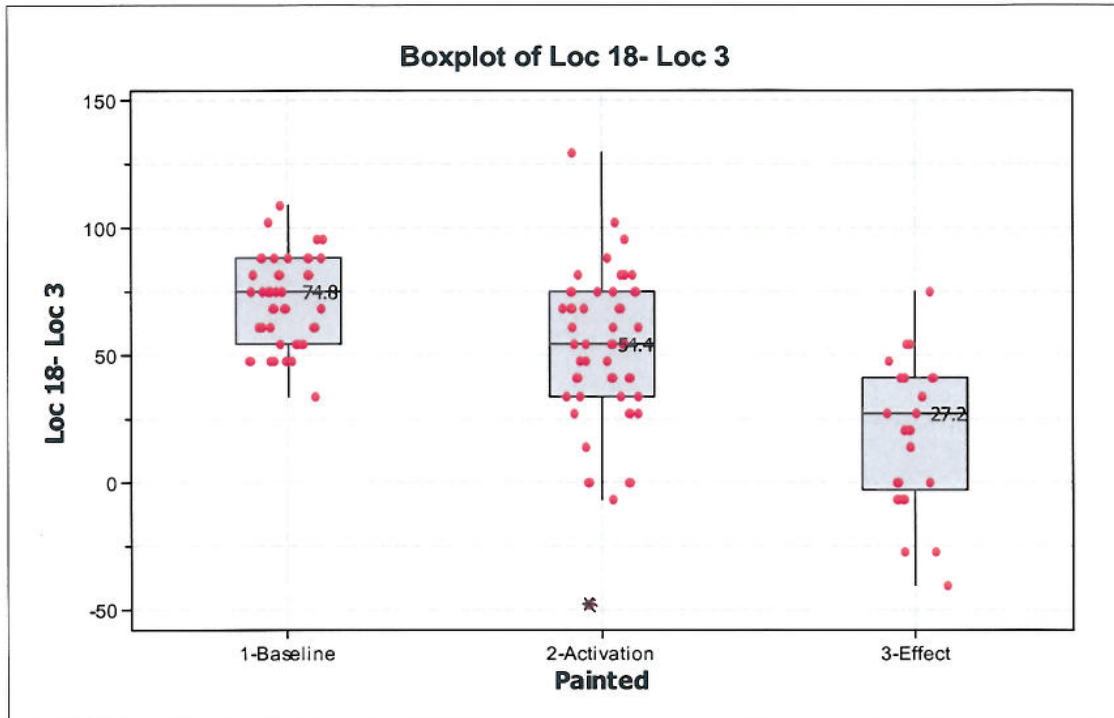


Fig.5

The actual reduction after a period of 6 months was shown to be 26%. Versus the based line, this was shown to be statistically significant. The activation period was chosen to be 2 months as the product does require some exposure to sun light and rain to remove adsorbed organics of the photocatalyst before it can become fully functional. This activation period is very paint specific, can differ and is largely very dependent on the exact composition and formulation. However, for interior car parks etc, It is now possible to make paint with little or no activation period, although all paints do show better performance with ageing.

Similar results are shown for other locations. The locations were chosen for their different exposure levels to sun light, wind speed as these are two factors which were clearly expected to affect the efficiency of the paint to reduce the NOx. The location 4 shown below is a very similar location with respect to confinement, wind speed and hours a daylight exposure. The reduction in NOx levels was also shown to be very similar. Once again, after activation period the levels of NOx dropped to 27% below the baseline figure. We should also point out that these numbers are clearly related to the amount of paint deployed. If we were to increase the surface area of the painted wall the percent reduction would also increase. We anticipate that a 5 fold factor in surface area with double the efficiency of the paint. Therefore for example if we were to increase the surface area from 500m² to 2,500m² we would expect to see reductions at the centre of the painted wall of as much as 50%.

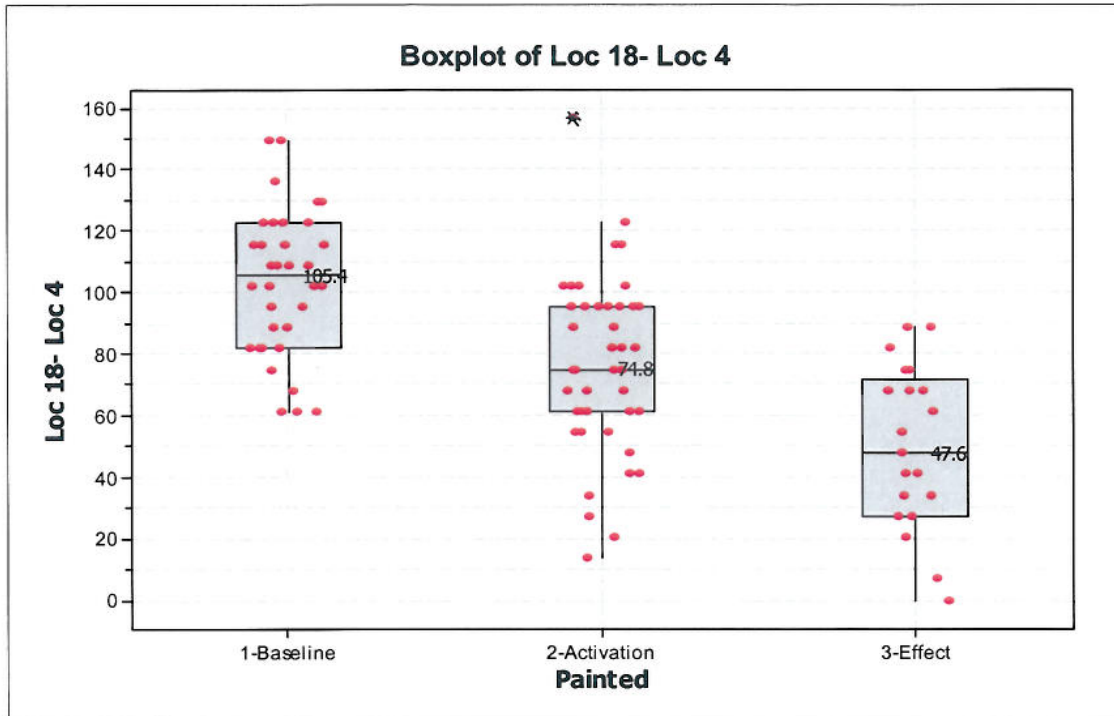


Fig. 6

Other locations were chosen to be at higher levels from the road, inside the MRT station with little or no direct sunlight, at the entrance of tunnels where direct sunlight is restricted, in total 13 locations were painted with photocatalytic paint. Of those 13 locations 8 are now showing statistically significant reductions in NO_x levels. This does not mean to say the other locations are not working, they almost certainly are, it's simply that the wind speed is probably too high to measure the effect. We know that the effect is easiest to detect with low wind speeds in enclosed areas. This was demonstrated in earlier trials and can also be seen in the London trial shown below.

Fig 7 shown below, once again shows a statistically significant drop in the levels of NO_x over a similar time frame to locations 3 and 4 however the magnitude of the drop is less than at locations 3 and 4 shown above. In this case we can measure only a 17% reduction. This does not mean the paint is working less well at location 5, it simply means the wind speed may be higher or the hours of direct sunlight were less.

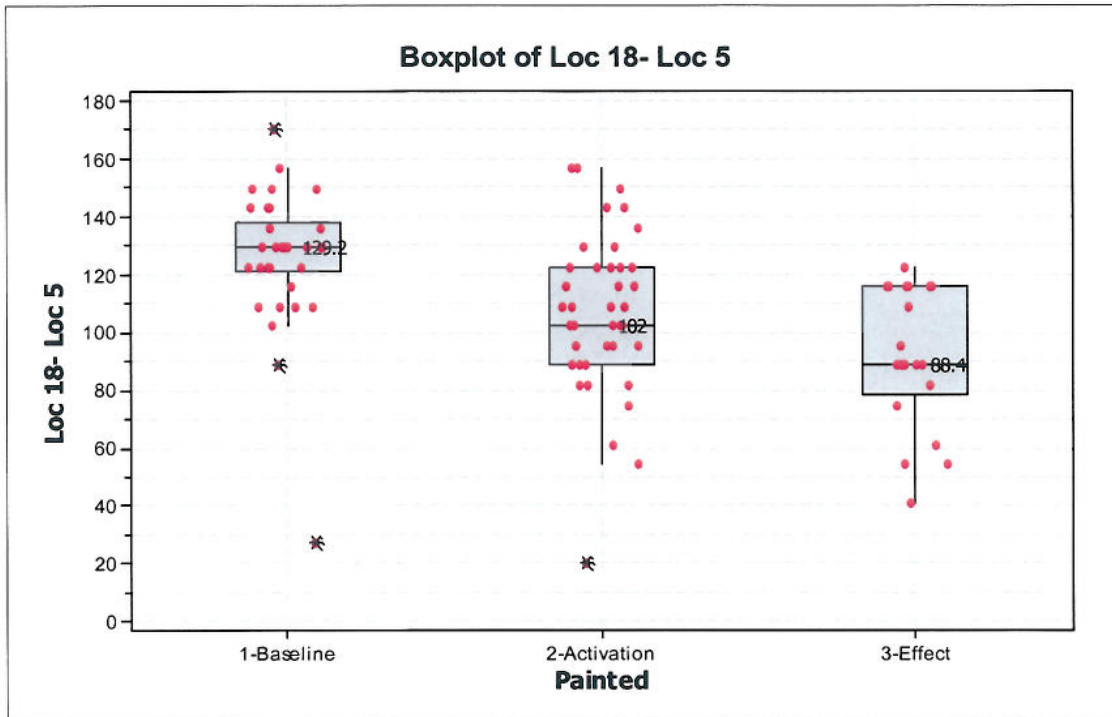


Fig. 7

3. Applications (Camden Trial)

Another trial which has been carried out was in the London Borough of Camden. Camden is very much central London as shown on the map below in Fig 8. This trial was carried out with Chemiluminescent monitoring (NO, NO₂, NO_x, wind speed/ direction and meteorological data collects) which was taking place every 15 min of every day. Unlike the diffusion tubes this method is more accurate and we have accumulated much more data, as the diffusion tube measurements were taken daily.

The trial was also constructed differently, we have taken one years background data at the site before coating the wall with a photocatalytic coating. We also have reference sites in other locations approx. 500m away.

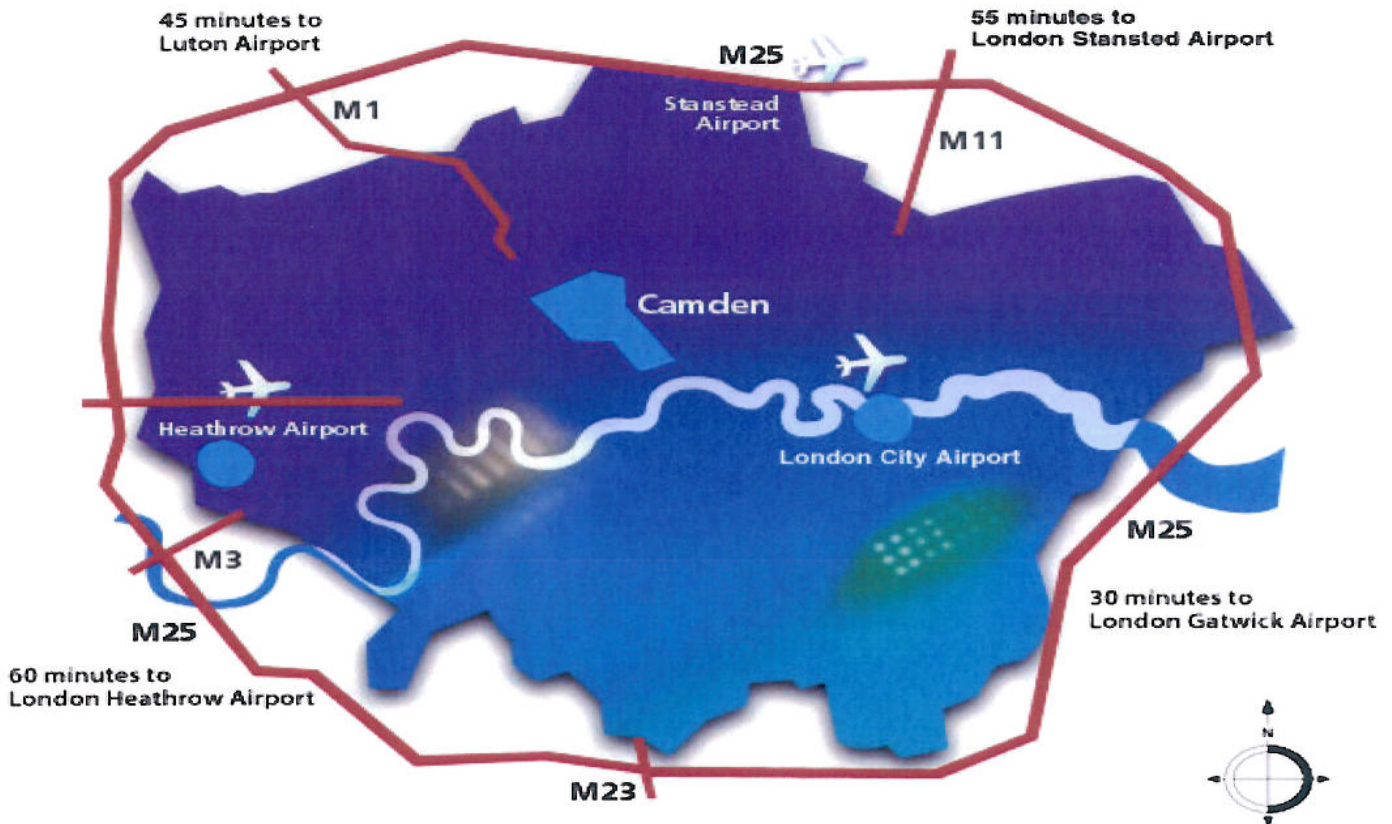


Fig 8

The actual trial site is shown in fig 9 below, the wall was completely re-furbished in late 2007 and the monitor was positioned with inlets at 15cm from the wall and 1.5 m from the wall as can be seen in the picture below.

Monitoring took place for the whole of 2008 to gain at least 1 full year of background data, this was essential to look at the seasonal effects of the pollution. It is well known in London that the variability from summer to winter can be very large. The actual photocatalytic product was chosen to a transparent sol which had been tested in the laboratory for 18 month prior to the application, the lab results suggested the product did not loose any activity over the 18 month period, when applied to a concrete paving block.

The same sol was then applied to the 300m² area of wall, shown in the picture below, mid March. Measurements where then taken at 15min intervals for the whole of 2009 and will continue to be taken until June 2010.



Fig 9

The results are shown in Fig 10. below. The box plot shows the data after the application to be lower than at anytime in the previous year. Particularly, compared to the same period in the previous year, which is the correct way to carry out the comparison because of diurnal effects. Fig 10 shows the comparison between a 24hr period in June 2008 with June 2009. In this case we can see the effect of the photocatalytic coating kicking in just after sunrise and becoming greatest around midday. The coating is seen to be effective until after 10pm at night just before sunset. The most interesting point is that the product is working with diffuse light as there is no direct sunlight on the wall until midday.

Furthermore, if we look at the comparison with the reference site for the same period shown in Fig 11, we see very little reduction in NO_x during daylight hour. Fig. 11 is for data collected at Shaftsbury avenue which is about 500m away form the St Martins College trial site.

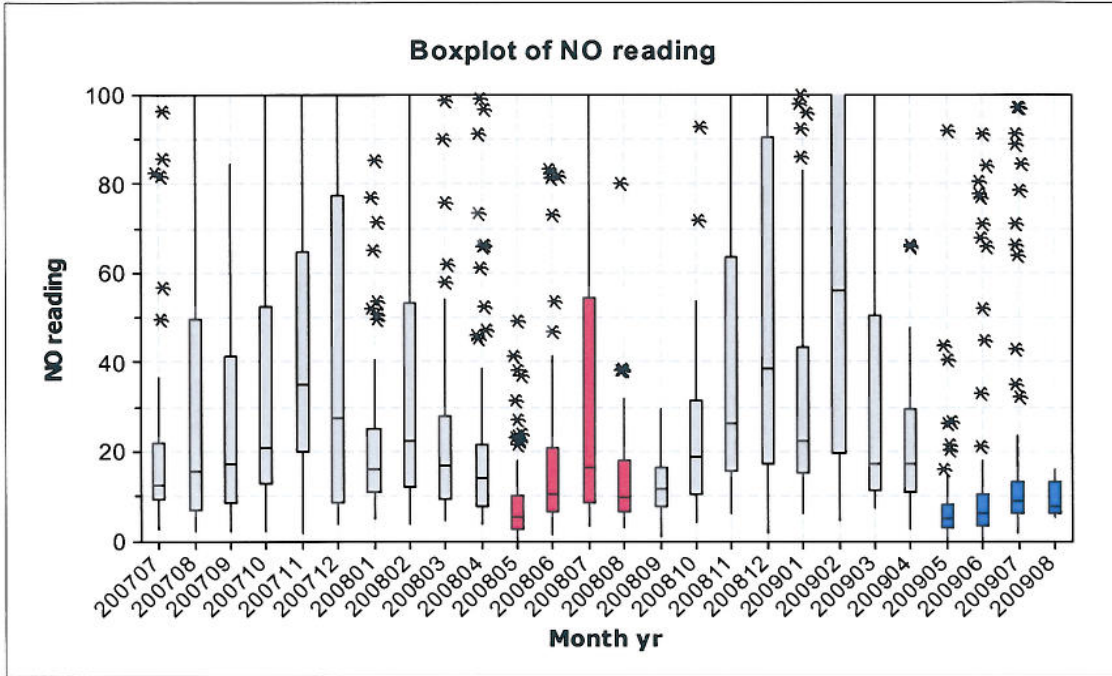


Fig.10

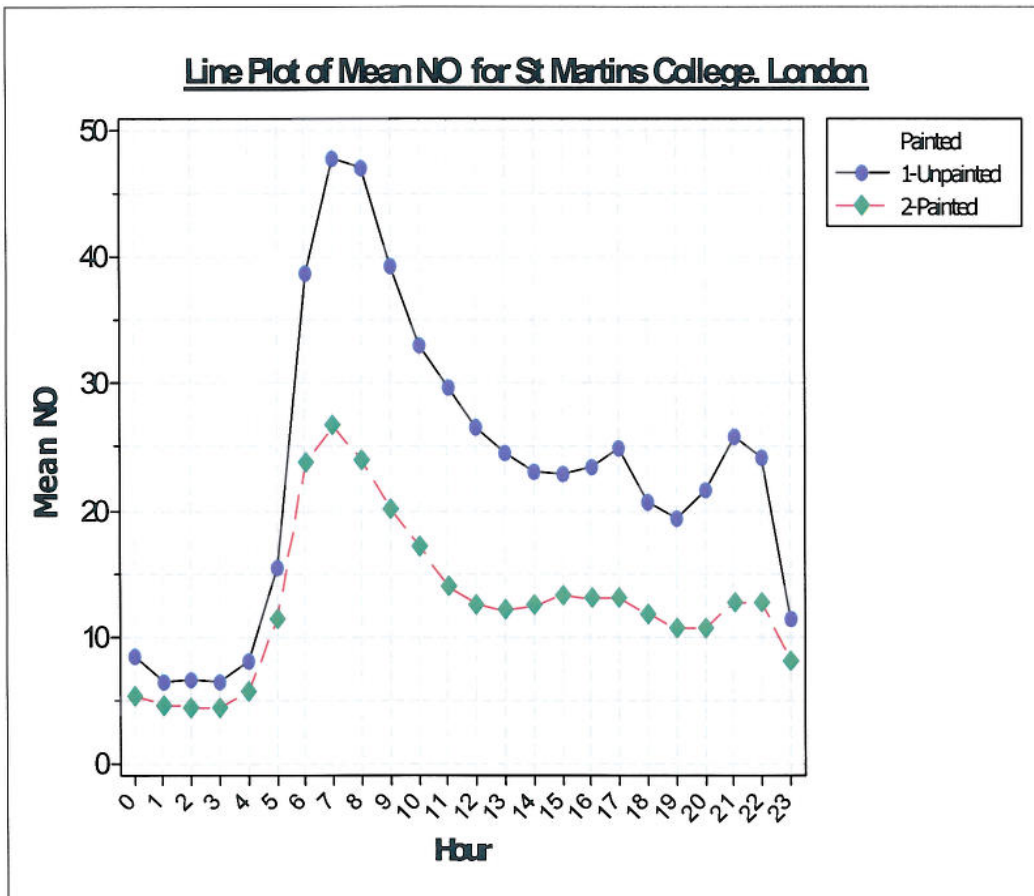


Fig. 11

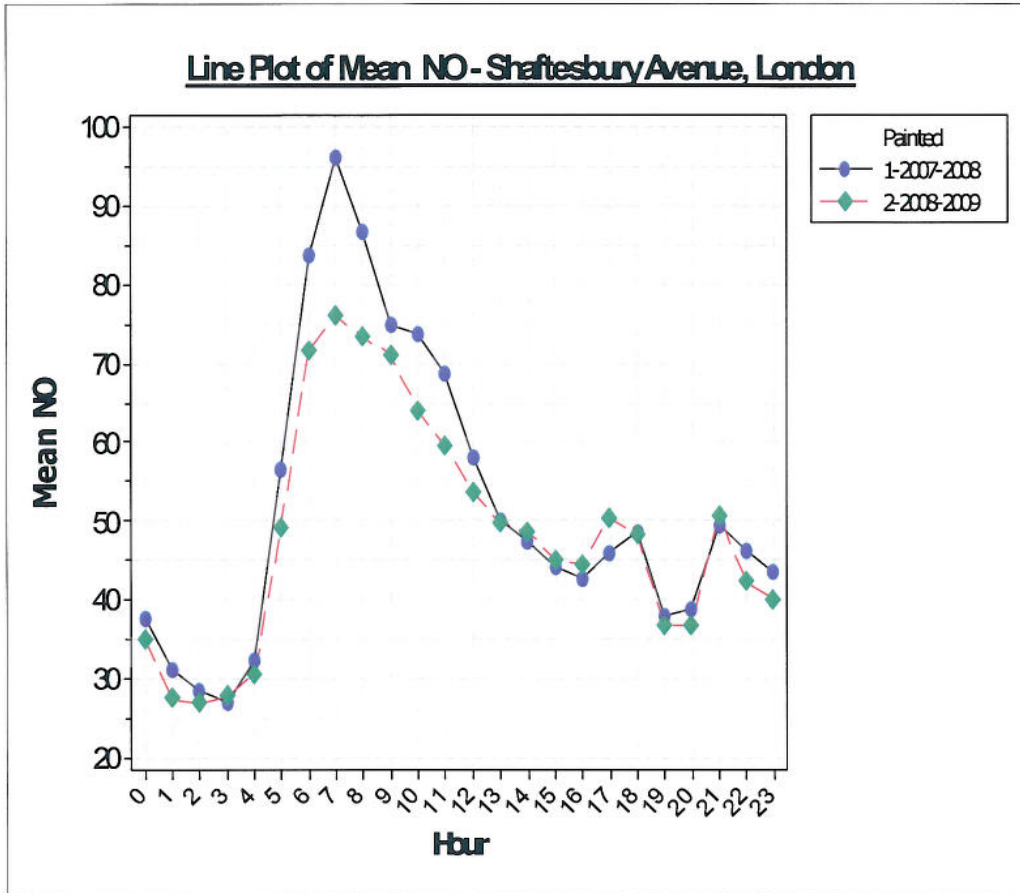


Fig 12

Conclusions

The above two trials demonstrate the effectiveness of Photocatalytic coatings for the use in pollution control. The trial in Manila was a conventional white paint containing photocatalyst called KNO_xOUT from Pacific Paints in Manila. The trial in London was made using a sol made with special peptising agents and binders for adhesion to concrete. Although we don't anticipate the sol to last as long as a paint, re-application may be necessary every 2-3 year to be most effective.

We know from laboratory testing the both of these products will also remove VOC's such as toluene, xylene, benzene and acetaldehyde etc. We need to carry out field trials to show just how effective these products can be for VOC's and also particulate matter. We know PM 2.5 and 0.1 are now becoming major issues for large cities in Europe and around the world.

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