Depollution Coatings using Photocatalysis
or
"How my back fence became a pollution filter"

Steve Forrest – Marketing Manager Asia Pacific
Cristal Global

Surface Coatings Association Australia
2009 Conference, Glenelg South Australia
Eco Footprints, Sustainable Coatings across Australasia

Abstract

It is estimated that 5,000 people in metropolitan Manila, in the Philippines, die prematurely each year as a direct result of air pollution. The World Health Organization estimate over 2,000,000 million people die each year world wide.

The most damaging components of outdoor air pollution are the various nitrogen oxides (collectively referred to as NOx) with the single biggest source of NOx being vehicle combustion engines. NOx reacts to form smog causing breathing problems. In addition, it damages crops and vegetation. NOx also reacts to form particulates and acid vapour that penetrate the lungs and can lead to emphysema, bronchitis or respiratory disease.

Cristal Global, a leading manufacturer of ultrafine titanium dioxide, has been engaged in trials monitoring the effectiveness of deploying photocatalytic coatings in polluted locations. These photocatalytic surface coatings are able to react with various air pollutants, principally NOx. Results demonstrate such coatings react with the pollutants removing them from the air and generating less harmful components.
It is encouraging to have coatings, manufactured and used, in ways that minimise their environmental footprint, but it is a paradigm shift to have a coating that actively improves air quality.

Introduction

Air pollution is a major environmental risk to health. The World Health Organization estimates air pollution is responsible for over 2,000,000 deaths world wide per year[i]. These effects are felt in both developed and developing countries.

Even in a country as relatively clean as Australia the numbers are significant. The Australian Bureau of Transport and Regional Economics (BTRE) estimates in the year 2000, motor vehicle pollution accounted for approximately[ii]:

- 900-2,000 premature deaths;
- 900-4,500 cases of morbidity from cardio-vascular disease, respiratory disease and bronchitis; and
- 700-2,050 asthma attacks (as a contributing factor)

The BTRE estimate the total economic costs of these health impacts in Australia to have been AUD$2.7 billion.[iii]

The photocatalytic properties of titanium dioxide (TiO_2) are well documented yet practical applications employing this technology are few. With the harnessing of the photocatalytic properties of titanium dioxide there is potential for it to be deployed against air pollution, specifically NOx, SOx and VOC's.

This paper will briefly discuss some of the contributing environmental issues related to air pollution and the mechanism of photocatalytic coatings, before focusing upon developments in depolluting coatings and on the trials that have been conducted.

Air Pollution

Some of the most damaging components of air pollution are the various nitrogen oxides collectively referred to as NOx. Combustion of fossil fuels in transportation or industrial applications emits NOx as gaseous by-products. For example, typical fuel combustion products would be:

$$\text{Fuel} + \text{Air} \;.\; \text{Hydrocarbons} + NO_x + CO_2 + CO + H_2O$$

Since the 1970 Clean Air Act the US Environmental Protection Agency (EPA) has been tracking the six major types of pollutants; carbon monoxide, lead, nitrogen oxides, particulates, sulphur dioxide and volatile organic compounds. Implementation of the various Acts has reduced the level of pollutants emitted and though all of the major six have decreased since monitoring began, NOx has been reduced the least. Lead emissions have been reduced by 98% and particulates by 80%, whilst NOx has been reduced by less than 30%[iv]. It has been stated that "*Reducing emissions of NOx is a crucial component of EPA's strategy for cleaner air*"[v]

Major sources of NOx

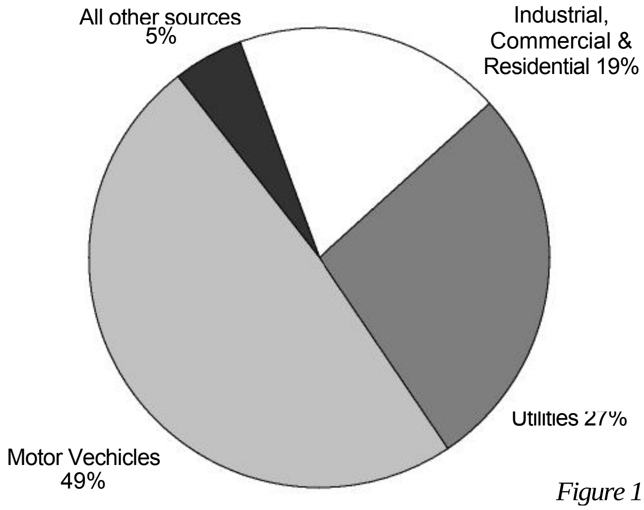

Figure 1

The single biggest source of NOx is from vehicle emissions. Utilities, industrial, commercial and residential sources are also significant contributors but individually are dwarfed by the out put by motor vehicles.

Health & Environmental Impacts

There are a number of inter related health and environmental impacts resulting from NOx emissions.

Ground Level Ozone (Smog) - NOx is a key component in the formation of photochemical smog. This forms from NOx and VOCs reacting under heat and sunlight. It can particularly impact upon children, elderly and people suffering from, or with a disposition towards, asthma. Those exposed to high concentrations or for prolonged periods are susceptible to lung tissue damage and reduced lung function.

Particulates – NOx in combination with ammonia, moisture and other compounds form nitric acid vapor and associated particulates. The vapor has potential to damage lung tissue whilst the small particulates can penetrate deeply into the lungs causing or exacerbating respiratory diseases like emphysema and bronchitis.

Acid Rain – NOx and SO_2 react in the atmosphere to form acids. These descend as rain, snow or dry particles damaging vegetation, superstructures and buildings. Decent into water ways can cause pH drops in lakes and rivers impacting wildlife.

Global Warming – one of the components of NOx is nitrous oxide (N_2O). Nitrous oxide is a serious green house gas rated as one of the top four most abundant greenhouse gases. Due to its atmospheric life time and ability to absorb and emit thermal radiation it is rated as almost 300 times more potent than carbon dioxide.

Impairment to Visibility – nitrate particles and nitrous oxide can block the transmission of light reducing visibility and contributes to the visible brown haze or plume noticeable above polluted cities.

Mobility - NOx and the pollutants formed from NOx, tend to have significant resonance times allowing them to be transported by prevailing winds over long distances. The problems associated with NOx, damage to crops and vegetation for example, are not confined to areas where the NOx is emitted.

Photoactivity

The photoactivity of titanium dioxide is well known. Absorption of light, of the relevant frequency (near UV), is sufficient to raise an electron from the valancy band to the conductive band, where they have mobility. This results in charge separation within the crystal, leaving a positively charged ‘hole’ in the valancy band. The electron and hole pair are refered to as a ‘exciton’. The light induced generation of excitons has traditionally been seen as a disadvantage in pigmentary applications as the resulting oxidizing nature is capable of degrading most polymer systems.

Three mechanisms characterizing the cyclic reaction of photo-induced oxidation of polymers by TiO_2 and generation of radicals are listed below[vi]:

1. Photoexcited TiO_2 forms an oxygen radical anion by electron transfer from molecular oxygen. A modification of this scheme involves a process of ion-annihilation to form singlet oxygen which then attacks any unsaturation in the polymer[vii].

$$TiO_2 + O_2 \xrightarrow{hv} TiO_2^{+\cdot} + O_2^{-\cdot}\ (I)$$
$$(I) \rightarrow TiO_2 + {}^1O_2\ (\textit{ion-annihilation})$$
$$(I) + H_2O \rightarrow TiO_2 + HO^{\cdot} + HO_2^{\cdot}$$
$$2HO_2^{\cdot} \rightarrow H_2O_2 + O_2$$
$$RCH_2{=}CHR' + {}^1O_2 \rightarrow RCH{=}CHCH(OOH)R'$$

2. Water catalysed by photoexcited of TiO_2 form reactive hydroxyl radicals by electron transfer. The Ti^{3+} ions are oxidised back to the stable Ti^{4+} ions to start the cycle over again.

$$H_2O \xrightarrow{(TiO_2)\ hv} H^+ + e'\ (Aqu) + {}^{\cdot}OH$$
$$[Ti^{4+}] + e' \rightarrow [Ti^{3+}]$$
$$[Ti^{3+}] + O_2 \rightarrow [Ti^{4+}]$$

3. An exciton (p) created by the irradiation of TiO_2, reacts with the surface hydroxyl groups of the TiO_2 to form a hydroxyl radical. Oxygen anions are also produced

which are adsorbed onto the surface of the pigment particle. These inturn produce active perhydroxyl radicals.

$$TiO_2 \xrightarrow{hv} e' + (p)$$
$$OH^- + (p) \rightarrow HO^\cdot$$
$$Ti^{4+} + e' \rightarrow Ti^{3+}$$
$$Ti^{3+} + O_2 \rightarrow [Ti^{4+} \ldots\ldots\ldots O^{2-}]\ \textit{adsorbed}$$
$$[Ti^{4+} \text{———} O^{2-}]\ \textit{adsorbed} + H_2O \rightarrow Ti^{4+} + HO^- + HO_2^\cdot$$

The result is a cyclic reaction, catalysed by TiO_2, resulting in hydroxyl radicals and perhydroxyl radicals generated whilst moisture, oxygen and light are available. As a catalyst the TiO_2 is not consumed in the reaction allowing continual generation under suitable conditions. Pigment manufacturers have gone to great lengths and conitnue to research methods to limit the photoactivity with lattice doping and inorganic surface treatments. In contrast, to utilise the photocatalytic properties of titanium dioxide, every effort is made to encourage its photoactivity.

Considerations for Photoactivity

Titanium dioxide pigments are commercially available in two morphological crystalline forms: anatase and rutile. They exhibit different levels of photoactivity, with the differences depending markedly upon the manufacturing history of the TiO_2. Surface characteristics are also an important factor in controlling photoactivity. The surface is covered with amphoteric hydroxyl groups formed by the adsorption of water. Those found on anatase are more acidic in character and less effectively bound than those on rutile. Therefore the third reaction mechanism, shown previously, occurs more slowly in the case of rutile. These accumilated differences results in anatase pigments being more photoactive than rutile types.

To further encourage photoactivity, size of the titanium dioxide becomes important. Photo-oxidation studies[vi] on coatings indicate a clear demarcation between nanostructured Ultrafine TiO_2 products (5-50nm) and pigmentry grade titanium dioxide (250-300nm). Ultrafine TiO_2 products are far more photoactive than pigmentry sized products as characterized by increased chalking and gloss reductions when incorporated into identical resins.

In combining an Ultrafine anatase TiO_2 with controlled manufacturing history and surface conditioning, a highly photocatalytic product can be generated.

Depollution Mechanism

Research has found that the highly reactive species generated from irradiated TiO_2 can be deployed against pollutants. A NOx reduction test has been established in which test coatings are applied to a sample plaque and sealed in a chamber that has a constant feed of NOx. The chamber is irradiated and a chemiluminescence detector measures the level of NOx leaving the chamber.

Experiments have illustrated that deploying photoactively enhanced Ultrafine TiO_2 particles in coatings gives the resultant film the ability to react with pollutants. Principally NOx, SOx and VOCs can be broken down to less harmful components. There are a number of variables in formulating a coating which markedly impacts the effectiveness of a given film, but a key component is the inclusion of a suitable calcium carbonate. The photocatalysis reaction with pollutants is summed up below;

1. NOx comes into contact with photocatalytic TiO_2 in the film and in the presence of moisture it is converted to nitric acid. This in turn is neutralized by calcium carbonate, also present in the coating, forming calcium nitrate within the film. Water and carbon dioxide are then released.

$$NO_x + H_2O \rightarrow TiO_2 \rightarrow HNO_3$$
$$HNO_3 + CaCO_3 \rightarrow Ca(NO_3)_2 + H_2O + CO_2$$

2. A similar reaction to NOx occurs for sulphur oxides or SOx. The SOx is converted to sulphuric acid. The acid is neutralized by calcium carbonate, water and carbon dioxide is emitted.

$$SO_x + H_2O \rightarrow TiO_2 \rightarrow H_2SO_4$$
$$H_2SO_4 + CaCO_3 \rightarrow Ca\ SO_4 + H_2O + CO_2$$

3. Volatile organic compounds are equally vulnerable to the photo activated TiO_2 in the film breaking down to water and carbon dioxide.

$$VOC + H_2O \rightarrow TiO_2 \rightarrow H_2O + CO_2$$

There may be the concern that a by product from these reactions is the emission of CO_2. No increase in CO_2 emissions is generally desirable but this has to be put into perspective. The NOx removed from the air is significantly more toxic from a health and global warming perspective. The volume of CO_2 given off by 1sq metre of photocatalytic paint has been measured at 1g per year. Contrasted against the average output from a single persons breathing, CO_2 emissions are on the order of 900g *per day* or greater than 320kg per year.

Coating Formulations

It should be noted that the role of the nanoparticle TiO_2 is purely as a catalyst and therefore it is not consumed during the process. This indicates that the reactivity of a film should not diminish over time. There are however two limitations on the useful life of a film.

Firstly the level of calcium carbonate consumed in the neutralization step could be an issue however the recommended level for effective formulations has been calculated to be sufficient for several decades of performance. The oldest films to date have not indicated a reduction in performance due to calcium carbonate consumption.

The second limitation is the '*life*' of the coating. The durability of a coating does have potential to become a limitation on expected performance. There are challenges formulating with such active ingredients. The very feature that makes Ultrafine TiO_2 suitable for depollution has a significant impact upon polymer considerations. The durability of most common polymers is tested if any length of service is to be considered. Ideally the coating must be photo-resistant to the effects of the TiO_2 and resistance to acids would be an advantage.

The final coating also benefits from being porous to allow increased contact between the nanoparticle TiO_2 surface and the pollutants.

It is not the intention of this paper to discuss, in detail, formulation development and polymer technologies associated with depollution coatings, as this is an area of on going research. Suffice to mention that there are patent applications on several specific polymer systems in conjunction with photocatalytic TiO_2 including polysiloxanes[viii] and alkali metal silicates.[ix]

Trials

There have been a number of trials to gauge an insight into the most effective deployment of depollution coatings. A selection are summarised in the following section.

PICADA & 'Street Canyon'

Started in January 2002, Millennium Inorganic Chemicals, now Cristal Global, was a leading member of an international consortium chartered to develop and validate pollution abatement using photocatalytic coatings. The PICADA (Photocatalytic Innovative Coverings Applications for Depollution Assessment) project was a European Union initiative that ran until December 2005, at a cost of 3.4 million Euros. It included leading organizations and universities in pollution modelling and urban testing as well as engineering firms to deploy and gauge the technologies potential.

Trials were a key component of the PICADA mission. One of the most significant tests was the construction of the 'Street Canyon' pilot site. Here a number of shipping containers were aligned to create two alley ways, 2.4 metres wide, 18 metres long and with sides 5.2 metres high. This was to simulate environmental conditions of a street in an urban setting. To simulate traffic a combustion engine was run and its emissions channelled down perforated pipes in each 'alley way'.

The intent was not to deploy and measure a depollution coating but to gauge how well computer modelling matched real pollution measurements taken on site. Sophisticated software attempted to predict pollution patterns modelled upon topography, pollution levels, weather and wind direction. A range of monitors were positioned to detect NOx and VOC levels. Detectors to measure meteorological changes; humidity, temperature, solar irradiation, wind velocity and direction were also employed.

What the 'Street Canyon' trial validated was that pollution modelling is a valid method to predict real pollution flows and dispersion, provided sufficient data can be accumulated concerning the specific location and level of pollutants. Having confirmed the reliability of this technology, future trials were able to be assessed and analysed with much greater precision.

Pedestrian and Road Tunnel, Porpora Street, Milan

In conjunction, Global Engineering of Milano, Italy and a member from the PICADA group, set up a depollution trial in a pedestrian and road tunnel under the Milano Lambrate railway in Milan. Pollution levels were considered heavy with traffic counts of up to 30,000 vehicles per day using the tunnel. Pedestrian walkways line both sides of the two lane road in this enclosed environment.

Global Engineering in development with Cristal Global provided and applied a separate photocatalytic coating, based upon a patented photocatalytic concrete road coating, to the ceilings and walls. The tunnel is a little over 100 metres long and 7 metres wide. Several UV lighting bars were installed along the length of the tunnel. Natural light only penetrated a short distance at either entrance. Multiple sampling points along the length and on both sides of the tunnel were installed.

An independent third party, Euro Quality Systems® conducted sampling before and after deployment of the photocatalytic coatings. Their testing over a six day period gave the following results;

- 67% reduction in NOx
- 47% reduction in SOx
- 47% reduction in PM 2.5

PM2.5 is a measure of particulate matter less than or equal to 2.5 microns. This fraction is considered a respiratory concern.

The results confirmed the de-pollution performance of the various coatings and the ability for effectiveness under less than ideal lighting conditions. It did illustrate the effectiveness of a combined deployment of photocatalytic coatings to both road and ceiling and walls.

Sir John Cass Primary School, Aldgate, London

The Sir John Cass primary School in central London was selected as a typical location where photocatalytic paint could be applied in an urban environment to improve air quality. A 300sq metre exterior wall was coated directly adjacent to the entrance of a children's playground area.

Continuous roadside air monitors provided 14 months of data for the area. These were supplemented with 4 sets of diffusion tubes to be used at multiple locations in the area. NO_2 levels were detected to be at an average of 37ppb, whilst European Directives are scheduled to come into affect in 2010 setting a 21ppb limit.

Nitrate boxes were also used and attached directly to the coated wall. These boxes are comprised of multiple panels, several coated with the photocatalytic coating and several 'blanks', panels coated with a regular non-photocatalytic coating. These were enclosed in a Perspex box which allowed illumination but providing protection from the elements whilst still allowing ventilation. The protection from the elements is to prevent calcium nitrate captured in the coating from being removed, as it is a water soluble compound. The boxes provide a sample of coating that can be taken away for ion chromatography analysis to determine how much nitrate is being captured.

Computational Fluid Dynamic (CFD) was used to model the effects of wind direction on pollutant concentrations and pluming around the site. This feature is a particularly important consideration in built up urban settings where the topography of buildings can channel pollutants creating areas of concentrated NOx adjacent to other areas.

Not surprisingly, results from the roadside monitors did not establish a detectable drop in pollution levels for the general area. The location of the road side monitors, several metres from the wall, suggests that changes in the immediate vicinity of the wall went undetected. The diffusion tubes did detect differences between the road side monitor locations and closer proximity to the coated wall. This indicated that for such a limited deployment the depollution affect did not extend beyond a couple of metres from the coated surface. Accumulation levels from panels in the nitrate box compared to blanks did nevertheless confirm a significant level of nitrate was being captured by the coating, shown in figure 2.

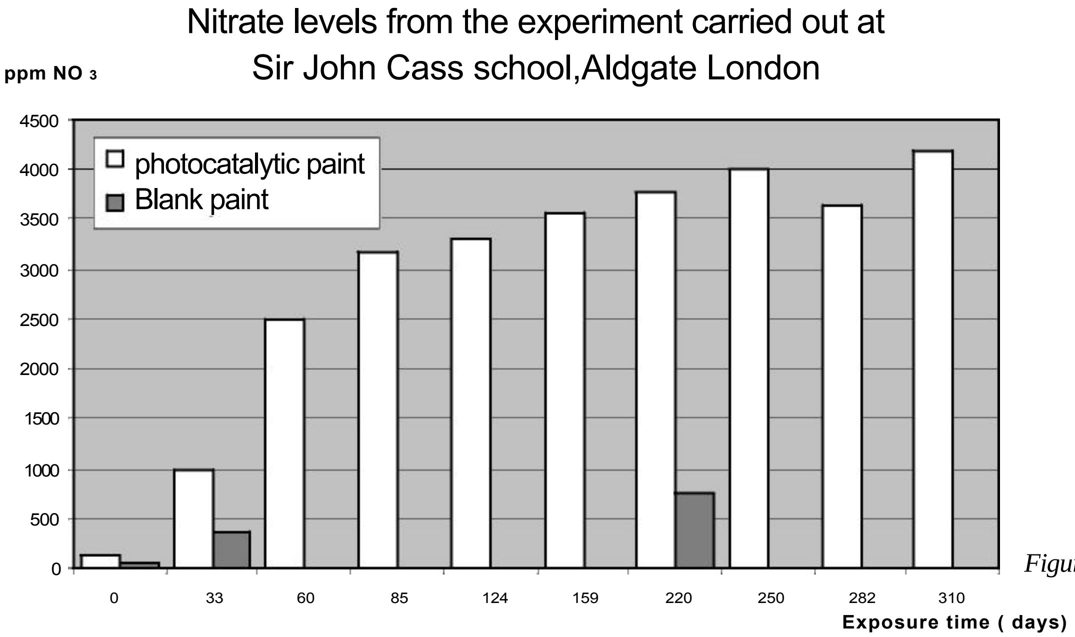

Figure 2

Based on the detected levels of nitrate captured on the coatings the following calculations were made concerning the 300sq metre deployment;

- At least 4.5g of NOx was being removed daily
- Volume of air being treated was 10,000m^3 per day
  - > Assumed reduction from 37ppb to 0ppb
- The coated area '*cleaned*' the equivalent of 2,000 passing vehicles per day
  - > Assuming 50:50 diesel:gasoline vehicles
  - > 1 sq metre purified the equivalence of 6 passing vehicles per day

Low level lighting – Car Park trial, Paris

To test aspects of low level lighting and polymer variations, a trial was designed for an enclosed underground car park in Paris. Coatings were applied, covering 1,800 sq metres of walls and ceilings. Nitrate accumulation in the coatings were measured at two locations; one near the entrance, exposed to diffuse natural light and another well within the car park exposed to only standard fluorescent lighting.

NOx levels in the car park area prior to testing were gauged at 1,000ppb, more than 47 times the European Directive for 2010. These readings highlight the dangers enclosed areas pose where combustion emissions can concentrate.

Another feature of this trial was gauging self-cleaning performance. Most car parks are painted grey or dark colours to hide soot build up. Hence increased lighting is required to sufficiently illuminate these types of underground locations. With a photocatalytic coating there is the potential that particulate matter will be reduced (suggested from the Milan tunnel experiment), which when combined with a level of self-cleaning diminishes the requirement of hiding soot build up. This provides the opportunity to deploy white or pale coloured coatings enhancing available illumination. This feature has the potential to reduce the level of lighting required in underground car parks and is an area of ongoing research.

Nitrate accumulation was measured in the car park for the two different formulations (A & B) at both locations. Calculated reductions from the prior baseline are shown;

Formulation A inside car park = 2.25g of NOx per day
  > 53.6% reduction in NOx

- Formulation A near the entrance = 3.64g of NOx per day
  > 90.1% reduction in NOx
- Formulation B inside car park = 3.75g of NOx per day
  > 89.4% reduction in NOx
- Formulation B near entrance = 7.54g of NOx per day
  > 100% reduction in NOx every 13.3 hours

This trial highlighted just how significant the influence of the coating is when developing an effective depollution coating. It also indicated that though reduced performance can be expected in interior locations it is possible for photocatalysis to occur even under fluorescent lighting.

Summary

It is encouraging having coatings, manufactured and used, in ways that minimise its environmental footprint, but it's a paradigm shift to have a functional coating that can actively improve air quality.

The photocatalytic properties of titanium dioxide are well documented yet practical applications of this technology are still relatively few. Ultrafine titanium dioxide embedded in a coating, combined with calcium carbonates, allows photocatalysis properties to be deployed against airborne pollutants, specifically NOx, SOx and VOC's.

This paper has touched upon some of the ongoing work in this field of research. Depollution coatings on their own are not the answer, but whilst combustion engines are still used, the deployment of depollution coatings offers a weapon in the arsenal against air pollution. The ability to coat any paintable surface, allows significant volumes to be deployed upon areas presented in a cityscape. Painting a building or a fence would not merely be improving the aesthetic appearance but could deploy an active contributor to improving the air quality for your family and neighbourhood.

References

[i] World Health Organization (2005). "*Air Quality & Health*". Retrieved 22 December 2007 from http://www.who.int/mediacentre/factsheets/fs313/en/index.html

[ii] BTRE (2004). "Health impacts of Transport emissions in Australia: Economic costs", p 90-91

[iii] BTRE (2004). "*Health impacts of Transport emissions in Australia: Economic costs*", p 105

[iv] DuPont, P., (2006). "*Don't be very Worried*". Wall Street Journal May 23 2006. Dow Jones

[v] US EPA office of Air Quality Planning & Standards (1998). "*How nitrogen oxides affect the way we live and breath*". EPA-456/F-98-005

[vi] Allen, N., Edge, M., Sandoval, G., Verran, J., Stratton, J. & Maltby, J. (2005). "*Enviromental Photocatalytic coatings applications*". Photochemistry & Photobiology, 2005, 81: 279-290

[vii] Laurenson, P., Arnaud, R., Lemaire, J., Quemner, J. & Roche, G. (1978). "*Photothermal Degradation of Polyethylene Films: II: Action of Photocatalytic Metallic Oxides*". Eur. Polym. J., (1978), 14, 129-137

[viii] Stratton, J. (2006). "*Composition useful for Providing NOx Removing Coating on Material Surfaces*". WIPO, WO2006/030250

[ix] Goodwin, G., Stratton, J. & McIntyre, R. (2005). "*Coating Composition having Surface Depolluting Properties*". WIPO, WO2005/083014