The Problem: Air Pollution

Significant improvements have been made on emissions control, but more work is needed to have cleaner air.

Several environmental agencies and NGOs are raising the awareness of the health risks related to pollution. In previous years, the major focus has been on CO₂ and Particulate Matter (PM10 and PM2.5), however NOx levels have become well known for their contribution to the pollution problem.

Photocatalysis provides a way of converting otherwise harmful pollutants into harmless materials.

Various studies have shown that the other several actions implemented to control pollution such as Low Emission Zones (LEZ), the use of eco-friendly engines and cleaner fuels have not provided the expected results and other technologies are required.

Exposure to NOx causes multiple respiratory complications for the global population including airway inflammation in healthy people and increased respiratory symptoms in people with asthma.

A recent study revealed that more than 1,100 schools in London are within 150m distance from roads carrying more than 10,000 vehicles a day. The same study showed that people living near roads carrying more than 10,000 vehicles a day are vulnerable to heart diseases and that air pollution could be responsible for 15 to 30% of all new cases of asthma in children.

The Health Costs

Air pollution has a relevant negative impact on our economy.

The cost of damage caused by emissions in 2009, just from the industrial facilities reporting into the E-PRTR (European Pollutant Release and Transfer Register), is estimated as being at least EUR 102–169 billion. Fifty per cent of the total damage cost occurs as a result of emissions from just 191 (or 2%) of the approximately 10,000 facilities that reported at least some data for releases to air in 2009. Three quarters of the total damage costs are caused by the emissions of 622 facilities, which comprise 6% of the total number.

AIR POLLUTION AND HOW IT IMPACTS OUR HEALTH

- Shorter life expectancy
- Pulmonary problems
- Reduces the effectiveness of asthma inhalers
- Causes and exacerbates asthma
- Increases risk of contracting pneumonia
- Heart problems
- Increases susceptibility to microbes
- Increases the risk of a low birth weight or lethargic baby

Source: European Environmental Agency
Focus on NOx

Sources
Nitrogen dioxide (NO$_2$) is a reactive gas that is mainly formed by oxidation of nitrogen monoxide (NO). High temperature combustion processes (e.g. those occurring in car engines and power plants) are the major sources of nitrogen oxides, NOx, the term used to describe the sum of NO and NO$_2$. NO makes up the majority of NOx emissions. A small part is directly emitted as NO$_2$, typically 5–10% for most combustion sources, with the exception of diesel vehicles. There are clear indications that for traffic emissions, the direct NO$_2$ component is increasing significantly due to increased penetration of diesel vehicles, especially newer diesel vehicles (Euro 4 and 5). Such vehicles can emit up to 50% of their NOx as NO$_2$ (e.g. Grice et al., 2009) because their exhaust after treatment systems increase the direct NO$_2$ emissions.

Effects on Human Health
Negative health effects can be seen as a result of short-term exposure to NO$_2$ (e.g. changes in lung function in sensitive population groups) and long-term exposure (e.g. increased susceptibility to respiratory infection). Epidemiological studies have shown that diseases such as bronchitis in asthmatic children increase in association with long-term exposure to NO$_2$. Reduced lung function is also linked to NO$_2$ at concentrations currently found in cities of Europe and North America (WHO, 2008). It should be noted that as NO$_2$ is highly correlated with other pollutants (in particular PM) it is difficult to differentiate the effects of nitrogen dioxide from those of other pollutants in epidemiological studies.

Nitrogen compounds have acidifying effects but are also important nutrients. Excess deposition of atmospheric nitrogen can lead to a surplus of nutrient N in ecosystems, causing eutrophication (nutrient oversupply) in terrestrial and aquatic ecosystems. Excess nitrogen supply can lead to changes in unique terrestrial, aquatic or marine animal and plant communities, including biodiversity loss (EEA, 2010).

Nitrogen oxides play a major role in the formation of ozone. They also contribute to the formation of secondary inorganic aerosols (SIAs), through nitrate formation, contributing to PM10 and PM2.5 concentrations.

Trends in NO$_2$ and NOx Concentrations
The trends in concentrations are linked to changes in emission sources. EU emissions of NOx fell 44% in the period 1990–2009 and 8% from 2008 to 2009. Nevertheless, total NOx emissions in 2009 were about 12% higher than the aggregated emissions ceiling set in the NEC (National Emissions Ceilings) Directive for 2010.

Transport is the dominant sector for NOx emissions, accounting for 49% of the total in 2009, followed by the energy sector, which contributed 20% of the total. These two sectors have substantially reduced emissions since 1990. Actual emissions from vehicles (often termed ‘real world emissions’) may exceed the allowed emissions specified in the Euro emission standards for each vehicle type. This is particularly the case for NOx emissions from light-duty diesel vehicles. EU Member States regularly update the emission factors used in their emission inventories and their previously reported emissions.

WORLD HEALTH ORGANIZATION, SEPTEMBER 2011

“Urban outdoor air pollution is estimated to cause 1.3 million deaths worldwide per year.”
**Photocatalysis**

*Adding new functionalities to a surface*

Photocatalysis is a natural reaction occurring in presence of light, water and oxygen. The reaction is accelerated by a catalyst (Titanium dioxide – TiO₂) and it is activated by the energy of the UV light (“photo”).

When TiO₂ is exposed to UV light, electron-hole pairs are generated, facilitating reduction and oxidation reactions through the formation of adsorbed free radicals on TiO₂ surface. These radicals are extremely highly reactive species, capable to degrade the pollutants hitting or absorbed onto the photocatalytic surface; the reaction of degradation converts harmful materials, such as nitrogen oxides, sulphur oxides, VOC (volatile organic compounds) into harmless substances.

The catalyst is not consumed by this reaction, ensuring a continuous process during the service life of a photocatalytic surface.

Titanium dioxide is a raw material widely used in various applications. It is the white pigment coloring most of the items we see and use in our daily life. Coatings, wall paints, plastics, and paper are just a few examples where TiO₂ is used, to achieve white color as well as to reach the required level of opacity. Titanium dioxide is present not only in white colored materials, but it’s a key component whenever opacity is needed. Specialty qualities of TiO₂ are used in ceramics, in electronics, in cosmetics and even in drugs and foodstuffs, as well as in catalytic applications for industrial processes.

Photocatalytic TiO₂ has specific properties and it is different from the pigmented version. The morphology and the characteristics of its ultrafine particles are developed to achieve the best catalytic activity and to allow an optimal incorporation into a variety of matrix. Specific photocatalysts are developed for use in paints, coatings, cement-based materials or for direct application on surfaces (for examples on filtering media for air treatment units).

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**ADDITIONAL FUNCTIONALITIES**

- De-pollution
- Self-cleaning
- VOC abatement
- Deodorizing
- Super-hydrophilicity
Proving the Concept

College Campus, Camden, UK

A depolluting trial was conducted with Camden Council and Kings College on an exterior wall of the Central St. Martins College of Art and Design. Background data of pollutants in the area were collected for a period of one year prior to a transparent photocatalytic coating being applied to the wall surface (135m²).

Chemiluminescence monitoring of NO, NO₂ and NOx was employed in order to record the pollution levels. Two detection probes were placed at different distances from the wall surface to detect the changes in pollution levels. Parallel monitoring of pollution in a nearby area was performed to establish an ongoing baseline of air quality levels as a basis of comparison. Meteorological data such as wind speed and direction, rainfall, temperature and humidity were also continuously monitored every 15 minutes.

Monitoring of the area continued for more than two years after the application of the photocatalytic coating. The results from this trial show NOx reductions of 35-65% depending upon the time of the year and local weather conditions.

The product showed the capacity to remove up to 0.5g/m²/day of NOx. A surface of 300m² coated with this CristalACTiv™ transparent can offset the NOx emission of 50 cars travelling 20km per day.

Metro Station, Manila, Philippines

In Manila, a trial was conducted in collaboration with Pacific Paints (Boysen), leading paint producer in the Philippines, and with a consulting company specialized in pollution monitoring. The test required coating selected areas of the MRT (Metro Rail Transit) Guadalupe station for a total of more than 6,000m².

The paint formulation is the result of Cristal’s extensive R&D activity in photocatalysis. The measured NOx reduction in the vicinity of the painted walls showed that each treated square meter removes up to 80g of NOx per year. The total surface coated with depolluting photocatalytic materials is able to decompose more than 300kg of NOx per year.

VOC Reduction

Photocatalytic Ultratine Titanium dioxide, when applied by means of paints, coatings or other surface treatments is shown to destroy atmospheric pollutants such as volatile organic compounds (VOC). Within a few days to a few months from application and depending on the formulation type, a properly formulated paint is shown to become a ‘negative VOC’ product. This means that the VOC degraded by the coating material in its service life are far more than the ones emitted by the paint itself and due to the organic components of the formulation.

Cristal used a combination of a Total Hydrocarbon Analyzer (THC) and a CO₂ Analyzer to measure the VOC photocatalytic degradation in a gas stream passing in the sample cell represented in the schema below.

Tests were made on an optimized paint formulation (Styrene-Acrylic, 72.5% Total PVC and containing CristalACTiv™PC500 photocatalyst), showing significant activity in VOC reduction. Laboratory measures were confirmed also by VOC monitoring in an industrial environment (paint production workshop)1.

The measurements of the VOC levels conducted, as requested by the Health and Safety procedures, showed significant decrease once the walls of the production unit were treated with a specifically formulated photocatalytic paint using CristalACTiv™ photocatalyst technology.

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<th>AREA 1</th>
<th>Y2009</th>
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<td>XYLENE</td>
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1 Data courtesy of Pacific Paints (Boysen) Philippines, Inc.
Cristal Offering

Much more than a TiO₂ photocatalyst

Cristal’s extensive experience in TiO₂ allows the development of specific photocatalysts, tailored to different applications and providing multiple functionalities.

Our photocatalysts are available as powder materials, but also as stable aqueous solutions (sol) and as concentrated dispersions.

These special TiO₂ products are developed by our R&D Centers in Baltimore, USA and in Stallingborough, UK and are manufactured in a dedicated plant in Thann, France.

The Expertise

The optimal photocatalytic performance can be achieved only using the most advanced photocatalysts in optimized formulations. Cristal’s expertise in photocatalysis results in our scientists developing proprietary patented formulations.

Our knowledge and experience include sophisticated monitoring techniques, both in laboratory scale or in real-life conditions to validate the performances of the photocatalytic treatments.

The data from our several significant field trials, verified by reliable third parties and our theoretical modeling competences are available to help you define the characteristics of a photocatalytic treatment required to achieve your goals.

Collaboration and Partnership

Cristal’s proprietary competencies in photocatalysts and their utilization are available for our selected partners.

Licensing of the Cristal technology and the CristalACTIV™ brand provides you with the reliability of more than a decade of developmental activities conducted by a leading player in the market of the Ultrafine and Specialty Titanium Dioxide.

Furthermore, we work in close collaboration with our partners on specific projects aiming to develop and optimize unique versions of our TiO₂ products and of our formulations.

Joint activities of promotion, marketing, market development, lobbying at regulatory level are part of our collaboration.

Contact us at photocatalysis@cristal.com for further information and to discuss partnership opportunities.

<table>
<thead>
<tr>
<th>CristalACTIV™ PC-105</th>
<th>CristalACTIV™ PC-500</th>
<th>CristalACTIV™ S5-300A</th>
<th>CristalACTIV™ S5-300B</th>
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<td>~ 1.1</td>
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</tbody>
</table>
Why Photocatalysis?

- Photocatalytic surfaces can dramatically reduce local NOx levels
  - Depolluting effect quantitatively assessed over extended periods
  - Computational Fluid Dynamics calculations allow defining optimum surface to be treated

- Photocatalytic coatings are cost-effective and easy to apply
  - A useful tool to support the NOx reduction in areas of non-attainment of air quality

- Photocatalytic materials are also effective at decomposing organic stains, mold and algae that accumulate on exposed surfaces
  - The self-cleaning effect has been repeatedly demonstrated on exterior building facades, on coated structures and on transportation infrastructures

- Air pollution and specially NOx pollutants remains a major issue in developed and emerging regions.
  - The issue forces local authorities to take actions.

- Photocatalysis, as a novel and proven solution can help local authorities to meet the legal ceilings.

- Specifiers, construction and estate management companies can differentiate their projects or business with low maintenance and depolluting materials.

- Construction materials and paint formulators are under increasing pressure to provide active products to meet low maintenance and depolluting requirements.

About Cristal

Cristal is a proven leader in ultrafine TiO₂-based products which are at the core of environmental catalysts technologies such as Selective Catalytic Reduction (SCR) for NOx abatement. Based on the experience gained in the treatment of air pollutants at source, CristalACTiV™ Photocatalysis Technology emerged as novel solutions to depollute the urban air in-situ.

Cristal is a leading TiO₂ producer with a broader global footprint than any other TiO₂ manufacturer. Headquartered in Jeddah, Saudi Arabia, Cristal operates eight TiO₂ manufacturing plants in six countries and on five continents and is well-positioned to serve existing and growing markets in all major world regions.

Cristal produces its CristalACTiV™ ultrafine TiO₂ for many catalysis applications at its Thann, France plant which was expanded in 2008 to sustain the growing global demand. Relying on its global reach and a strong technology base, Cristal leads and adapts to innovations in the marketplace, ensuring that environmental catalysts will contribute to a cleaner world.

For more information, visit our websites:

www.cristal.com and www.cristalactiv.com

Contact us at: photocatalysis@cristal.com

EUROPE - MIDDLE EAST - AFRICA - ASIA/PACIFIC
24, Rue du Sentier, 75002 Paris, France
Phone: +33.1.5504.8930
Fax: +33.1.5504.8940

AMERICAS
20 Wight Avenue, Suite 100, Hunt Valley, MD 21030, USA
Phone: +1.410.229.4441
Fax: +1.410.229.4415

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Phone: +33.1.5504.8930
Fax: +33.1.5504.8940

AMERICAS
20 Wight Avenue, Suite 100, Hunt Valley, MD 21030, USA
Phone: +1.410.229.4441
Fax: +1.410.229.4415
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For earth-friendly coatings