Beyond zero: a negative VOC paint that reduces VOCs in the air

Johnson Ongking, Gretchen Fontejon, Pacific Paint (Boysen) Philippines, **Julie Maltby Kerrod, Robert McIntyre,** Cristal Global, discuss the introduction of photocatalytic paints that can remove more VOCs than is used to make the product

The main focus in the development of environmentally friendly coatings has been to bring down the levels of volatile organic compounds (VOCs) in paint formulations, with zero VOC paint becoming the green standard of the industry. But is zero really as low as we can go?

A commercially available photocatalytic paint introduces the concept of a 'negative VOC paint' – a coating that can remove more VOC than is used to make the product. Within a few days to a few months of application, depending on environmental conditions, the product is shown to consume far more VOC, emitted from local traffic and other sources, than was used to produce it.

It is also demonstrated how the product can be used in a commercial factory environment to dramatically reduce VOC levels. In the process, a new paradigm for green coatings is introduced – from reducing potential pollution a coating may cause to the environment to one that actually reduces pollution in the environment.

PHOTOCATALYTIC PAINT FOR REDUCTION OF AIR POLLUTANTS

The potential for photocatalytic paints containing ultrafine titanium dioxide (TiO_2) to break down harmful air pollutants such as nitrogen oxides (NOx) and VOCs has been known for many years.

TiO_2 is a semi-conductor and exhibits a characteristic energy gap of 3.23eV or 3.06eV between the valence band and the conduction band for anatase and rutile, respectively. Wavelengths shorter than 390nm for anatase and 405nm for rutile – corresponding to higher energy than the threshold energy – will excite electrons from the valence to the conduction band.

In the presence of oxygen (air) and water (humidity), this makes possible the creation of hydroxyl and peroxyl radicals or 'free radicals', at the surface of the TiO_2. These are the reactive species that break down pollutants that come into contact with the coating.

Once activated, the film reacts with any pollutants, such as nitrogen oxides (NOx) that come into contact with the surface. Harmful NOx gas is converted to nitric acid that is rapidly neutralised by alkaline calcium carbonate particles in the paint, producing harmless quantities of calcium nitrate and negligible amounts of carbon dioxide (CO_2) and water; while VOCs coming into contact with an activated film are converted to carbon dioxide and water (***Figure 1***).

Several laboratory and field trials involving CristalActiv, a form of ultrafine TiO_2 from Cristal Global and KNOxOUT, a commercial photocatalytic paint developed by Pacific Paint (Boysen) Philippines, Inc containing CristalActiv, have shown that properly formulated photocatalytic coatings can be effective in reducing NOx levels[1].

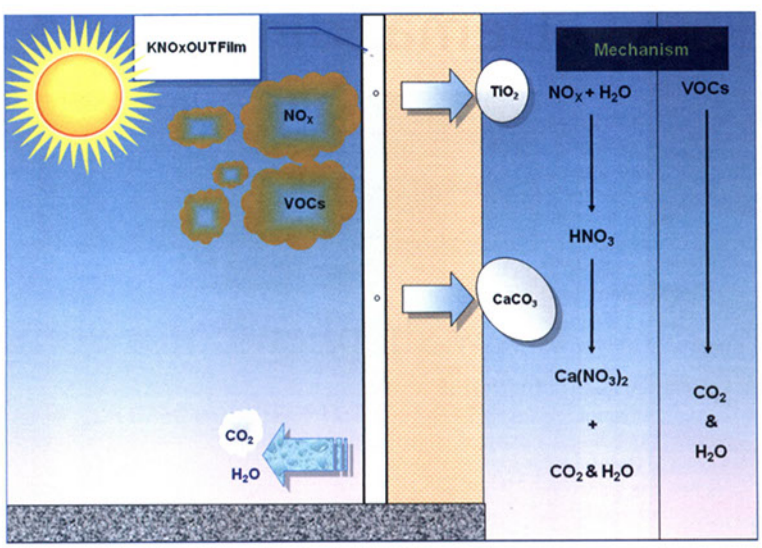

Figure 1. Scheme demonstrating ultrafine TiO_2 use of UV light, oxygen and water to reduce levels of smog forming air pollutants

VOC REMOVAL: LABORTORY TESTING USING ACETALDEHYDE

Another series of laboratory tests has been conducted to show that the KNOxOUT product is very effective at removing VOC.

Figure 2 shows laboratory test apparatus used to evaluate the performance of products with respect to VOC removal, a Total Hydrocarbon Analyser (THC) and a CO_2 analyser (from Signal Instruments) are used to measure levels of hydrocarbon and CO_2 in a gas stream. Acetaldehyde, which has been chosen by the ISO committee as an appropriate test gas for VOC removal by photocatalytic products, is used as a model VOC[2].

The advantage of this setup is that it will respond to any organic species. The disadvantage is that because the THC **will** respond to **any** organic species, differentiation between them is difficult due to the response being measured in terms of a calibration gas; in this case this is propane in nitrogen.

Thus a similar set-up using a Gas Chromatography (GC) analyser (from Varian

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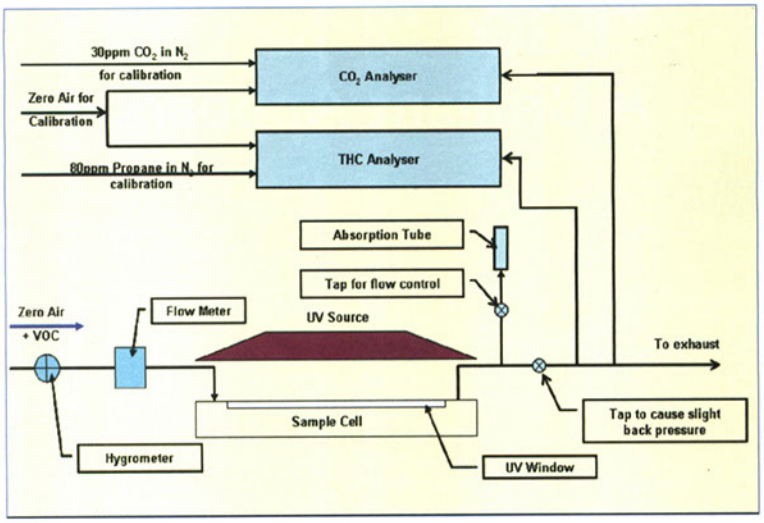

Figure 2: Scheme depicting test apparatus (THC & CO2 Analysers) used for determining the performance of materials for VOC removal

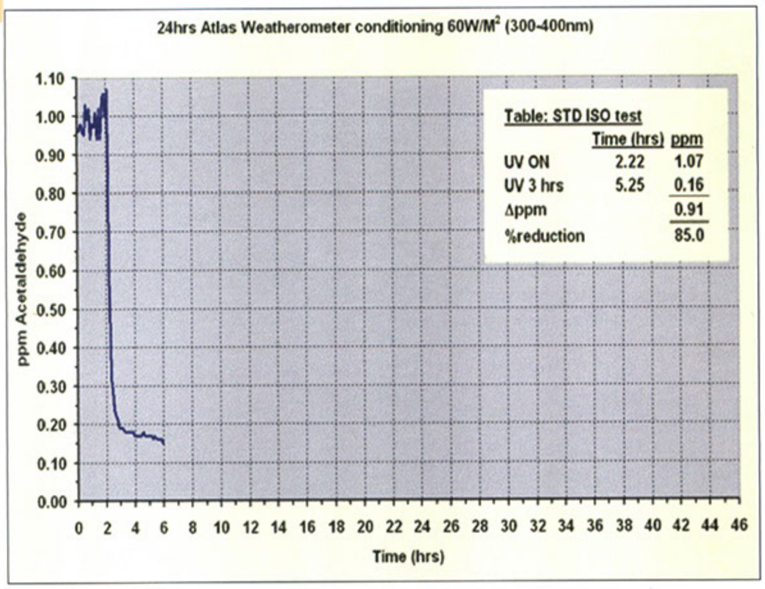

Figure 3: Acetaldehyde removal, as measured by GC analysis, using KNOxOUT conditioned by Atlas weatherometer

Instruments) for the VOC measurement was also conducted. The advantage of this method is that the instrument can be calibrated directly to the organic under test and consequently it will measure just that organic without interference from other organic species.

The inlet gas stream consists of 'Zero Air' (Total Hydrocarbon <0.01ppm, CO_2 <0.5ppm) and a set level of VOC flowing at constant rate over the sample under test. In this test the level of acetaldehyde is a nominal one ppm at a flow rate of one litre/minute.

With both test setups the sample is irradiated with UVA or longer wavelength light. For these laboratory tests KNOxOUT with CristalActiv was prepared.

An experiment showed that Texanol, an organic coalescing solvent in coatings, is released into the atmosphere over a two-day period after application; this was monitored as a response from the THC. After two weeks organic emissions from the paint could no longer be detected.

It was found that all photocatalytic paints improve with conditioning by irradiation and washing. It was also shown by analysis of the wash water that the performance improvement correlates quite well with the amount of dispersant and thickener washed out of the paint. In a real world situation the dispersant and thickener are removed by natural irradiation, being washed by rain or, in fact, a combination of both. In climates where there is little rain it may take up to two months to fully activate the paint.

For climates with heavy rainfall the product can become fully active after several hours of heavy rain. ***Figure 3*** shows that after 24hrs in an Atlas weatherometer, which provides simulated sunlight and rainfall, the product is fully active giving 85% reduction in the standard ISO test method after 3hrs irradiation. Similar performance can be achieved by conditioning to UVA light and water soaking. These tests used the GC setup for evaluation.

VOC REMOVAL CALCULATIONS

Calculations were carried out to determine the time required for Acetaldehyde removal equivalent to the Texanol content of the paint film.

Mol wt of Acetaldehyde	44.053g mol^{-1}
Mass of carbon/mol acetaldehyde	24.022g
Mol wt of Texanol	216.3g mol^{-1}
Mass of carbon/mol Texanol	144.132g mol^{-1}
Molar gas volume at 0°C & 1atm pressure	22.414 l
Amount of Texanol present in 1m² of paint film	0.5g
Area of test paint film	0.015m²
Flow rate of cell	1l min^{-1}
Initial concentration of Acetaldehyde	1ppm v/v
Minimum acetaldehyde removal	16%
Maximum acetaldehyde removal	86%

The calculations below are based on the test strip area of paint film.

Volume of acetaldehyde introduced	0.0000010 l min^{-1}
Mols of acetaldehyde introduced	4.461 exp -08 mol min^{-1}
Mols of acetaldehyde removed	7.138 exp -09 mol min^{-1}

The calculations below are for 1m²

Mols of acetaldehyde removed	4.758 exp -07 mol $min^{-1}m^{-2}$
Carbon removed	1.143 exp -05 g min^{-1} m^{-2}
Carbon removed	0.01646g day^{-1} m^{-2}
Mass of carbon emitted from 1m² film due to Texanol	0.333g m^{-2}
Time required for 1m² of film to remove VOC equivalent to Texanol in the paint assuming 16% efficiency	29,144mins
Time required for 1m² of film to remove VOC equivalent to Texanol in the paint assuming 16% efficiency	20.2days
Time required for 1m² of film to remove VOC equivalent to Texanol in the paint film assuming 86% efficiency	3.75days

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Area	Xylene (mg/m^3)			
	Y2009	Y2010	Y2011	% Change 2011 vs 2009
Area 1	55.36	0.0002	0.0033	-99.99%
Area 2	0.27	0.0034	0.0036	-98.67%
Area 3	0.27	0.0025	0.0012	-99.56%
Area 4	15.38	0.00040	0.0012	-99.99%
Area 5	8.65	0.0004	0.0034	-99.96%
Area 6	2.27	0.0014	0.0033	-99.85%
Area 7	2.02	0.0031	0.0033	-99.84%

Table 1, Concentrations of Xylene before (2009) and after (2010, 2011) application of KNOxOUT

Area	Benzene (mg/m^3)			
	Y2009	Y2010	Y2011	% Change 2011 vs 2009
Area 1	0.17	0.0001	0.0033	-98.06%
Area 2	0.17	0.0047	0.0033	-98.06%
Area 3	0.17	0.0032	0.0010	-99.41%
Area 4	0.17	0.00040	0.0012	-99.29%
Area 5	0.17	0.0001	0.0033	-98.06%
Area 6	0.17	0.0024	0.0033	-98.06%
Area 7	0.17	0.0037	0.0033	-98.06%

Table 2: Concentrations of Benzene before (2009) and after (2010, 2011) application of KNOxOUT

VOC REMOVAL: MANILA PAINT PLANT

EnvironAir Asia Inc conducted work environmental measurements at the Pacific Paint (Boysen) plant located at 292-D Tuazon St, Quezon City on November 4, 2009, December 15, 2010 and November 10-11, 2011 as part of the company's compliance of the Occupational Safety and Health Standards of the Philippine government.

Sampling of organic BTEX solvents were included in the measurements and were taken via area monitoring, which used the average of seven readings in a work area over a 15min period; and personal monitoring, in which monitors were attached on workers over an eight hour shift.

Previous tests had shown that BTEX solvents could be oxidised by photocatalytic materials[3], albeit with more difficulty than acetaldehyde because of their conjugated aromatic rings. During photocatalytic oxidation, smaller molecules like acetaldehyde are directly broken down to CO_2 and water; larger molecules like toluene and ethyl benzene are first broken down into intermediate organic acids and alcohols and are eventually oxidised to CO_2 and water.

Tables 1 and ***2*** show the monitoring results carried out on xylene and benzene levels in seven areas in the plant in 2009, 2010 and 2011. Results for toluene, and ethyl benzene were very similar. There were no changes in the structure or ventilation in the plant during this time period and the plant was making basically the same products with slightly higher volumes in 2010 and 2011 compared to 2009. Therefore, if anything, the areas were exposed to more solvents in 2010 and 2011 than 2009. In first quarter 2010, the interior of the whole factory, a total of 2056m² of wall area, was painted with the photocatalytic paint, KNOxOUT.

An important factor in the degree of reduction of VOC levels in a given area is the amount of VOCs in an area compared to the amount of photocatalytic active surface in that area. Given the relatively high area of photocatalytic painted surface and the low levels of VOCs in the plant (compared to the threshold values), it is not surprising that a high percentage of the VOCs in the work areas are dramatically reduced.

CONCLUSIONS

The above laboratory and paint plant data shows just how effective photocatalytic coatings can be for VOC removal. The lab tests and the paint plant both used KNOxOUT with CristalActiv. The laboratory results show that within 3-20 days of application (depending on the location, light levels, humidity and the levels of VOCs it is exposed to) the paint will be 'VOC neutral' – it will photocatalytically degrade an amount of VOC equivalent to that in the paint formula.

Any additional VOC oxidised by KNOxOUT after that makes it a 'negative VOC' paint. As the ultra-fine TiO_2 is a catalyst and not consumed in the photocatalytic reaction, the paint will continue to oxidise any VOCs it comes into contact with for many years. Instead of being a source of VOC emissions, paint can now be an effective way to reduce VOCs in the air; in the process setting a new paradigm of how green coatings can go beyond neutrality and actually make the environment safer and healthier for us. *APCJ*

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Asia Pacific largest market for epoxy resins

The report *'Global Epoxy Resin Market by Application & Geography – Market Estimates Up To 2017'*, produced by MarketsandMarkets, defines and segments the global epoxy resins market with analysis and forecasting of the global volume and revenue for epoxy resins. It also identifies driving and restraining factors for the global epoxy resins market with analysis of trends, opportunities, burning issues, winning imperatives and challenges. The market is segmented and revenues are forecasted on the basis of major regions such as North America, Europe, Asia Pacific and Rest of the World.

The key countries are covered and forecasted for each region. Further, market is segmented and revenues are forecasted on the basis of applications.

Bisphenol A and Epichlorohydrin are major raw materials in the production of epoxy resins and any change in the demand and supply of these raw materials could have a major impact on the epoxy resin industry.

The global market for epoxy resins in terms of revenue was estimated to be worth around US$5.5bn in 2011 and is expected to reach US$8.4bn by 2017, growing at an estimated CAGR of 7.3% from 2012 to 2017. Asia Pacific is the largest market and demand is expected to rise here due to robust growth in end-user industries of China and India.

Key market participants in the global Epoxy resins market are The Dow Chemical Company (USA), Momentive Performance Material Holding LLC (USA), Nan Ya Plastics (Taiwan), Kukdo Chemical (South Korea), Huntsman Corporation (USA), NAMA Chemicals (Saudi Arabia), BASF SE (Germany), 3M (USA), Spolchemie AS (Czech Republic), etc.

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