LEADING JOURNAL FOR THE COATINGS INDUSTRY IN EUROPE AND THE MIDDLE EAST

# PPCJ

POLYMERS PAINT COLOUR JOURNAL

VOL 207 – NO 4636 NOVEMBER 2017

**Inside:** Appealing aspects of coil coatings

**Inside:** All change in Italy

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# The Coatings Group

## FORTHCOMING EVENTS

***Global links for coatings professionals***

### Middle East Coatings Show Dubai 2018

19 – 21 March 2018
DWTC, Dubai UAE

### Coatings For Africa

The Southern Africa Coatings Show

29 – 31 May 2018
Sandton Convention Centre
South Africa

### Asia Pacific Coatings Show 2018

13 – 14 September 2018
KLCC, Kuala Lumpur
Malaysia

### North African Coatings Congress 2018

17 – 18 October
Hyatt Hotel, Casablanca
Morocco

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FOR UP-TO-DATE INFORMATION ON ANY OF THE ABOVE EVENTS, PLEASE CONTACT THE COATINGS GROUP


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# Never a dull moment in coatings

AkzoNobel hit the headlines again towards the end of last month; when it was revealed that the company is in the process of discussing a merger with smaller US rival, Axalta Coatings Systems to create a US$30bn company.

Axalta, as you may remember, was formerly DuPont Performance Coatings, which was sold to the private equity firm the Carlyle Group for US$4.9bn in February 2013. Axalta went public on the New York Stock Exchange in November 2014 and since then has become fully independent, the Carlyle Group having exited their last ownership stake in Axalta in 2015.

It's interesting to note that AkzoNobel's new Chief Executive, Thierry Vanlancker, previously led operations in polymers, performance coatings and chemicals at DuPont.

AkzoNobel said it was in "constructive talks" about a "merger of equals", while Axalta said it was engaged in talks but cautiously added that there was no certainty that a definitive agreement between the parties will be reached. Does this all mean that PPG has now definitely given up on its bid for AkzoNobel? As they say: watch this space...

## Merger abandoned

Talking of mergers and acquisitions, last month also saw Clariant forced to abandon its US$20bn merger with Huntsman after the continued accumulation of Clariant shares by activist investor, White Tale Holdings and its opposition to the transaction. The merger 'destroys existing Clariant shareholder value', White Tale Holdings wrote in an open letter. The group, which owns more than 20% of Clariant's shares, indicated that 'the proposed transaction has no strategic merit' and undervalues Clariant's shares.

For a complete round-up of the year's M&A news, do make sure you get hold of the February issue of *PPCJ*.

## Time to celebrate

We're all feeling decidedly autumnal, this month, at Coatings Group HQ here in Redhill. Post Halloween and the clocks going back; the nights are starting to draw in, bonfire night is over and, as I write, there are only 49 shopping days to you know what. Any thought of diets and healthy eating are thrown out of the window as various celebrations are entered into the diary. One key date coming up is November 23, which is the date for this year's British Coatings Federation (BCF) Awards. As reported on p5, this year the awards have received the highest number of entries in the event's eight-year history.

The awards showcase organisational brilliance and celebrate the achievements of the BCF members and the students from their Coatings Training Institute (CTI). Awards for 2017 include: Sustainable Innovation; Customer Service; Excellence in Training; Young Leader of the Year; Corporate Social Responsibility; Student of the Year; Coatings Care Progress Award; and Coatings Care Overall Best Performer. Finalists include: AkzoNobel; HMG Paints; Crown Paints; Farrow and Ball; Jotun; PPG; and Teal & Mackrill to name just a few. Good luck to all the finalists. We will carry a full list of winners in the December issue of *PPCJ*.

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## NEWS IN BRIEF

### Clariant on track to meet 2017 outlook

Clariant has announced nine months 2017 sales of CHF4.698bn, compared to CHF4.299bn yr-on-yr. This corresponds to a 10% growth in local currency driven by contributions from all Business Areas, with notable double-digit gains from Catalysis and Natural Resources. Organic sales rose by 6% in local currency, as a result of higher volumes. Growth was strongest in North America and in the Middle East & Africa, where sales in both regions rose by 16% in local currency. In Plastics & Coatings, sales advanced by 5%.

### Saving fuel costs

Owners and operators are saving fuel costs and reducing carbon emissions with AkzoNobel's patented biocidal antifouling coating Intercept 8500 LPP, part of the International product range. The coating, which has seen rapid adoption among customers with more than 100 applications since its launch in March 2016, has been estimated to have saved vessels US$25.5M in fuel costs and 274,000t of $CO_2$.

### Solar challenge success

Axalta Coating Systems has celebrated the success of two student teams at the Bridgestone World Solar Challenge 2017, a competition of experimental solar cars that took place last month in Australia. The Bochum SolarCar Team and The Punch Powertrain Solar Team both developed effective and reliable solar vehicles that successfully completed a 3021km race from Darwin to Adelaide. Both teams were supported by Axalta, who provided them with coatings, as well as technical assistance and expertise.

# Siegwerk opens production facility designated for inkjet inks

Siegwerk, a leading global providers of printing inks for packaging applications and labels, has expanded its Technical Center in Annemasse (France) with a new production facility for inkjet inks. The investment follows the construction of a dedicated inkjet laboratory last year that was built to already extend the company's R&D capabilities in this area. Siegwerk is committed to further drive the development of inkjet inks that meet all printing process functionality and efficiency requirements and address the specific challenges of the labels and packaging segments.

**L-R: Jens Adrio, (Head of Corporate Development), Veronique Danois (President of Siegwerk France), Herbert Forker (CEO) and Matthieu Carni (BDM)**

Today, the site in Annemasse is home to 275 employees and counts as Siegwerk's European leading plant for water-based printing inks and varnishes. The so-called Center of Excellence produces more than 25,000t/yr of printing ink. Over the past three years the company invested €3M to specifically build up its development, production and testing capacities in the inkjet technology.

Siegwerk has already invested nearly €11M over the past 12 years to build up a sustainable and successful Technical Center in France.

# Clariant and White Tale engaged in talks

Clariant, a world leader in speciality chemicals, has noted White Tale's press release and the demands published therein. Clariant notes that after the announcement of the termination of the merger agreement between Clariant and Huntsman on October 27, 2017, Clariant and its shareholder White Tale have engaged in an initial discussion regarding the new situation for the company and ways to work together in the future.

Clariant's management has offered to White Tale its readiness to present its existing growth strategy, listen to White Tale's plans and discuss appropriate concrete ways forward, including White Tale's wish for seats on the Board of Directors. According to Swiss governance, the requests of White Tale will be discussed in the next Board of Directors meeting.

Like White Tale, Clariant continues to be confident in the future opportunities for long-term value creation for all stakeholders, as a leader in speciality chemicals. In order to deepen the discussions, Clariant invited White Tale to hold further talks. In the coming weeks, Clariant will also continue the existing dialogue with all its shareholders, having shown long-term interest in the company.

# AkzoNobel's cargo tank coating wins ICIS Innovation Awards

AkzoNobel scooped two prestigious honours at the recent ICIS Innovation Awards for the Interline 9001 ultra-performance cargo tank coating supplied through its International brand.

As well as being awarded with the overall Innovation Award, Interline 9001 also received the Best Product Innovation Award from ICIS, the trusted information provider for the global chemical and energy industries.

The awards recognise the impact the new coating has had on the chemical tanker industry, specifically how it tackles the issue of absorption from aggressive cargoes, such as methanol, acetone and ethylene glycol. These issues can often result in cargo cycling restrictions, increased risk of subsequent contamination and the need for repeated resource and time-intensive washing procedures.

# Ashland and Phoseon UV LED initiative

Ashland and Phoseon Technology have announced a global UV LED initiative, combining Ashland's product development expertise in UV LED coatings and laminating adhesives and Phoseon's UV LED curing lamp technology for the labels and packaging industry. This relationship, in the energy curable value chain, will provide the converter base with proven plug and play solutions combining compatible UV LED coatings and laminating adhesives with the appropriate UV LED lamp technology.

# Wacker expands technical centre for cyclodextrin in Adrian, Michigan

Munich-based chemicals group Wacker has announced it is expanding the service portfolio of its technical centre in Adrian, Michigan, USA. For the first time, Wacker is establishing a global laboratory dedicated to developing and commercialising new industrial applications for its cyclodextrin products.

These organic, ring-shaped sugar molecules are capable of binding, releasing or stabilising substances. Because of these abilities, cyclodextrins are used in numerous industries, from household and personal care to pharma, cosmetics, textiles, food and agrochemicals, as well as in the coatings sector. The

new laboratory enables Wacker to develop together with its customers novel, tailored product solutions and to open new markets for cyclodextrins.

Research areas are for example innovative polymer systems based on cyclodextrins for self-healing coatings. Wacker is co-operating with leading scientists to tap the potentials of this new material, as the plant-based sugar molecules offer a novel and environmentally sound alternative to many traditional materials. Further current projects are exploring the capabilities of cyclodextrin in water or air treatment applications, for instance to filter unwanted odours or pollutants.

## Sika opens second production facility in Angola

Sika is expanding its presence in Africa by opening a new facility in the Angolan capital, Luanda. In addition to the production of concrete admixtures in an existing factory, mortar products – one of the Sika Group's fastest-growing areas of business – will also be manufactured locally.

With the additional production capacities in Angola, Sika is moving further toward its goal of covering about 70% of the market potential on the African continent with its own subsidiaries and production facilities. In this West African nation, the construction industry is receiving considerable impetus from major investments in infrastructure and in residential, industrial and commercial properties. Sika has also recently commissioned mortar production facilities in the countries of Nigeria and Ivory Coast.

Ivo Schädler, Regional Manager EMEA: "In the last five years alone, we have greatly strengthened our presence on the African continent and now have 19 national subsidiaries and 18 production facilities. We are positioning ourselves in the markets early so that we can benefit from the construction boom triggered by rapid population growth and urbanisation. We have been highly successful with this strategy in Africa: in the last five years we have seen 22% annual growth."

## Croda Invests in new plant

Croda International Plc has celebrated the upcoming commissioning of its latest investment at its Atlas Point manufacturing site in New Castle, Delaware.

The first of its type in the USA, the new plant is capable of producing 100% renewable, 100% bio-based non-ionic surfactants, which are active emulsifying agents used in a wide range of consumer products including coatings in the automotive industry. The plant will add 30 new, full-time employees to the workforce at Atlas Point.

## HB Fuller poised for global growth

Boosting HB Fuller's problem-solving potential, the company has finalised its acquisition of Royal Adhesives & Sealants for US$1.575bn. HB Fuller, combined with Royal, deepens its expertise in speciality and high-value applications used in a range of sectors, including electronics, hygiene, medical, transportation, clean energy, construction and more. Together, the companies will enable an interconnected world, support better use of the world's finite resources, improve food security and access to clean drinking water and address the challenges of a globally disperse and ageing population.

The acquisition expands HB Fuller's product offering in engineering, durable assembly and construction adhesives and makes it the world's largest supplier of adhesives for insulating glass and commercial roofing applications. Of the top adhesives manufacturers, HB Fuller is the only one singularly focused on adhesive and sealant technologies. The combined companies' comprehensive suite of products support innovative product design with the potential to touch everything from our clothes, homes and workspaces to how we communicate and travel.

## NEWS IN BRIEF

### Siegwerk acquires Van Son Liquids to expand WB inks

Siegwerk has signed a contract to purchase Van Son Liquids BV located in Hilversum, The Netherlands. The family-owned company manufactures high-quality water-based flexo and gravure printing inks for more than 25 years.

### IMCD opens coatings laboratory in Pennsylvania

IMCD NV, a leading speciality chemicals and food ingredients distributor, has announced an expansion of its technical capabilities with the addition of a coatings laboratory in King of Prussia (Pennsylvania), USA. The lab is the newest addition to the company's rapidly growing technical base and in combination with the recent acquisition of LV Lomas provides IMCD with market focused technical centres in North America covering the coatings, personal care and food markets.

### Finalists announced for the BCF Awards 2017

The British Coatings Federation (BCF) has revealed the finalists for its annual Awards celebration, which recognises excellence within the coatings industry. The BCF Awards received the highest number of entries in its eight-year history. BCF Chief Executive, Tom Bowtell commented "With a two-fold increase in entries received from our members, the BCF Awards 2017 will be the biggest and best yet. Congratulations to those who have been shortlisted and I look forward to announcing our winners next month."
The winners will be announced on Thursday, November 23. Visit www.coatings.org.uk/bcfawards

## NEWS IN BRIEF

### BASF signs distribution agreement with GMZ

BASF has recently signed an expanded distribution agreement with GMZ, a CASE distributor of Azelis Americas. Through this expansion, GMZ becomes the sole distributor of BASF's Dispersions & Resins Division portfolio of products across the Midwest and Northeast markets including Illinois, Wisconsin, Minnesota, Indiana and Michigan.

### Wacker raises prices for silicone products

As of November 1, Wacker, raised its prices for silicone polymers, silicone fluids and silicones from downstream production stages. Wacker's pyrogenic silica HDK is also affected. Depending on product family, region and business field, the price increase will range up to 25%, if permitted by existing customer contracts. This measure is necessitated by rising production expenses due to increasing raw-material and energy costs.

### Azelis to distribute Huntsman's Tecnothane

The polyurethanes division of global chemical company Huntsman has strengthened its relationship with Azelis – a leading distributor and supplier of speciality chemicals. Azelis has been appointed official distributor of Huntsman Tecnoelastomeri's Tecnothane products in France and Benelux.

### Venator celebrates

Venator's Duisburg, Germany facility recently celebrated its 125th anniversary with a large outdoor event. The facility produces a broad range of titanium dioxide pigments and functional additives.

# PPG donates coatings to help restore US A-12 spy plane

When the US Space & Rocket Center (USSRC) in Huntsville, Alabama, began restoring an A-12 Oxcart, it took only a local telephone call to obtain the aerospace coatings required to paint the legendary spy plane. Tom Meyer, PPG Plant Manager, aerospace transparencies facility in Huntsville, arranged for PPG to donate military aerospace coatings for repainting the Cold War reconnaissance plane operated by the CIA.

Military aerospace coatings expert Duane Utter, PPG Global Segment Manager, military coatings and defense


products, worked with the USSRC's curator in selecting the best products for the job. Instead of flat paint like the original, the curator requested a topcoat with a high-gloss finish that would weather better in the aircraft's outdoor environment.

PPG donated nearly 90gal of PPG Desothane HS 8201/F gloss military topcoat in midnight for the livery and four additional colours for markings. The company also contributed 30gal of PPG Desoprime HS 7233 military epoxy primer.

The A-12 Oxcart has been on display outside the USSRC's main museum entrance since it was received in 1989 on loan from the National Museum of the US Air Force.

## Bureau Veritas joins RECOMMS drones project

Bureau Veritas has joined RECOMMS (Remote Evaluation of Coatings / Corrosion on Offshore Machinery and Marine Structures / Ships), a joint investment project (JIP), to develop drones with the capability to inspect steel structures in enclosed spaces. The JIP's primary objectives are to develop a steady, stable and reliable drone capable of following programmable flight paths, either pre-determined by 3D imagery software or flown by a pilot, using 3D simulator ship specific training programmes developed in unison with the drone design. This will lead to the development of a complete and marketable inspection drone when delivered with the required software package.

Key investment partners for the confined space ambitions include AkzoNobel, Barrier Group, Bureau Veritas, Drone Ops, Hempel Paints A/S, Marine Technical Limits and a major oil company. Safinah Ltd, coating specialists and consultants, are the RECOMM project managers.

It is estimated that eliminating the need for staging erected for class renewal surveys could save in the region of US$90,000 for a VLCC or US$40,500 for a capesize bulk carrier (based on dry-docking costs in China for ships of 10 years and older).

## Brenntag South Africa launches

Brenntag, a global market leader in chemical distribution, has officially founded Brenntag South Africa (Pty) Ltd. Following the merger of the separate operating entities Lionheart, Plastichem, Multilube and Warren Chem Specialities, Brenntag South Africa officially launched on October 1, 2017. The business includes chemical distribution and services in Life Science (food, nutrition, pharma and personal care), Material Science (plastics, rubbers, polymers and lubricants), as well as Industrial Sales and Services.

Michael Thomson, President Brenntag Africa: "The new company has a focused commercial set-up, specifically tailored to Customer Industry Sectors and leveraging on the expertise and skills of the former individual companies, ensuring that the business is strategically and operationally better positioned to realise growth. Bringing the individual companies together has allowed for the development of a customer centred approach, aided by dedicated Product Management, strengthened departments for Safety, Quality & Regulatory Affairs and more streamlined and efficient Operations functions."

The new company has about 180 employees and locations in Cape Town, Johannesburg and Durban.

## CE certification for Cortec products

Cortec Corporation has announced it is now certified to use CE marking on six Migrating Corrosion Inhibitor (MCI) products for the protection and repair of concrete structures: MCI CorrVerter, MCI-2018, MCI-2019, MCI-2021, MCI Architectural Coating, and MCI Wall Defense. The marking certifies that Cortec meets the 2+ certification system requirements for assessing and verifying the constancy of these products under the EN 1504 standard and allows the products to be sold freely across the European Union.

# Europeans join forces on $CO_2$

The use of carbon dioxide and other waste gases as a new source of raw materials is increasingly a topic of interest at the European level. A new consortium of 14 partners from seven countries, led by materials manufacturer Covestro, is now planning to investigate how flue gas from the steel industry can be used to produce plastics in a particularly efficient and sustainable way. This will save crude oil, the raw material used in conventional methods. The cross-sector project called Carbon4PUR receives funding from the European Union.

"Together, we are on the path to a crucial innovation: waste gas mixtures from the steel industry can provide carbon for a chemical processes and ultimately be used to produce insulation materials and coatings," explained Dr. Markus Steilemann, the Covestro Board Member responsible for Innovation, Marketing and Sales. "This helps us to broaden our resource base and to reduce the climate footprint for the entire value chain. At the same time, we are joining our forces by partnering with industrial and academic partners throughout Europe."


Specifically, the project aims to use mixtures of carbon dioxide and carbon monoxide, which are generated during steel production, to produce polyols key components of polyurethane-based insulating materials and coatings that are otherwise obtained from crude oil.

Last year, Covestro began using carbon dioxide to produce a precursor for soft polyurethane foam, which is designed for use in upholstered furniture and mattresses. Meanwhile, the company is researching additional areas of application for $CO_2$-based raw materials.

## AkzoNobel adds colourful appeal to new exhibition at Van Gogh Museum in Amsterdam

A dazzling exhibition of paintings at Amsterdam's Van Gogh Museum which depicts Paris as seen through the eyes of eight Dutch artists has been designed with the help of AkzoNobel's colour expertise.

*The Dutch in Paris 1789-1914* – which opened last month – contains more than 120 works, including loans from museums and private collections around the world. The exhibition space was created by well-known designer Peter de Kimpe, who used a specially selected paint palette supplied by the company's Sikkens brand.

**Ruud Joosten (left), COO AkzoNobel and Axel Rüger, Director Van Gogh Museum**

As well as featuring works by Van Gogh himself, the exhibition also includes paintings by Van Spaendonck, Scheffer, Jongkind, Kaemmerer, Breitner, Van Dongen and Mondrian. The format – which shows their work for the first time alongside their French contemporaries – draws from the inspiration the Dutch artists found in Paris, their encounters with French artists and how these experiences impacted their art.

## Latest conference from the BCF underscores the importance of behavioural safety approaches

The British Coatings Federation (BCF) hosted a Safety Conference last month in Nottingham focusing on behaviour-based safety and human factors. The coatings companies in membership of the BCF have demonstrated an ongoing commitment to safety, which is illustrated in recent results from the BCF's Coatings Care programme which show a 75% reduction in the number of accidents per year. Despite the improved safety record, incidents still do occur and the BCF's Safety Conference explored how to prevent accidents in the workplace by focusing on the human element of health and safety and improvement of the company's safety culture.

Health and safety is a key focus of coatings companies, and with the Sentencing Council's new guidelines six times higher than before, the financial impact on businesses when something goes wrong can be devastating to a business financially, as well as taking an emotional toll. Speakers at the BCF's Safety Conference presented a compelling range of talks including Richard Scaife (The Keil Centre), Huw Jones (Health, Safety, Environmental Risk Management), Eddie McCullough (DEKRA Organisational Reliability) and Michael Tans (Ramboll Environ).

## NEWS IN BRIEF

### Evonik increases prices for Vestamin IPD

Evonik has announced it is to raise the prices for its isophorone diamine, offered under the brand name VestaminIPD by 10% on a global basis. Due to significant higher costs attributed to geographical supply and demand imbalances this unavoidable increase came into effect November 1, 2017.

### New website for Datacolor

Datacolor has launched the redesigned Datacolor.com, the company's flagship online presence and primary source for Datacolor solutions, support and education. The website has been translated into four languages: English, simplified Chinese, French (new) and German (new).

### RepRap distributes DuPont 3D printing materials

DuPont and German RepRap have announced that customers can now purchase DuPont Hytrel thermoplastic elastomers and DuPont Zytel nylon-based filaments for 3D printing in EMEA through German RepRap. The expansion of these high-performance materials into the realm of 3D printing enable users to achieve greater design freedom, lightweighting, reduced product development cycles and much more, allowing for rapid prototyping, part production, tooling and customisation.

### Wanda VR range now available in Spain

AkzoNobel has expanded its products available for bodyshops with the introduction of its global vehicle refinishes brand Wanda in Spain through it's long-term partner HELLA SA. It will be introduced in other European countries from 2018 onwards.

# DIARY

**February 4-9, 2018**
**The Waterborne Symposium**
Astor Crowne Plaza, Louisiana, USA
www.waterbornesymposium.com

**March 8-10, 2018**
**PAINTINDIA 2018**
Bombay Exhibition Centre,
Goregaon, Mumbai, India
www.paintindia.in

**March 19-21, 2018**
**Middle East Coatings Show**
DWTC, Dubai, UAE
www.coatingsgroup.com

**April 10-12, 2018**
**American Coatings Show**
Indiana Convention Center
Indianapolis, IN 46225, USA
www.american-coatings-show.com

**April 17-20, 2018**
**PaintExpo**
Karlsruhe Exhibition Centre
Rheinstetten, Germany
www.paintexpo.de

**May 22-23, 2018**
**Surfex**
Ricoh Arena, Coventry, UK
www.surfex.co.uk

**May 29-31, 2018**
**Coatings for Africa**
Johannesburg, South Africa
www.coatingsgroup.com

**May 29-31, 2018**
**UTECH Europe 2018**
MECC, Maastricht
The Netherlands
www.utecheurope.eu

**September 12-14, 2018**
**FEICA 2018 European Adhesive & Sealant Conference and EXPO**
Radisson Blu Latvija, Riga, Latvia
www.feica.eu

**September 13-14, 2018**
**Asia Pacific Coatings Show**
KLCC, Kuala Lumpur
Malaysia
www.coatingsgroup.com

**October 17-18, 2018**
**North African Coatings Congress**
Hyatt Hotel, Casablanca, Morocco
www.coatingsgroup.com

# EU round up: ECHA warns British coatings companies of major trading rule changes following Brexit

The European Chemicals Agency (ECHA) has warned of the major impact on British coatings companies and their trading partners in Europe, should the UK push ahead with quitting the European Union (EU) as planned, on March 29, 2019.

It has released a database seeking to advise chemical producers of how their legal obligations will change. ECHA warns British companies: "If your business is in any way part of a supply chain that links you to businesses located within the 27 EU member states remaining after the UK's withdrawal, you will face some fundamental changes."

Importantly, UK paints and coatings companies will have an obligation by May 2018 to register chemicals under EU chemical control system REACH that are made or imported in annual quantities of between one and 100 tonnes. And yet, on March 29, those registrations will become null and void, following Brexit.

As a result, customers based in the EU (or the European Economic Area – EEA – countries of Norway, Iceland and Liechtenstein), may have to re-register such chemicals themselves, if they want to continue buying them from the British supplier that registered them in the first place.

There are two other options, said the ECHA guidance. The British manufacturer will have to relocate to the remaining EU or EEA or appoint what is called an 'Only Representative' within the remaining EU/EEA. This is a company or person who is authorised to make the relevant filing under REACH and be legally responsible for ensuring a British exporter complies with EU rules.

Also, there are significant changes where a UK company was a lead registrant for registrations of chemicals involving other companies, including those in the remaining EU. After Brexit, these registrations would also expire, warned ECHA and companies wanting to ensure their products can be legally sold under REACH would have to appoint a new lead registrant, the British lead registrant would have to move to the remaining EU, or it would become an EU-based 'Only Representative'. See https://echa.europa.eu/advice-to-companies-q-as/general

• Meanwhile, ECHA's biocidal products committee has agreed that the biocide azoxystrobin should be approved for use across the EU as a biocidal preservative product in paints, silicon coatings, mineral and silicon sealants and grout products, by professionals and non-professionals. The assessment was part of the ongoing screening of biocides through the EU's biocidal products regulation.

## People

**Axalta appoints Ferris**
Axalta Coating Systems has appointed Mr Robert Ferris (pictured) as VP of Corporate Affairs and CCO. As chief company spokesperson, he will be responsible for developing and executing internal and external communications strategy and will also oversee the company's global corporate social responsibility (CSR) initiatives. In tandem with Mr Ferris' appointment, Matthew Winokur, formerly VP, Corporate Affairs, has been named Axalta's VP of Sustainability. In this new position at the company, he will partner closely with Axalta's business leaders, customers, and other stakeholders to integrate, optimise and communicate the company's sustainability initiatives.

**HB Fuller names director**
HB Fuller Company has appointed Ruth Kimmelshue to the company's board of directors, effective October 4. Kimmelshue serves as Cargill's Corporate SVP, Business Operations & Supply Chain and is a member of the executive team. Before taking her current role, Kimmelshue held a number of leadership positions for Cargill's businesses.

**New CFO for IGM Resins**
IGM Resins has appointed John G Knudsen IV – CPA, MAC as CFO reporting to CEO Edward Frindt. He will be responsible for providing strong strategic, financial and operational leadership to IGM. He will directly manage the corporate finance team and will be accountable for the administrative, financial, cash and risk management operations of the company.


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BÜHLER

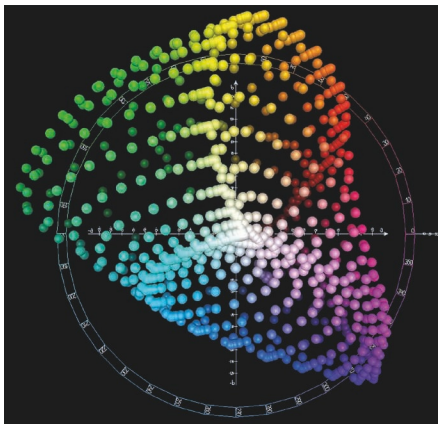
*Cynthia Challener* discusses the history of the systems and instruments used to measure colour

# Colour measurement continues to evolve

With the globalisation of many industries, the components found in complex products from consumer electronics to automotives can be manufactured in many different locations around the world and assembled in yet another. Despite potentially being made of different materials and coated using different application methods and even different paint formulations, components used to assemble a final product must all have the same appearance properties and exhibit colour harmony. Colour measurement is, therefore, an essential aspect of process and quality control. Both the equations used to describe colour and technologies applied in the design of instruments to measure colour have evolved significantly over time.

## TYPES OF SPECTROPHOTOMETER

Currently there are two types of spectrophotometers used to measure colour: the 45°c:0° and d:8° geometries. The former uses 45° circumferential illumination and 0° viewing perpendicular to the sample plane, simulating the normal conditions used for colour evaluation and measuring "colour as you see it", according to Anita Fehr, Product Manager for Color with BYK-Gardner. This geometry is typically used for batch-to-batch control in production. A d:8° geometry instrument illuminates the sample diffusely using a white coated integrating sphere and measurement is performed using an 8° viewing angle. In specular included (spin) mode, the total reflected light [diffuse reflection (colour) + direct reflection (gloss)] is measured and colour is determined independent of the sample's gloss or surface texture. Such instruments are typically used for evaluation of incoming goods and determination of colour strength as a function of dispersion time, according to Fehr. Colours created using metallic and effect pigments are analysed using multi-angle instruments. Various standards define multi-angle colour values to allow objective description of the colour of metallic finishes. Fehr notes that research studies have shown that a minimum of three, and optimally six, viewing angles are required.



**CIE Lab colour space top view**

## CIE LAB SYSTEM

Solid colour measurement was initially achieved using three-filter colour sensors and based on the standard spectral value function CIE 1931 (DIN5033). The introduction of spectrophotometers for solid colour measurement several decades ago created a need for an alternative colour measurement system. Currently, multi-angle spectrophotometers are applied for the colour measurement of modern paints and coatings. The system widely used today for solid colour measurement is the CIE Lab system developed by the International Commission on Illumination (French Commission internationale de l'éclairage), according to Fehr. This system describes all of the colours visible to the human eye and was created to serve as a device-independent, reference model. "The intention of the CIELab system was to create a uniform colour space, meaning that the same dE* value is perceived as the same magnitude of difference no matter which colour is evaluated," says Fehr. Unfortunately, however, she notes that CIELab colour differences correlate poorly with visual assessments due to the fact that differences in hue and lightness are perceived more strongly than differences in chroma, which results in visual assessments often leading to elliptical tolerances. In addition, chromatic colours have larger ellipsoids than achromatic colours. "The sizes and shapes of the ellipses are different depending on the hue," she explains. "The minimum requirement should, therefore, be to build tolerances for colour families," she adds.

## SINGLE TOLERANCE FOR ALL COLOURS GOAL

During the past 30 years, several iterations of difference equations and colour spaces have been developed in an attempt to overcome the short comings of the non-uniform CIELab system and improve the correlation between visual perception and instrumentally measured values. The goal has also been to permit the use of a single tolerance for all colours, according to Fehr. The CMC formula was based on the visual evaluation of textile samples by the Color Measurement Committee of The Society of Dyers and Colorists and introduced in 1984. This formula modified the CIELAB equation, such that the ellipses representing acceptable shade variations could be described with one value referred to as the DE(CMC). In 1995, the CIE published an equation called CIE94. "The CIE94 tolerancing method is conceptually similar to CMC 2:1 but lacks some of the hue and lightness adjustments. However, while it matched the colour difference perception of the human eye more closely, it lacked some accuracy in the blue-violet region of the colour space," notes Fehr.

▷ 12

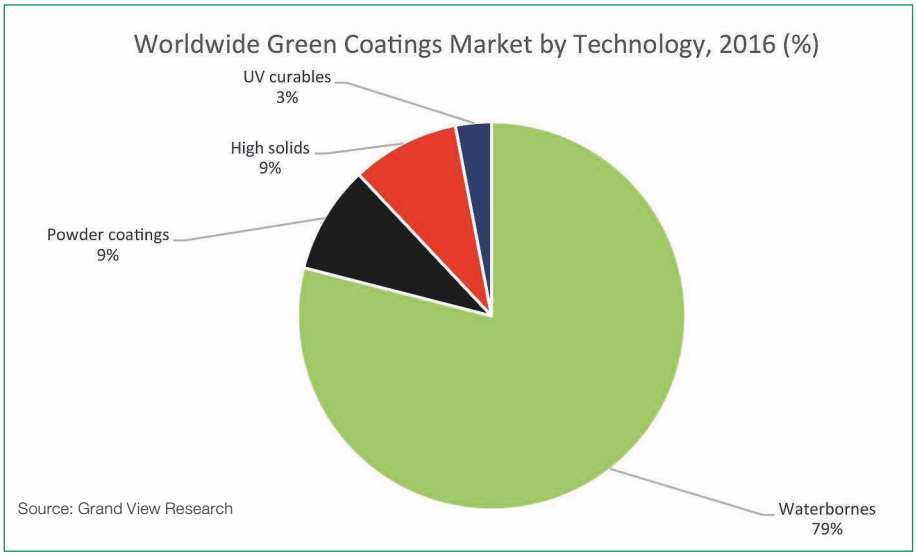
In his column this month, *Terry Knowles* looks at the global green coatings market

# Delving into compliant coatings globally

This month, I'm covering just a single study which has taken all of the environmentally-friendly coatings technologies and lumped them into a title which calls them 'green coatings', although 'compliant coatings' would have been a better choice when considering the title of the study.

That said, the study in question from Grand View Research clearly has a broad scope, which will attract raw materials companies and formulators alike. The global green coating market size was valued at US$115.19bn in 2016. Increasingly stringent government regulations associated with VOCs are expected to propel demand for their more compliant alternatives. Rising demand for waterborne and powder technology to replace solventborne coatings, especially in the architectural and automotive applications, is expected to drive industry growth.

The global green coatings market is expected to reach US$209.2bn by 2025. The market looks set to experience a CAGR of 6.9% over the forecast period, owing to increasing product penetration in construction and automotive applications at the expense of the use of high-VOC coatings in these fields.




## SOME INSIGHTS FOR THE EMEA REGION

Europe has been a major consumer of waterborne paints owing to the stringent government regulations, early uptake of the technology and high consumer awareness regarding product benefits. Initiatives taken by industry players to manufacture environmentally-friendly products in order to comply with regulatory norms including EU's VOC Regulation 2004/42/EC and US EPA's Clean Act is expected to propel industry growth.

Europe is likely to witness growth owing to growing population and economic developments in the UK, Spain and Italy. Various infrastructure projects – seaports and airports among them – have been planned in the UK National Infrastructure Delivery Plan 2016-2021, which are likely to drive the market demand over the next eight years.

The Middle East & Africa is expected to witness significant growth owing to rapid urbanisation and industrialisation in the region. The growth of application industries, coupled with the expansion of major coating manufacturers in this region, is expected to have a positive impact on the industry trends over the next eight years.

## OUTLOOK FOR OTHER PARTS OF THE WORLD

In the USA, stringent regulations imposed by the EPA on the paints and coatings industry to limit VOCs are expected to have a positive impact on the industry trend. Innovation on the part of automotive manufacturers in the region to use powder and UV-cured coatings in vehicle manufacturing is also expected to contribute to their greater use in the coming years.

Asia Pacific accounted for 33.4% of overall green coatings market share in 2016 and is expected to grow at the fastest rate, owing to rapid growth of the automotive assembly industries in India and China.

India is expected to be the key market for green coatings and is expected to grow at a CAGR of 7.6% from 2017 to 2025. The rapid growth of the manufacturing sector in the country owing to the 'Make in India' initiative taken by the Indian government is expected to open new avenues for the market over the projected period.

## SOME TECHNOLOGICAL VIEWS

Unsurprisingly, given the general dominance of the decorative sector, waterborne technology dominated the industry in 2016 and is likely to grow at a CAGR of 6.8% from 2017 to 2025, as a result of rising consumer preferences for environmentally friendly products in architectural and (increasingly) automotive applications.

- Waterborne coatings dominated the industry owing to the early adoption

of the technology especially in architectural application across Europe and North America. The technology is expected to grow at a significant rate owing to higher product demand from the automotive and wider industrial coatings sectors, particularly in Brazil and India.

- Powder technology is expected to grow at CAGR of 7.2% from 2017 to 2025, on account of its superior properties including zero VOC, superior corrosion resistance, reduced drying time and high-quality finish.
- High solids coatings are likely to witness a growth of 6.6% from 2017 to 2025, owing to its superior water resistance, cost effectiveness and excellent viscoelastic properties. The demand for high solids coatings was placed at US$10.01bn in 2016 and is expected to grow on account of their rising use in aerospace, automotive and packaging applications.
- In 2016, automotive uses of UV cured technology accounted for 23% of the total and these are expected to grow significantly in line with increasing demand for sunroof seals, window seals and paint touch-up applications.

## TRENDS IN END USES

The architectural industry was the largest application segment for waterborne coatings, accounting to close to 80% of the overall demand in 2016. Increasing infrastructure spending coupled with rising economic development in Asia Pacific and the Middle East are expected to drive market growth over the next eight years.

Surging demand for domestic appliances including freezer cabinets, washing machines and microwave ovens are expected to augment growth in the powder coatings market. The demand for the technology for manufacturing consumer goods is expected to grow at a CAGR of 8.1% from 2017 to 2025, owing to the OEMs' changing preference for powder coatings at the expense of their liquid forerunners.

Rising consumer disposable incomes and changing consumer lifestyles in Brazil are expected to have a positive impact on the construction industry in the region, thereby, impacting the green coatings market in a positive way. The government's efforts to offset the country's housing deficit, low-interest rates and expanding middle-class population is expected to drive growth.

High energy consumption associated with the product manufacturing and use is projected to restrain industry expansion. Manufacturers are expected to invest in R&D to design new products with low cost, shorter drying times and superior water- and chemical-resistance in order to attract consumer attention.

**PPCJ**

**Report details**

1. *Green Coating Market Analysis By Technology (Waterborne, Powder, High Solid, UV Cured), By Region (North America, Europe, Asia Pacific, Central & South America, MEA), And Segment Forecasts, 2014 - 2025* was published by Grand View Research in August 2017. A single user licence for the whole report costs US$4950 but individual sections from the report can be purchased and downloaded from the website, www.grandviewresearch.com

**Author:** Terry Knowles, Freelance Writer
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◁ **10** The latest update, ΔE2000, was introduced in 2000. This formula, according to Fehr, contains a so-called rotational term for the blue-violet region to address the shortcomings of the ΔE94 formula. "How well these new colour equations will penetrate the market remains to be seen. Even though they offer advantages over the CIELAB system, changing peoples minds and habits can take some time," she says.

With respect to advances in instrumentation for colour measurements, Fehr points to the improved performance of handheld devices and the advent of multifunctional instruments as two important developments. "As smaller and smaller components with similar quality and performance capabilities to those of original, larger components have become available, portable instruments have been introduced with accuracy comparable to that of larger instruments," she observes. "Modern" instruments also often provide more than colour measurement information. BYK-Gardner, for instance, has a solid colour spectrophotometer that performs colour and gloss measurements simultaneously. The company has also introduced a multi-angle spectrophotometer that provides effect measurement (sparkle, graininess and the Int-Emission value) in addition to colour measurement data for six different angles.


**The BYK-mac i spectrophotometer objectively measures total colour impression under different viewing angles and lighting conditions. Additionally, it detects and quantifies fluorescent light in the visible range**

Digital standards are also increasingly important for multi-instrument users that have access to instruments with excellent inter-instrument agreement. Historically, a physical standard was sent to different members of the supply chain, with each member having to perform measurements using their own specific colour instrument. With a digital standard and instruments with excellent inter-instrument agreement, the physical standard only needs to be measured once and then shared with all other members of the supply chain. "This approach saves both time and money, but inter-instrument agreement is the key," comments Fehr.

BYK-Gardner has developed LED technology to address the need for a robust light source that provides excellent repeatability and reproducibility. "LED technology has many other advantages as well, including high energy efficiency, very long lifetimes, no heat development, a homogeneous illumination area and no warm-up time," Fehr says.

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*PPCJ*'s columnist, ***Joe Powder***, provides answers to readers questions on aspects of the powder coating process

# Ask Joe Powder

**Good day Joe – Please assist if you can.**

**In South Africa it is very difficult and very expensive to get piped gas into my plant. We are starting up a powder coating section for architectural extrusions. I would like to get some input as to whether I should select my ovens to be gas/diesel or infrared. Is there a SWOT analysis that has been done to determine the best options?**

**Regards and thank you in anticipation.**

*Belinda Rossouw*
*Rivonia, Johannesburg, South Africa*

**A.** Good day, back atcha Belinda. This is a very common problem in the African continent. We ran into a similar problem in Nairobi. The coating operation there could either pay for gas lines to be laid to their plant (cost prohibitive and would take an indeterminate amount of time for installation) or install a large gas storage tank and buy a year's worth of gas (also cost prohibitive). They elected to use electric resistance heating for their finishing line. I felt this was the lowest cost option for capital expenditure, however operating costs are quite high.

For your situation I recommend a combination of infrared and electric resistance heat. The infrared will have to be electric as opposed to gas fired or gas-catalytic infrared for the reasons you mention above. I think it will be best to use a medium to long wavelength infrared system as it provides better heat-up consistency and is less sensitive to coating colour differences as compared to short wavelength types. It is important to orient the elements so they do not cause 'striping' from localised focal points of IR energy. IR energy is relatively 'line-of-sight' and will preferentially heat up the surfaces it 'sees' (lots of quotations today). Because of this localised delivery of heat it is wise to follow the infrared zones with convection heat, in your case resistance electric. Convection heat will even out the overall temperature of your parts and is 'colour-blind' as opposed to infrared. This way, you can be assured of thorough, even cure across your parts.

I would avoid diesel fuelled ovens. They are rather inexpensive to purchase and operate, however the combustion is not as clean as that of natural gas and can cause inconsistencies in colour. If your target market was less critical than architectural you could contemplate using a diesel fuelled oven but I don't think this is an option for you.

I hope that this helps you in your quest for a curing system for your powder coating shop. Good luck and let me know if you have any further queries.

Best regards,
Joe Powder

**Dear Joe – One of my customers in Thailand is facing an unknown problem when they use polyester products. The coated pieces have an ALM profile and their application is vertical. The unknown compound is similar to snow and mostly found inside the baking oven and is the cause of the defect on the coated surface. It seems to happen from my powder and is the usual condition at the customer's line oven, in my opinion. Can you advise from your experience what it is and how it happens?**

**Thank you in advance**,

*Pongbodin Deacha*
*Factory Manager (Powder), Thailand*

**A.** Dear Pongbodin Deacha – Thank you for your question. I have seen this problem before. It can be summed up in one word: BENZOIN. Nearly all powder coating formulas use a degassing agent to assist in film formation of the coating, while it is melting in the oven. Degassing is needed because as the particles coalesce air pockets form in between the particles (I like to call it interstitial air). Incorporating benzoin allows the bubbles to escape during this melt phase. Sounds great so far. Part of the mechanism of degassing involves the volatilisation of the benzoin as its melting point is 132°C and it tends to sublime above this temperature. How do we know this? I have taken samples of the snowflake-like residue found in powder cure ovens and had our analytical lab characterise it. What they found was the majority of the residue is benzoin.

So how do you minimise/stop this problem? My experience with finding high concentrations of benzoin in a cure oven usually indicated a very 'tight' oven. By that I mean an oven with very little exhaust. This is a common issue as some oven designers think that since powder coatings are promoted as having no VOCs (volatile organic compounds) that they do not have any volatiles. This is not the case. VOCs refer to regulated organic compounds that present a deleterious effect on the atmosphere. Powder volatiles do not but they still exist. Hence the solution to your problem is to 1. Thoroughly clean/vacuum your oven and 2. Provide more exhaust to the oven.

This should eliminate the problem.

Oh, and one other thing, have a trusted analytical laboratory analyse the residue with infrared spectroscopy. Benzoin absorption bands are unmistakable.

Best regards and let me know if you have further questions.

Joe Powder

**PPCJ**

**Please send your questions and comments to: askjoepowder@yahoo.com**

Letters to and responses from Joe Powder have been edited for space and style – Ed

*Akio Umino*, *Hirotake Fukuoka* and *Ichiro Azuma*, DIC Corporation, discuss the latest UV curable, water-based alkyd resin, which offers excellent adhesion to various substrates

# Heat resistant, ultra-smooth UV curable alkyd primers for PVD

Physical vacuum deposition (PVD) systems have been used in automotive parts, such as headlamps and cosmetic containers, to achieve mirror surface designs. When PVD is applied directly on plastics, the mirror surface design is not achieved because of irregularities on the surface of plastics. The smoothness of the plastic surface can be improved and final mirror effect greatly improved by applying a UV-cured primer layer (**Figure 1**).

In particular, excellent heat resistance is required for use in vehicle headlamps (**Figure 2**). Depending on the type of the light bulb, the surface temperature of the reflector reaches 230°C at maximum when the headlamp is turned on, so a substrate with high heat resistance, such as PPS or BMC, is used. At the same time, excellent heat resistance is also required for the primer. On the other hand, a substrate having excellent processability, such as PET / PBT alloy or ABS, is used as the extension installed apart from the light bulb at vehicle headlamps. Conventionally, UV-curable acrylic resin compositions are individually designed for each of these substrates.

The authors of this paper have developed a novel alkyd resin and completed a primer paint that can be used for all substrates. This alkyd resin has been adopted by the world's leading headlamp manufacturer, realising the reduction of environmental burden due to painting loss and a reduction of working cost; demand continues to increase year over year.

This paper explores the design of the novel alkyd resin which realises excellent heat resistance to form a crosslinked structure with an acrylate compound via UV irradiation and also exhibits excellent surface smoothness. Furthermore, the development of waterborne alkyd resins suitable for this application will be discussed.

## UV CURE CONCEPT OF ALKYD RESINS

In alkyd resins, vegetable oil is used as a raw material and this lowers the polarity of the resin, allowing for an affinity to various substrates and provides excellent adhesion. On the other hand, crosslinking density is lowered due to the influence of the vegetable oil's long alkyl chain and heat, as well as chemical resistance become poor.

The authors considered that heat resistance and chemical resistance can be improved by reacting unsaturated double bonds of alkyd resin with UV irradiation to increase the crosslinking density (**Figure 3**). In addition to the excellent substrate adhesion that alkyd resins provide, if we can realise excellent heat resistance and chemical resistance, an alkyd resin can be developed for various uses. For example, moisture-curable urethane coatings for wood and UV-curing flexo inks can utilise this novel alkyd resin.

## ALKYD RESIN SYNTHESIS AND PAINT FORMULATION

The three resins of synthesized alkyd resin shown in **Table 1** (long oil type, medium oil type, short oil type) and a conventional acrylic resin were hybridised with an acrylate compound and diluted with ethyl acetate to obtain the 70% non-volatile content, UV-curable coating for PVD primer shown in **Table 2**. The acrylate group concentration in the table indicates the number of moles of acrylate group present in 1g of the amount of active ingredients. For the composition, 4 weight % of photoinitiator and 0.3 weight % of levelling

**Figure 1. Expression of mirror surface design by primer of PVD. (From the left, BMC substrate, BMC / Deposited aluminium (no primer), BMC / Primer / Aluminium)**

**Figure 2. Substrate of headlamp and its requirement of heat resistance**

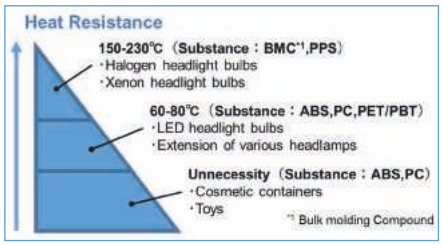
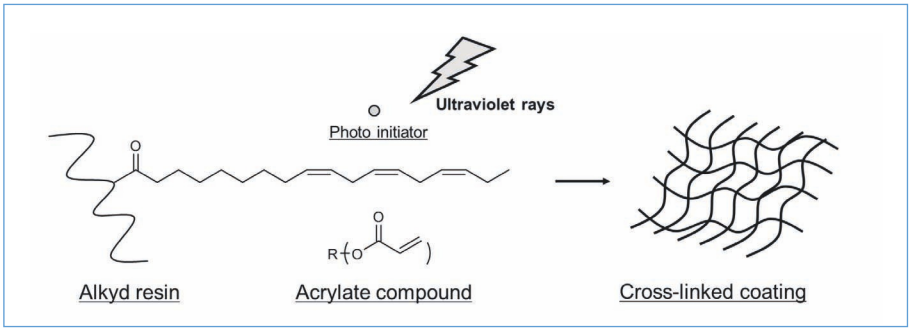



**Figure 3. Crosslinking of alkyd resin and acrylate compound by UV irradiation**



| Type | Oil length [%] | Acid value [mgKOH/g] | SP | Mw (x10$^3$) | Mw/Mn |
|---|---|---|---|---|---|
| Long oil | 74 | 7.0 | 9.0 | 7 | 2.5 |
| Medium oil | 45 | 10.1 | 9.3 | 114 | 32.2 |
| Short oil | 28 | 9.3 | 9.7 | 203 | 68.8 |

**Table 1. Synthesised alkyd resin**

| Prototype | Acrylic resin | Alkyd resin Long oil | Medium oil | Short oil | Acrylate compounds A*2 | B*2 | Acrylate group concentration [mmol/g] |
|---|---|---|---|---|---|---|---|
| 1 | 50 | | | | 50 | | 4.9 |
| 2 | | 50 | | | 50 | | 4.9 |
| 3 | | | 50 | | 50 | | 4.9 |
| 4 | | | | 50 | 50 | | 4.9 |
| 5 | 50 | | | | | 50 | 4.4 |
| 6 | | | 50 | | | 50 | 4.4 |

**Table 2. Composition of UV curable coating for PVD primer**
*2 Any formulation by Miramer M600, Miramer M340, Miramer M2370 and Miramer M220

| Product name | Detail | Manufacturer | NV | Weight [g] |
|---|---|---|---|---|
| Composition | UV curable coating | DIC | 70% | 100.00 |
| Irgacure 500 | Photoinitiator | BASF | 100% | 2.80 |
| MEGAFACE F-477 | Levelling agent | DIC | 100% | 0.21 |
| **TOTAL** | | | | **103.01** |

**Table 3. Formulation of test paint**

| Prototype | Appearance Initial | 230°C 24hr | Cross-hatched adhesion test (DIN EN ISO 2409) Initial | 230°C 24hr |
|---|---|---|---|---|
| 1 | Excellent | Excellent | Gt0 | Gt5 |
| 2 | Poor [Turbidity] | Poor [Turbidity] | Gt0 | Gt0 |
| 3 | Excellent | Excellent | Gt0 | Gt0 |
| **4** | Excellent | Excellent | Gt0 | Gt4 |
| **5** | Excellent | Good [Prismatic pattern] | Gt0 | Gt5 |
| **6** | Excellent | Good [Prismatic pattern] | Gt0 | Gt0 |

**Table 4. Results of heat resistance test of Prototype 1 to 6 on a PPS substrate**

agent (on the amount of active ingredient) were added to prepare the test paint. The formulation of paints are shown in **Table 3**.

## Spray, Curing, and PVD condition

Spray, UV-curing, and PVD were carried out with the following method.

**1.** After diluting with a mixed solvent*3, sprayed with 20µm thickness on PPS*4 substrates.
**2.** Set at 25°C for five minutes and dried at 60°C for five minutes.
**3.** Irradiated with 1500mJ/cm$^2$ of UV light.
**4.** Physical vacuum deposited layer of 100nm of aluminium metal.

**3 Ethyl acetate/Butyl acetate/n-Butanol = 30/30/40 (wt %); *4 DIC·PPS FZ-8600 BLACK manufactured by DIC Corporation.*

## Appearance and cross-hatched adhesion test results in a PPS substrate

After preparing metal laminates with primer layers of Prototype 1 to 6 on a PPS substrate, Prototype 2 (long oil alkyd resin) did not form a smooth primer layer and did not have a good appearance, even initially. The long oil alkyd resin has poor compatibility with the acrylate compound because the ratio of oil in the raw material is high. Therefore, it became an unsuitable primer surface.

## Heat resistance evaluation

Heat resistance was tested via a change of appearance and cross-hatched adhesion test after storing the laminated substrate at 230°C for 24hr. The results of the appearance after the heat resistance test are shown in **Figure 4** and the results of adhesion test are combined and summarised in **Table 4**. The laminated substrate of Prototype 3 (medium oil alkyd resin composition) had excellent heat resistance but Prototype 1 (acrylic resin composition) and Prototype 4 (short oil alkyd resin composition) had insufficient PPS substrate adhesion after the heat resistance test. Also, the laminated substrate of the composition (Prototypes 5 and 6) with low acrylate concentration produced a Prismatic pattern after the heat resistance test, resulting in poor appearance.

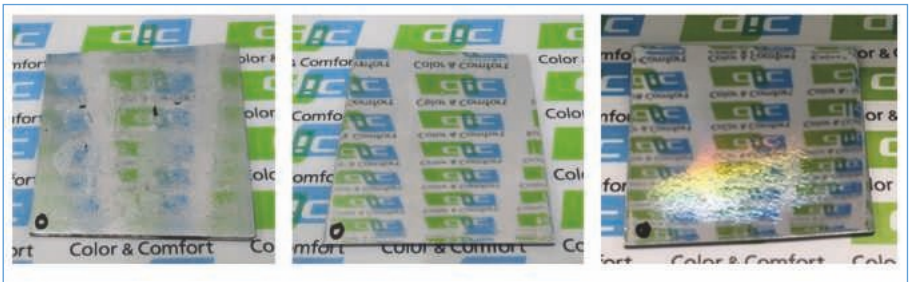
## IR spectra before and after UV-irradiation

The infrared absorption spectra of the acrylate compound (Miramer M 340) (a), linseed oil constituting alkyd resin (b), Prototype 3 before UV irradiation (c), and Prototype 3 after UV irradiation (d) are shown in **Figure 5**. In the alkyd resin composition (c), peaks (1620, 1430-1410, 820-810cm-1) indicate the acryloyl group of the acrylate compound (a). At the same time, peaks (3000-3100, 1650cm-1) indicate the vinyl group of linseed oil constituting alkyd resin (b). Focusing on the spectra of (c) and (d), since the peak indicated the vinyl group of linseed oil disappeared after UV irradiation, it was confirmed that the alkyd resin was crosslinked by UV irradiation. Thus, it can be confirmed that the crosslinking of not only the acrylate group of the acrylate compound but also the vinyl group of the alkyd resin is progressing in Prototype 3.

## Observation of surface shape

Using laser microscopy, the Prismatic pattern on the surface of the laminated substrate of Prototype 5 was observed (**Figure 6**). Surface roughness at the submicron level is formed in the prismatic pattern and it is presumed that visible light is irregularly reflected off it, resulting in poor appearance. This is presumed to be a result of a partial differential in UV curability due to insufficient acrylate concentration

**Figure 4. Appearance result after heat resistance test at 230°C**




A: Prototype 2 B: Prototype 3 C: Prototype 5

# Middle East Coatings Show Dubai 2018

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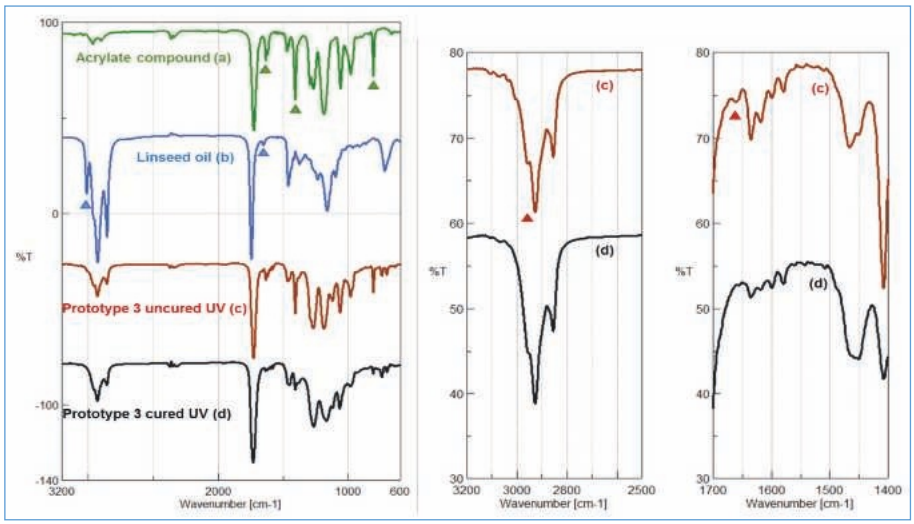



**Figure 5. Infrared absorption spectrum of Prototype 3 before and after UV irradiation**

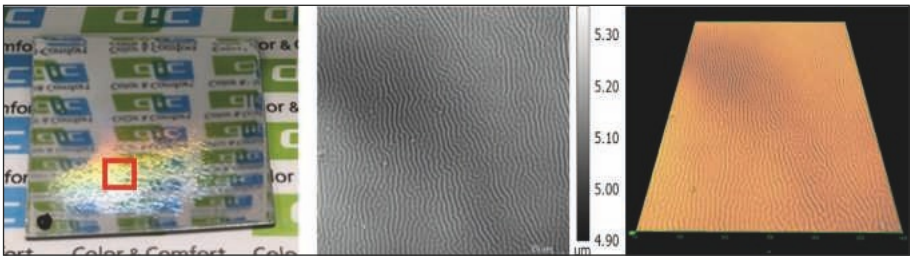



**Figure 6. Surface observation results of the Prismatic pattern in Prototype 5**

as well as poor compatibility of the polymer and acrylate compound.

### Cross-hatched adhesion test for various substrates

An adhesion test was carried out on various substrates using Prototype 3, which showed excellent heat resistance as a primer. Temperature suitable for each substrate was applied as conditions for the heat resistance test (**Table 5**).

### Characteristic of alkyd by each Thermomechanical analyser (TMA) and Thermogravimetry Differential thermal analysis(TGA-DTA)

Prototype 1 (acrylic resin composition) and Prototype 3 (medium oil alkyd resin composition) with the same acrylate concentration were coated with an applicator and cured by the method described above to prepare a sample for thermal analysis with 150μm of film thickness. We simulated the volume change of the primer layer in the 230 degree heat resistance test using a TMA 1st-run measurement (**Figure 7 left**). In both samples, volume expansion of the film was observed with heating. After that, in Prototype 1, cure shrinkage of residual acrylate compound was observed from approximately 130 degrees, whereas Prototype 3 did not cause cure shrinkage.

After being cooled to room temperature, the Volume Shrinkage Rate of Prototype 1 was observed to be about 4% but Prototype 3 was only about 2%. This less shrinkage can be explained by the excellent adhesion of Prototype 3 after the heat test. Furthermore, the TGA-DTA measurement results of film samples utilising Prototype 1 and Prototype 3 are shown in **Figure 7 right**. Prototype 1 starts to decrease in weight from approximately 130°C and accelerates with heating. However, it was observed that Prototype 3 started weight loss from approximately 200°C and slowly decreased in weight to 300°C, which is the decomposition temperature of general organic substances. Taken comprehensively, in the primer layer using the acrylic resin composition, decomposition and curing shrinkage of the primer layer result in the high temperature heat resistance test.

Therefore, by using the novel alkyd resin composition, the UV curability of the primer layer is improved and these defects derived from the residual acrylate compound can be suppressed. Therefore, the novel alky resin provides excellent adhesion to various substrates.

## DESIGN OF UV CURABLE WATER-BASED ALKYD RESIN DISPERSION

Following the alkyd resin design technology that is excellent in heat resistance, we began developing environmentally friendly water-based primer paints. The image of UV curable waterborne polymers is shown in **Figure 8**. Alkyd polymers with a hydrophilic group (called the 'shell segment' in this article) is surrounding the hydrophobic acrylate compounds (called the 'core segment'). The shell segment provides stability of dispersed particles in water and adhesion on substrates. On the other hand, the core segment provides thermal resistance.

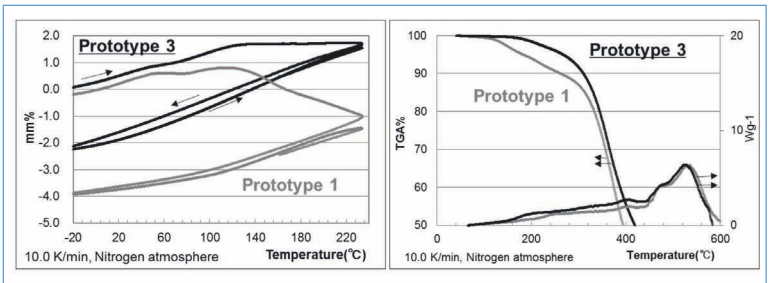
### Synthesis of water-based alkyd resin

A synthetic summary of the water-based alkyd resin used for the shell segment is shown in **Figure 9**. In the first step, we redesigned the middle oil alkyd resin, which is excellent in heat resistance and lowered its molecular weight. In the second step, hydrophilicity was enhanced by modifying the PEG chain in the main chain. In the third step, carboxylic acid was added to the side chain so that it could be dispersed in

**Table 5. Results of cross-hatched adhesion test on various substrates on initial and after heat resistance test**

| Substrate | | Cross-hatched adhesion test (DIN EN ISO 2409) Prototype1 | Prototype3 |
|---|---|---|---|
| ABS | Initial | Gt0 | Gt5 |
| | 80°C 24hr | Gt3 | Gt0 |
| PC | Initial | – | Gt0 |
| | 80°C 24hr | – | Gt0 |
| BMC | Initial | – | Gt0 |
| | 180°C 24hr | – | Gt0 |
| PET | Initial | – | Gt0 |
| Poly amide | Initial | – | Gt0 |

**Figure 7. Comparison of alkyd with acrylic by thermal equipment analysis**




- Left figure; Result of expansion rate of primer layer by TMA
- Right figure; Result of thermal decomposition temperature of primer layer by TGA-DTA

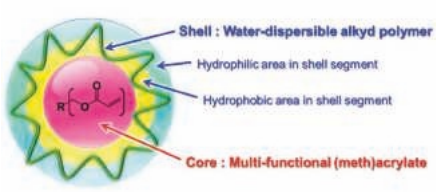



**Figure 8. Image of UV curable waterborne polymers**

| | UV curable water-based paints: Prototype 7 |
|---|---|
| Appearance | Milky white |
| Solid content [wt %] | 34-36 |
| Viscosity [mPa•sec] | 200 - 500 |
| pH | 6.0 - 9.0 |
| Acrylate concentration [mmol/g] | 3.0 |
| Organic solvent [wt %] | MEK (less than 1wt%) |

**Table 6. Technical Data of UV curable water-based paints**

water. We made an ester reaction between an acrylic resin with high acid value and the hydroxyl group of the alkyd resin. In the final step, after being pre-dispersed with the acrylate compound, water was continuously added to obtain a dispersion solution.

The technical data of the dispersion solution are shown in **Table 6**. In this emulsification sequence, the hydrophilic group in the polymer chain is oriented to the surface of the dispersed particle due to compatibility with a water molecule. On the other hand, the hydrophobic acrylate compounds are oriented to the inside of the dispersed particle to avoid interaction with water molecules. As a result of that, the dispersion particle with a core/shell construction is formed without any emulsifier.

### Paint formulation

For the dispersion, 4 weight % of photoinitiator and 0.3 weight % of levelling agent (on the amount of active ingredient) were added to prepare the test paint. The formulation of paints is shown in **Table 7**.

### Spray, Curing and PVD condition

Spray, UV curing, and PVD were carried out with the following method.

**1.** After diluting with water, sprayed with 20μm thickness on PPS*4 substrates.
**2.** Set at 25°C for 10mins and dried at 80°C for 10min.
**3.** Irradiated with 1500mJ/cm$^2$ of UV light.
**4.** Physical vacuum deposited layer of 100nm of aluminium metal.

### Appearance and cross-hatched adhesion test results for various substrates

The laminated substrates on which the primer layer of Prototype 7 was formed were taken out of a heater after 24hr and returned to a temperature corresponding to each substrate. After cooling for several hours at room temperature, the heat resistance was evaluated by appearance and cross-hatched adhesion test. These results are shown in **Table 8**.

The heat resistance of the high grade is lower than that of the solvent type, but the intermediate grade (for LED head lamps) reached level comparable to the solvent type. We are continuing to improve the stability of the dispersion and the biomass ratio.

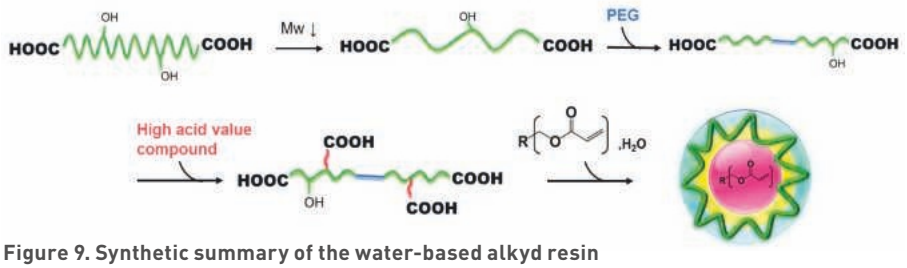



**Figure 9. Synthetic summary of the water-based alkyd resin**

| Product name | Detail | Manufacturer | NV | Weight [g] |
|---|---|---|---|---|
| Composition | UV curable coating | DIC | 30% | 100.00 |
| Irgacure 500 | Photoinitiator | BASF | 100% | 1.20 |
| Byk-345 | Levelling agent | BYK Chemie | 100% | 0.09 |
| **TOTAL** | | | | **101.29** |

**Table 7. Formulation of test paint**

| Substrate | Appearance Prototype 7 | Prototype 3 | Cross-hatched adhesion test (DIN EN ISO 2409) Prototype 7 | Prototype 3 |
|---|---|---|---|---|
| BMC | Initial | Excellent | Gt3 | Gt0 |
| | 180°C 24hr | Excellent | Gt4 | Gt0 |
| ABS | Initial | Excellent | Gt0 | Gt0 |
| | 80°C 24hr | Excellent | Gt0 | Gt0 |
| PC | Initial | Excellent | Gt0 | Gt0 |
| | 80°C 24hr | Excellent | Gt0 | Gt0 |

**Table 8. Comparison of application test results between water-base and solvent**

## CONCLUSION

A physical vacuum deposited metal laminate was prepared using a UV-curable composition that is hybridised with an acrylic resin and three alkyd resins as a main material before being hybridised again with acrylate compounds as a primer. Cured coating films of these primers were prepared and analysed with thermal analysis instruments. In addition, we reported on the development status of environmentally-friendly, UV-curable water-based alkyd resins. These results are summarised below.

- By using our medium oil alkyd resin as the material of the primer, excellent adhesion, which cannot be achieved with conventional acrylic resins, can be realised on various substrates. (Patent pending)
- A UV-curable, water-based alkyd resin was developed. It was also confirmed that the resin has excellent adhesion to various substrates, similar to a solvent system. (Patent pending) **PPCJ**

This article is taken from a paper given at the 2017 ECC, in Nuremberg, Germany

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*Michael L Gould*, RAHN USA/RAHN AG, discusses the company's work in choosing both photoinitiator and oligomer choices that will work with commercial UV/LED lamps

# Raw material selection for UV/LED

Until recently, UV curing applications required the use of high power mercury (Hg) lamps to provide the energy and wavelength distribution necessary for effecting complete cure of UV formulations (eg, inks, coatings, adhesives and composites). Traditional photoinitiators work well with mercury lamps due to many peak wavelengths in a typical Hg spectrum being matched to the many possible photoinitiator choices available commercially and these lamps continue to do the bulk of work in the industrial UV world.

Over the past 10 years, development of high power UV/LED lamps has provided another option for UV curable applications. UV/LED lamps are more energy efficient, quieter and easily repositioned, provide 'instant on/off' capability and last much longer with little decay of the lamp output. They are different from mercury lamps in one key respect: spectral output is very narrow and centred on the specific LED chosen, most commonly 395, 385 or 365nm lamps. Work continues to move toward other high intensity wavelengths but for now, UV/LED requires careful formulation with fewer photoinitiator choices.

Significant work in RAHN's UV laboratories has quantified and optimised to some extent, both photoinitiator and oligomer choices that will work with commercial UV/LED lamps. (This work has been limited to 395 and 385nm lamps.) This article will summarise the highlights of that work in order to guide material choices for use in UV/LED curing

Of critical importance is to understand the assessment paradigm within which evaluations were done. The majority of work was completed with high power 15W/cm$^2$ lamps. Emphasis of this work was on speed of cure, ie, how fast printed or coated substrate could move under the lamps while still achieving full cure (mar-free surfaces). Work was done in two phases, one emphasising photoinitiator choice and levels and the other focused on oligomer choices.

The 'lock and key' nature of photoinitiators – ie, creation of adequate free radicals only occurs when a PI absorbs light of specific wavelength(s) – limits PI choices when the lamp output spectrum is narrow. Based on a 395nm UV/LED lamp, DETX/ITX, TPO, EMK, TPO-L, BAPO and BDMM are the most logical photoinitiator candidates but the quantum efficiency of those products is not addressed simply choosing by absorption spectrum. Combinations of photoinitiators can participate in radical transfer reactions that sometimes prove more efficient than one PI alone but the efficacy of those combinations can change from formula to formula. Furthermore, required PI levels can vary significantly from clear coatings, where 3-4% PI may be adequate, to black or white inks where 15-20% PI may be required.

RAHN oligomers were tested in a clear formulation that was held constant across all experiments and applied to white card stock at a film thickness of 12µm. Photoinitiators were TPO at five parts and DETX at 0.1 part. Drawdowns were assessed for cure by both 'thumb twist' and 'fingernail scratch' qualitative assessments to determine the maximum speed at which full cure was reached. Nearly all products cured faster at 385nm versus 395nm and lamp distance, while possibly optimal around 25-35mm, accounted for little variation in cure response.

## RESULTS FOLLOW ONE TREND

Among the several dozen oligomers assessed, results clearly followed one specific trend: greatest curing efficacy is realised when oligomers combine moderate to high amine value with moderate to high (3-6) acrylate functionality. Mercaptan functionality also contributes significantly to robust cure but stability considerations can be challenging with mercaptans.

In general, typical oligomer reactivity is slow, particularly at 395nm and is greatly influenced by the diluting monomer. (Photoinitiator was held constant at 4.9% total, since the test formulas were clear coats and many of them were sufficiently reactive at that PI level.) Among products tested, oligoamines were the most reactive, followed by amine-modified polyether acrylates (or mercaptan-containing formulas), highly functional urethane acrylates then lower functional urethane acrylates and epoxy acrylates.

Summarising the study results, the top 10 RAHN LED oligomers are: GENOMER* 5695, GENOMER* 5275/5271, GENOMER* 2253, GENOMER* 3414, GENOMER* 3457, GENOMER* 3497, GENOMER* 2235, GENOMER* 4590/PP and GENOMER* 7302. The full version of this new Lab Report is available from the RAHN company website.

**PPCJ**

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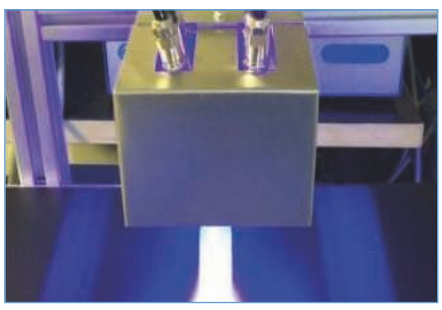



*Sarah Gibbons* reports on the latest technical standards for space paints and reviews the latest products

# New European technical standards system for space paints under development

Standards are being drawn up to ensure international best practice is consistently applied in durability testing of coatings for use in space projects.

The European Cooperation for Space Standardization (ECSS) is an initiative established to develop a coherent, single set of user-friendly standards for all European space activities – and its experts are now drafting technical rules for coatings used on satellites, rockets, probes and other space equipment.

This will allow coatings to be tested regarding their ability to cope with extreme thermal conditions (heat and cold), radiation, UV, vacuum conditions, toxicity, corrosion, debris deflection, humidity, abrasion and surface resistivity.

Space coatings have a high quality bar to clear. They must be environmentally-friendly (both terrestrially and in space); have appropriate reflecting and anti-reflecting properties and optical sensitivity according to their application; be very adherent; with low flammability; and should not release gases (off-gassing).

An ECSS note on the project, launched in February this year, said: "Many different environmental factors can have an effect on coating durability for space applications. This includes in-orbit effects, such as thermal cycling and particle radiation, as well as ground based effects, such as cleaning, contamination and humidity."

## AMBIGUOUS DEFINITIONS

It said that space projects have typically been free to choose their own test requirements, based on a combination of existing standards and specific mission demands. This approach can lead to ambiguous definitions about when a coating is 'space qualified'. Suppliers and customers often re-negotiate general aspects of coating qualification for each new project as a result. So, the intention of developing a new standard is to capture best practice across a wide range of existing national and international standards, "to specify a minimum set of durability requirements for coating use in space applications," said the note. That said, despite the drafting of new more comprehensive standards, mission-specific testing will continue to be encouraged alongside the generic durability tests, reflecting the diverse nature of space missions, the ECSS confirmed.

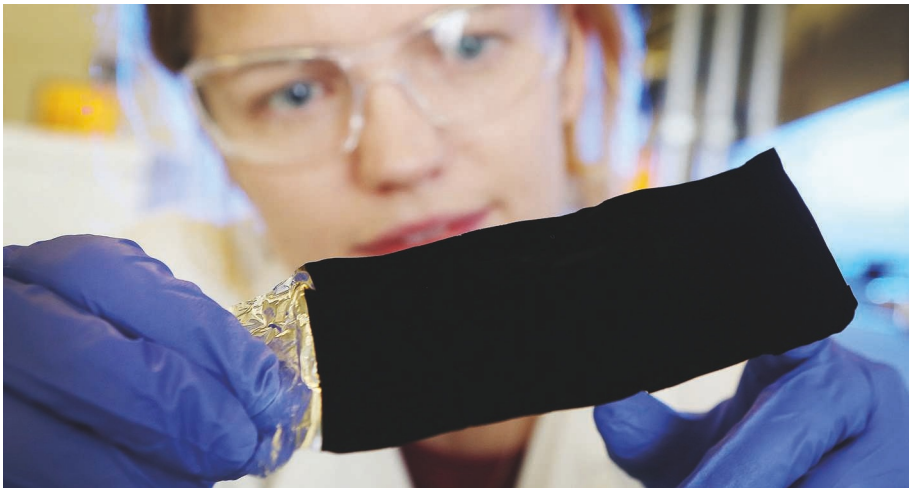
Some coatings, after all, are 'ablative' and last one mission only, sacrificed to protect the object they are covering. Such coatings can, for instance, protect astronauts from heat during re-entry into the earth's atmosphere.

They consume energy from a fire, releasing it in the form of gases as they char to form a cool insulation layer to the craft and they take an exceptionally long time to burn, said a note from licensed industrial coating and painting contractor, Cor-Ray Painting Co, based in California. Terrestrial uses for such coatings include on oil and gas pipes and electrical cables.

Many of the coatings applied to various components of space-bound craft and instruments need to exhibit a combination of reflective and absorptive properties at different wavelengths of the electromagnetic spectrum to maintain the interior temperature of spacecraft and prevent damage to scientific equipment attached to them.

## LOGOS IN SPACE

AZ Technology, based in Alabama, supplies NASA and a large number of other international space programmes with paint and coatings for a wide variety of space objects and instruments and currently has its products on the International Space Station. It is the only company officially licensed by NASA to paint the agency's red, white and blue logo on the ISS.



**Vantablack S-VIS: An air applied coating with incredibly low reflectance**

The company also developed a 'space-stable' sky-blue colour paint for the European Space Agency (ESA) logo. Most of its products, developed under vacuum conditions on its production site, have also been tested in space next to the ISS. This is part of NASA's Materials International Space Station Experiment, testing more than 2000 materials, such as thermal coatings and polymers, alongside objects including switches and mirrors.

A spokesman for AZ said its products sell from around US$300 a pint for a basic paint and those which include a lot of rare earth minerals, mined in China, which determines pricing, have a "highly variable price costing between US$7000-9000 a pint, before applying". This is no domestic paint, he added: "I describe it as light fluffy sprayable cement. The pigment is denser than ordinary paint and to spray it evenly is difficult. Curing is by a slow humidity drop over days because you don't want it to crack."

## COLOUR IS KEY

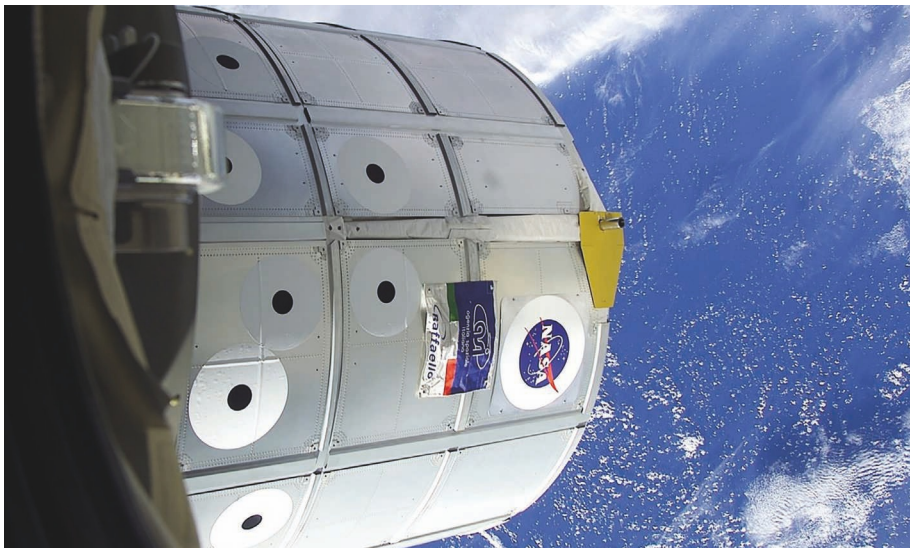
One key quality of space paint is colour – such as Vantablack, developed by the UK's Surrey NanoSystems, a coating which absorbs 99.965% of all light, first used in space in late 2015, improving the quality of optical systems on a star tracker satellite.

In future, it is anticipated it will help reduce the weight of optical systems, a crucial factor in space mission where every gram costs money.

A Surrey NanoSystems spokesman said: "Vantablack has the highest thermal conductivity and lowest mass-volume of any material that can be used in high-emissivity applications. It has virtually undetectable levels of outgassing and particle fallout, thus eliminating a key source of contamination in sensitive imaging systems. It withstands launch shock, staging and long-term vibration and is suitable for coating internal components, such as apertures, baffles, cold shields and micro electro mechanical systems…."

It is available in two versions, either directly applied to surfaces using vacuum-deposition technology or, Vantablack S-VIS - by spraying and post-processing.

"It reflects so little light that it is often described as the closest thing to a black hole we'll ever see," the spokesman added. "When it's applied to a three-dimensional object, Vantablack is so black that it becomes extremely difficult to discern any surface features and three-dimensional objects appear to become two-dimensional. Vantablack absorbs more than just visible light and is equally effective across a whole range of the spectrum that is invisible to the human eye," he added.




**AZ Technology produced black and white assembly targets on the Raffaello logistics module (used to transfer supplies and equipment to and from the International Space Station), with AZ produced NASA logo and ASI produced sign**

It is created from carbon nanotubes, each 20 nanometres in diameter (about 3500 times smaller than the diameter of the average human hair), and between 14µm to 50µm long. A surface area of one $cm^2$ contains around 1,000M nanotubes. It can coat high-performance infrared cameras, sensors, scientific instruments and satellite-borne calibration sources.

## INSPIRING WORK IN OTHER FIELDS

James Fesmire, Senior Principal Investigator for NASA and co-founder of the Cryogenics Test Lab at the Kennedy Space Center, said the now abandoned space shuttle programme had driven coatings innovation with every mission revealing new challenges. Now, he said, ISS work – satellite pay-loads, scientific apparatus and life support systems spark research and development:

"We just have to prove coatings are effective in an environment that's more extreme but it's not special because it's space or NASA but it's special for its properties."

NASA is working closely with the oil and gas industry to produce new efficient coatings for pipes to prevent metal corrosion and subsequent explosion.

Kennedy scientists have developed an environmentally-friendly smart coating with corrosion inhibitors packaged inside tiny micro-capsules or micro-containers, which are porous and less than one-tenth the size of the diameter of a human hair.

Dr Luz Marina Calle, Technical Lead for Kennedy's Corrosion Technology Laboratory, said micro capsules remain dormant until corrosion begins underneath: "That's where the smart portion of the technology kicks in," he said. "The shell of the micro capsules are designed to break open and deploy the corrosion inhibitor. Basically, the shells break down and deliver the corrosion inhibitor, and then they disintegrate."

This is particularly useful regarding corrosion to large bolts, where the surface looks good but the corrosion is taking place inside. Calle's team is working on encapsulating colour-changing corrosion indicators in coatings.

"If we have a coating with micro capsules that contain a corrosion indicator that changes colour when corrosion is present on the inside, then it will be evident from the outside that there is a problem," Calle said.

Meanwhile space coatings research projects working with the automotive industry is trying to protect vacuum jackets needed for tanks on hydrogen-powered cars to ensure their long-term performance.

Fesmire said: "When spacecraft fly into the vacuum of space, they need similar insulation materials to ensure the keeping of the cryogenic propellants for extended periods of time."

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Unique coil coated product can be formed and integrated into new office product shapes, while providing better performance than traditional options

# Helping office product manufacturers to think outside the box

While dry erase boards have long been a staple in just about every boardroom, classroom and meeting room, manufacturers typically have been forced to choose from expensive, heavy glass or porcelain construction or cheap melamine products that, to a large degree, had to be manufactured into rectangular boards or panels and inserted into frames.

Furthermore, the less costly options tend to ghost (erase incompletely), often require thorough cleaning with liquid cleaners and wear more easily, leading to premature replacement.

Now advanced coatings applied to steel coil substrate are enabling office product manufacturers to think outside the box by allowing cutting, bending and forming of a dry erase surface not only as doors, wall panels, and cubicle partitions but also as curved surfaces and even 3D shapes.

In addition to cutting down the weight, the dry erase coating also reduces ghosting and even allows for sublimation printing of logos and branding. This could include photo quality images or other graphics for industry or customer specific purposes.

## POST FORMABLE DRY ERASE COATINGS

While traditional dry erase materials are readily used in standard whiteboard shapes and sizes, they are not compatible with more complex forms. As such, they tend to corral office product manufacturers into rectangular 'inside the box' thinking.

"Porcelain and glass covered dry erase surfaces cannot be formed, which limits their potential use in a wider array of office products," says Dan Chin, President of Universal Chemicals & Coatings (Unichem), a custom adhesives and coating formulator. "Their weight also poses limits in the size, application and mounting of the dry erase boards."

A new approach of a specially formulated coating to aluminium and steel coil substrate is promising to dramatically expand the possibilities of how a dry erase surface can be used and incorporated into office products.

Coil coating, a high speed efficient coating process, involves the use of aluminium, cold rolled steel or hot dipped galvanised steel, which can be efficiently coated, re-coiled and then shipped for later fabrication and forming into parts or products.

Unlike porcelain and glass, a coil coated substrate with a special dry erase coating can be precision slit, stamped, sheared, roll formed and incorporated into virtually any size or shape that coated coiled metal can be configured.

Manufacturers like Unichem, for instance, have developed coatings for coil substrate that can be post formed to accommodate a manufacturer that wants to form whiteboards into wall panels, partitions, or office furniture installations. In fact, their coatings are used on the dry erase panels at one of the world's leading office furniture manufacturers.

Because of how flexibly the coated coil substrate can be formed, it is also suitable for entirely new applications, including aesthetically curved or 3D surfaces, which manufacturers, architects and interior designers may dream up.

Additionally, dry erase installations utilising the speciality coating weigh only a fraction of comparable porcelain applications and similar glass applications. This can simplify any wall or partition mounted installation, as well as make furniture lighter and more easily moved and shipped.

## BETTER ERASABILITY, LESS GHOSTING

In addition to the increased design options, manufacturers are also solving the omnipresent issue of ghosting and shadowing at a substantially lower cost than either glass or porcelain.

Some coil coated substrates, in fact, have been tested with more than 100 markers from a wide array of manufacturers, even some permanent marker manufacturers.

▷ 27

*Marco Heuer* and *Fabian Eichenberger*, Evonik, discuss two new silicone-free flow and levelling additives developed for use in solventborne can and coil coatings

# Appealing surfaces of coil coatings

Coil coatings are well-known in the market for providing high quality at low overall cost to end-users[1]. The transfer efficiency of the roller application is one of the major reasons for its popularity. Over the past few years, the Asia Pacific region has surpassed Europe as the leading consumer of coil coatings[2].

Pre-coated aluminium and steel coils applied by a roller-coater are a very economical way to create colour-coated goods without using a paint shop. Along with architectural elements (façades, roofs) and consumer goods (furniture, washing machines), food containers like cans are ideal for for such an application. The expected demand for coil-coated substrates will increase by more than 7%/yr in Asia Pacific[2]. There are three major reasons for this above-CAGR increase:

- The roller-coating application process is very effective; it is almost completely free of overspray, so very little coating is wasted. The high line speed allows for a high output during production.
- Thermal combustion systems are state-of-the-art for solventborne coatings. No air-polluting solvents are released into the environment and the energy of the combustion is used for heating up the curing oven for the roller-coater. This system allows for high throughput combined with an environmentally friendly and resource-efficient application process. This leads to an overall reduction in emissions at work sites.
- After application and curing of the coating, the coated substrates will be coiled, stored or shipped for an extended period of time. When necessary, the substrate can be wound up, cut, drilled and bent into the desired shape and into the desired amounts. This is a much more flexible means of production than, for example, a process involving cast iron, where the ready-made shape can only be sprayed and cured with a lot of overspray, drying time, etc. All of these factors lend to a production rate lower than that of the roller-coater process, where just one coating facility added to the beginning of the economic value chain can serve hundreds of metal-working facilities efficiently.

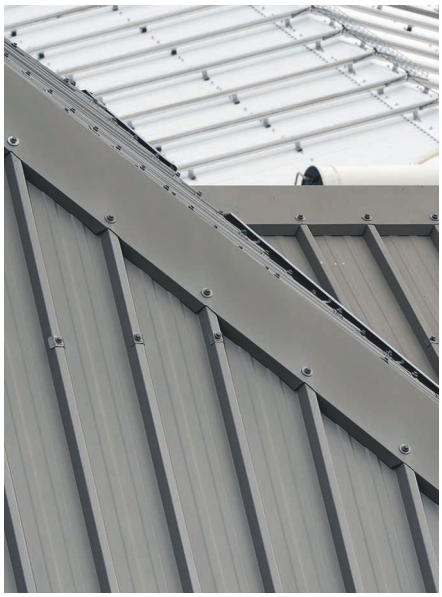
## INCREASING QUALITY DEMANDS FOR COIL COATINGS

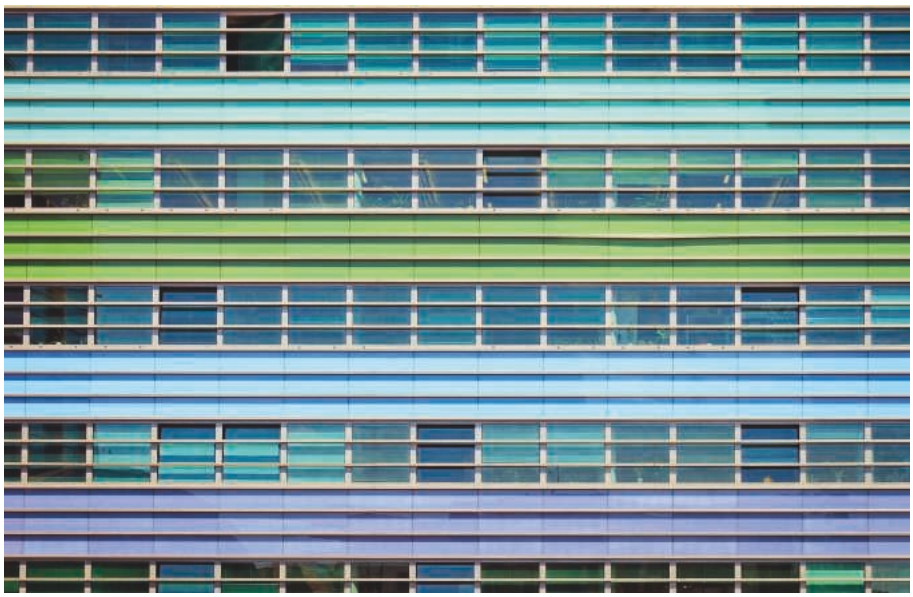
Because of extended warranties for long-lasting products like house panelling, roofing and windows, the producers of coil coatings are faced with increasing quality requirements leading to improved optical quality of the coated surfaces. The high line speeds of these industrial band coating operations and the subsequent deformation of the coated sheets demand extraordinary requirements regarding the optical appearance of coil coatings. They must provide excellent levelling, be free of foam and bubbles and have surface characteristics, such as smoothness, scratch resistance and abrasion resistance.

## FLOW ADDITIVES PROVIDE EXCELLENT OPTICAL APPEARANCE

Polyacrylates are well-established as flow additives for coil coatings. By their chemical nature, they are stable to the high curing temperature in the coil coating process. They impart smooth surfaces properties immediately after the coating is applied. Because the surface energy of the dried coating is not reduced, the wetting properties of the subsequent layer are not critical, making them very suitable for multi-layer coatings[3].

Two new, silicone-free flow and levelling additives are specifically developed for





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| Table 1. Improved optical appearance via flow promotion | | |
|---|---|---|
| Properties | Formulation * without additive | Addition of 0.4% new flow additive (1) to the formulation* |
| Gloss @ 20°C | 96 | 96 |
| Appearance in liquid formulation | clear | clear |
| Long wave | 17 | 6 |
| Short wave | 30 | 8 |

* Testing system based on Polyester -/Melamine

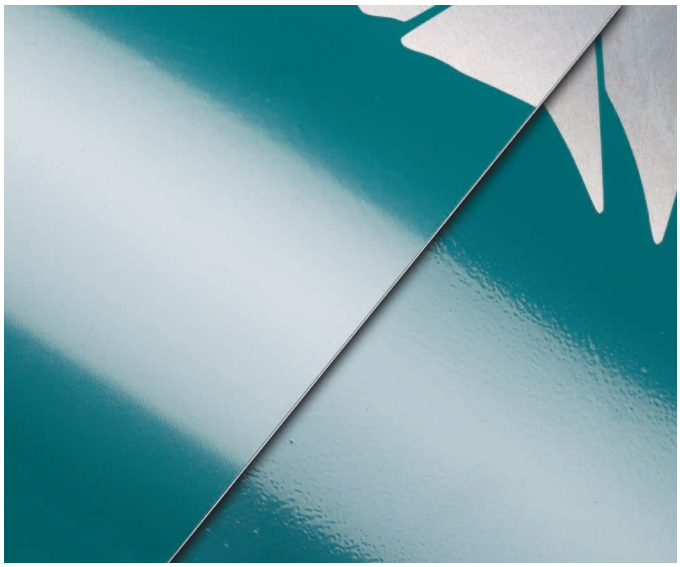

**Figure 1. Excellent flow promotion by addition of 0.4% new flow additive (1) to the formulation*, applied by spin coater**

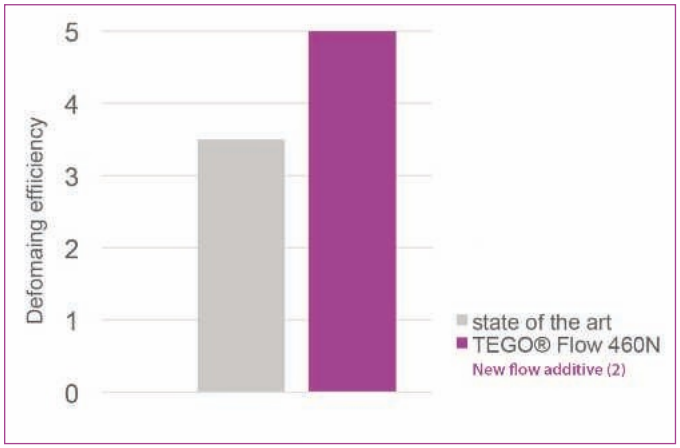


**Figure 2. Improved defoaming properties in the formulation Testing system based on Polyester-/Melamine[4]**

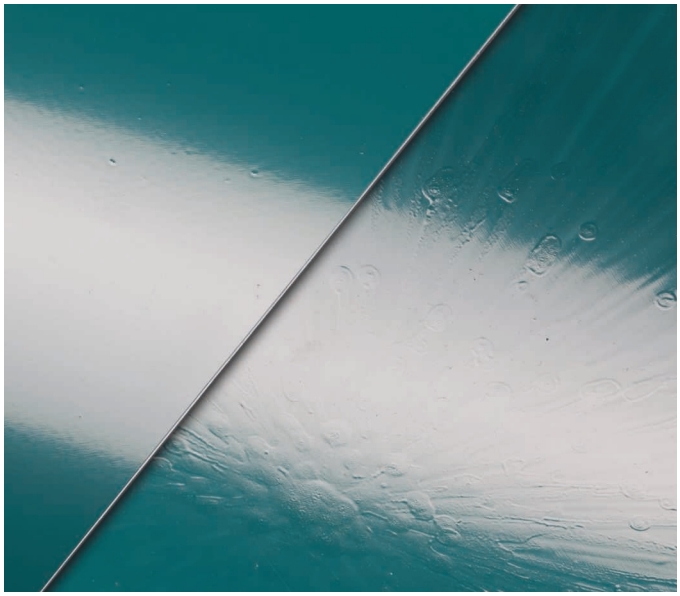

**Figure 3. (Right) Excellent optical appearance via improved defoaming properties by addition of 0.4% -new flow additive (1) to the formulation*, applied by spin coater**

use in solventborne can and coil coatings. The backbone of both products is based on unique and reliable polyacrylate chemistry, providing excellent recoatability for usage in, for example, primer/topcoat systems or lithographic images. To meet current and future demands regarding health and the environment, neither product contains any aromatic solvent like xylene, toluene, or higher aromatics. Additionally, neither halogens, formaldehyde, nor BPA are contained in the compositions.

The first additive provides an excellent broad binder compatibility for universal use in coil and can coatings. This leads to an outstanding optical appearance with no haze in the cured system, especially for transparent applications. This effect is demonstrated by the following lab results:

The second additive provides flow improvement as well as an additional deaerating effect. Due to its relatively hydrophobic nature, it avoids entrapment of foam during application. This additive was developed for use in pigmented systems. Achieving these two important properties for can and coil coatings reduces complexity. This effect is demonstrated by the lab results in **Table 1**.

The second additive provides flow improvement, as well as an additional deaerating effect. Due to its relatively hydrophobic nature, it avoids entrapment of foam during application. This additive was developed for use in pigmented systems. Achieving these two important properties for can and coil coatings reduces complexity. This effect is demonstrated by the lab results in **Figure 2**.

Neither of the new flow additives will influence the pigment stabilisation in solventborne can and coil coatings during manufacturing, storage or application.

## ■ OUTLOOK: FURTHER INCREASE IN OPTICAL REQUIREMENTS

Demands made upon the surface appearance of the bake-cured enamels are constantly increasing. The goal for the future is to create Class A surfaces via the roller-coating process. Currently, Class A surfaces can only be created via spray bell or spray gun application. Therefore, high-gloss surfaces for premium goods (such as cars or consumer electronics) cannot be attained by a roller coating process. Next to the orientation of metallic and effect pigment particles, the most important factor for Class A surfaces is the visual appearance of the coated surface. Only smooth surfaces with a very low short wave and long wave haze provide a surface suitable for premium goods. Both additives can be used in coatings formulations to optimise long wave/short wave up to 80%! This enables coatings producers to follow the global trend of premium optical appearance.

## ■ FAR-REACHING LISTING AND REGISTRATION GLOBALLY

Due to global demands of coatings producers and applicators, it was decided at a very early stage of product development that global listing

is absolutely necessary to support customers and end-users needs. So both additives are listed in all major chemical inventories for universal use (EINECS, TSCA, DSL, ENCS, AICS, ECL, PICCS, IECSC, TSCI, NZIoC) and fulfill the 21 CFR FDA regulations 175.300. Also, all components are also listed in Annex 6 in the lists for evaluated (A) or not evaluated (B) substances according to Swiss Ordinance (SR 817.023.21). These universal registrations minimise the complexity for coatings manufacturers in handling, logistics and formulation and allow diversified application. This means coatings manufacturers can use the same additive for more diverse end-uses like roof-toppings or food cans.

## SUMMARY

End customers' decisions are ultimately determined by quality and high demand for excellent visual appearance. The new surface additives improve processing and visual appearance significantly. In solvent-based can and coil coatings, such specially developed polyacrylates provide excellent appearance. The products' composition and their far-reaching listings and registration leads to universal application. Recoatability is excellent, due to the fact that they do not impair the surface energy of cured films. Both new additives fulfill 21 CFR FDA regulations 175.300 and all components are listed in Annex 6 in the lists for evaluated (A) or not evaluated (B) substances according to Swiss Ordinance (SR 817.023.21).

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**Marco Heuer** studied chemistry and technology of paints and coatings at the University of Paderborn, Germany. He graduated with a diploma in chemical engineering in 1995. After several years as R&D manager for different German paint manufacturers he joined the former nanoresins AG and hanse-chemie AG, Geesthacht, Germany in 2006. Since Evonik´s aquisition of both companies in 2011 he was responsible as Senior Technical Service Manager for nanoresins at Evonik Coatings & Additives. Since April 2015 he is serving the Applied Technology Department as Director Industrial Coatings for Coating Additives at Ressource Efficiency.

**Fabian Eichenberger** Studied bio- and nanotechnologies at the South Westphalia University of Applied Sciences where he graduated as a Diplom-Ingenieur (FH) in 2009. After working for two years in the paint industry in the R&D department of a manufacturer of automotive finishes, Fabian joined Evonik Industries AG in 2011. He currently serves as Senior Manager Applied Technology within the business line Coating Additives for the segment Plastics, Can, Coil, Leather Coatings.

- The new flow additive (1) shows a broad compatibility with all binders and high optical transparency.
- The new flow additive (2) provides flow improvement as well as an additional deaerating effect.
- Both products are free of hazardous ingredients like BPA, aromatics and halogens.

The excellent optical appearance attracts can and coil coating customers worldwide.

**PPCJ**

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◁ 23 With more than 10,000 cycles of erasability, heat and humidity cycling and cleanability, the finish exceeds the industry's stringent requirements, so even permanent markers clean off with spray cleaners.

As a matter of fact, a Fortune 20 technology company recently chose to apply one such coating, called Uni-rase, on all the white boards at its new world headquarters.

"In the erasability tests, the coating has to show little to no wear through all the mark-erase cycles," says Chin. "It's also important to build in resistance to moisture because some common dry erase products tend to ghost severely in high humidity climates."

## PHOTO QUALITY GRAPHICS

A dry erase board by definition is designed so ink will not stick. As such, typical dry erase materials usually provide only a simple graphics capability by printing.

However, the availability today of photographic quality sublimation inks, along with specialised coatings, makes the printing more impactful, complex images that enhance the brand possible.

"Now you can infuse (sublimate) permanent inks into the coating – such as for photos, logos, patterns, calendars, or industry specific formats or graphics – yet retain dry erase board erasability," says Chin. "The image in the coating is every bit as good as the actual printed photo, so it enhances visual impact and aesthetics."

The sublimation process used to achieve this and essentially introduces heat to turn solid ink particles directly into a gas, which permanently colours the surface and sub-surface of the dry erase board, so the ink will not wash away, according to Chin.

Though the dry erase market has changed relatively little in decades, the recent introduction of unique coatings is now changing the industry and providing office product manufacturers with creative new ways to better serve their customers.

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*PPCJ* caught up with a spokesperson from Axalta to discover more about the company's automotive coatings

# OEM vs refinish coatings

***Q. What are the different kinds of OEM paints that Axalta offers, particularly with regards to heavy goods vehicles manufacturers?***

**A.** In general, there are two different kinds of coating technologies used to paint new-build heavy-duty trucks (HDT). You have truck OEMs using 1K (one-component) technologies, which are similar to what is used on OEM passenger cars. These coatings are cured at 140°C to 160°C. In addition to this high-bake technology, polyurethane-based 2K (two-component) OEM coatings are used which typically cure at 80°C.

From a chemical perspective, 2K PU coatings are even more robust but they have the added advantage that they can be used on the plastic parts. This simplifies the process and ensures exceptional colour accuracy because these plastic components are coated using the same OEM paint system as the cab itself. A further advantage of 2K coatings is that they require less energy and, therefore, can have a positive impact on $CO_2$ emissions.

***Q. How do they differ from refinish paints?***

**A.** 2K PU-isocyanate coatings technology is also used in the aftermarket segment for repairs or refurbishment. It is typically cured at lower temperatures, around 60°C, as, at higher temperatures, plastic parts might deform or the sophisticated electronic components inside the vehicle might be damaged.

These refinish HDT coatings are probably best known in the market as Imron Fleet Line from Cromax, Permafleet from Spies Hecker and Standofleet from Standox, which have been formulated to be applied manually. By contrast, Axalta's 2K paint for the HDT OEM segment – Imron – is formulated for robotic application but is also based on a concentrated tints and binder system. What this means for bodyshops is that it is even easier to deliver a true colour match during repairs or refurbishment because both the OEM paint and the refinish paint use a concentrated tints and binders system. On HDT or bus OEM production sites, refinish paint is used for end-of-line repairs and touch-ups.

***Q. How does their implementation differ from the paints used in the refinish sector?***

**A.** It is not only the curing temperature that is a differentiator between HDT OEM and refinish but also the application is completely different. Similar to OEM passenger car coating application, all our HDT customers use robotic application, while in refinish manual application is typically used. In the bus segment, you find both robotic and manual application methods for new-build buses. End-of-line repairs are always done manually.

***Q. What are the training sessions and client support/ follow up offered by Axalta to its OEM clients?***

**A.** Axalta has a complete application centre in Wuppertal, Germany, where we can simulate the OEM line conditions including their specific bell cups. This helps a customer ensure that newly developed technologies or key colours can be tested upfront. This facility is also very valuable when a customer is installing a new paint-line, as the paint and colour performance can be checked upfront. In addition to the robotic training and simulation, we also offer repair and polishing training.

For more information on Axalta visit: axalta.com and follow Axalta on Twitter and on LinkedIn.

**PPCJ**

# Science inspires Lexus to create Structural Blue

The development of Lexus' latest automotive colour Structural Blue began with unusual inspiration: the keen observation of the morpho butterfly. Its wings appear blue but closer inspection reveals that they actually have no colour of their own. The effect is the result of microscopic details that scatter light and show only the colour wavelengths of the iridescent blue we perceive in their vibrant wings.

For Lexus, this science inspired the creation of 'Structural Blue'. By carefully re-creating the layers of nanostructures that produce this effect, the miniscule flakes and patterns could be crafted to produce a first-of-its-kind paint that controls brightness and colour purity to emit a new shade of blue. Most paints reflect 50% of incoming light but this approach enabled Structural Blue to reflect nearly 100%, making it more vibrant and dynamic than any other blue in the world. The advanced technology that creates this effect is the culmination of more than 15 years of research and development work.

Structural Blue pigment reflects light much like a tiny mirror. It creates a vibrant colour when viewed directly but when viewed off-angle it appears dark. When applied to Lexus LC, Structural Blue highlights the car's dynamic design and features, giving its unique shape the appearance of motion.

# Water-repellent coatings enable easy ice removal

Water-repellent surfaces and coatings could make ice removal a literal breeze by forcing ice to grow up rather than just skate by, says a new study from the University of Nebraska-Lincoln, USA and several Chinese institutions.

The researchers discovered that ice grows differently on absorbent vs water-repellent surfaces, demonstrating that a gust of air can blow away ice that forms on the latter. Their findings suggest that applying water-repellent coatings to windscreens before winter storms – or engineering surfaces that inherently repel water – could enable a strong breeze to handle the burden of ice removal.

In contrast, droplets on an absorbent surface crystallised into ice that grew along that surface, making it more difficult to remove. Molecular-level simulations suggested that these droplets almost immediately began forming two stacked layers of hexagonal 2-D ice, a form that Zeng previously discovered and dubbed Nebraska Ice. This ultra-thin ice encourages water molecules to essentially skate across it and colonise other areas of the surface, Zeng said.

"If the water and the surface don't have much chemistry in the beginning – they don't like each other – it's kind of like a divorce or separation," said Zeng, Chancellor's University Professor of Chemistry. "But if they like each other, they marry and stay together for a long time. That's when the ice grows along the surface. In the winter, if you have that kind of ice on a windshield, you have to use a scraper to get it off."

## ONWARD OR UPWARD

Temperature and pressure mostly dictate how water droplets crystallise in open air, and those variables do factor into ice formation on solid surfaces, Zeng said. But the team's study suggests that a surface's contact angle – the angle formed where a water droplet meets a solid surface – determines whether ice will grow along or off the surface. Whereas a hydrophilic surface allows water to spread across it at a small contact angle, a water-repelling hydrophobic surface will force droplets to bead up and form a larger angle.

"Whether water freezes in one way or the other is up to the surface, not the temperature," Zeng said. "It's almost entirely dependent on the contact angle."

On a defect-free surface fabricated in the lab or modelled in a computer simulation, ice transitions from along-surface to off-surface growth at a contact angle of somewhere between 30 and 40 degrees, the team found. The researchers also discovered that increasing the roughness of a surface by enlarging its nanoscopic pores actually decreased this angular threshold, meaning that rougher surfaces need not be as water-repellent to foster the growth of more-easily removed ice.

## BREAKING THE ICE

To compare the two forms of ice growth, the researchers designed a transparent surface split into halves: one hydrophilic, one hydrophobic. They then attached a high-speed camera to a microscope, capturing video of the respective processes both from beneath and from a side profile.

When the researchers subjected both halves to puffs of air, they found that ice abandoned the hydrophobic half but steadfastly held to the hydrophilic side. And ice that advanced across the hydrophilic half abruptly halted when it neared hydrophobic territory.

"People have been studying how water interacts with surfaces for a long, long time," Zeng said. "But this phenomenon was off the radar until now."

Zeng and the team reported its findings in the journal *Proceedings of the National Academy of Sciences*.

**PPCJ**

# PPG unveils top colours for European cars

PPG has unveiled its automotive colour trends and data, citing blue as the fastest-growing colour for cars worldwide, while white remains the most popular choice for cars in Europe.

While consumers' preference for white decreased this year by one percent, from 33% in 2016, the shade remains the overall top pick for vehicles in five of the six European countries surveyed for the data. As a whole, the colour's favourability has grown by five percent over the past five years in this region. Throughout Europe, both metallic and solid versions of white are the most popular options for luxury, compact and mini-van automobiles. But, European consumers prefer blue on sports cars more frequently than any other car type.

"PPG's leading position in paint and colour forecasting allows us to analyse cross-cultural and cross-industry trends with our 20 global colour stylists from seven countries," said Jane Harrington, PPG Manager, Automotive Colour styling. "While we know that automotive colour trends are inspired by multiple industries, they are unique compared to fashion or home décor since the trends evolve and change slowly over time instead of significantly year-to-year. While white, black, grey and silver continue to be popular colour choices, we're seeing a steady increase in the desire for cars in varying blue and brown shades."

**Europe:** White (32%), grey (18%), black (17%) and silver (9%) remained almost consistent with 2016, while blue (9%) saw an increase in consumer preference.

Comforting neutrals that consumers are craving in fashion, technology and their homes cause silver and grey to continue to be popular in automotive colours across all types of vehicles due to slight nuances in colour and classic roots, Harrington noted.

# Sales and acquisitions dominating Italian market

Brenda Dionisi reports from Milan, on the factors affecting the Italian paint market and the recent activities of some of its major players

Despite relatively stagnant year-end results in 2016 for the paints and coatings market in Italy, last year proved unexpectedly dynamic in terms of sales and acquisitions, with several companies in the sector moving to increase their market share in specific subsectors of the market. The paint and varnish sector is an important industrial segment of Italy's larger chemical industry, boasting a production value of more than €3bn, according to trade association AVISA, a division of Federchimica, the national chemicals industry association. Following Germany, Italy is Europe's second biggest coatings producer in terms of volume, with more than 700 companies operating in the sector domestically. AVISA represents the majority of Italian manufacturers of adhesives, sealants, paints, coatings and inks in the paints and coatings sector. Werther Colonna, President of AVISA, offered *PPCJ* an inside view on the overall state of the market: "Italy's paint and coatings companies – through the quality of their products, innovation and the ability to effectively respond to customer needs – are often examples of the world-renowned success that has the Made in Italy label so well known in the world. A significant and growing part of production output in the sector is dedicated to foreign markets."

**Frederico Geremia, President of Colorificio San Marco SpA surrounded by members of his family. The family-run San Marco Group is celebrating its 80th anniversary this year**

> *"Following Germany, Italy is Europe's second biggest coatings producer in terms of volume, with more than 700 companies operating in the sector domestically."*

## STAGNANT DOMESTIC CONSTRUCTION SECTOR

However, despite such excellence, market performance has been below expected levels in recent years, Colonna revealed. "On the whole, the entire year of 2016 was marked by difficulty and characterised, in most segments, by a succession of alternating signs of vigour and distress, translating, on the whole, into very bearish monthly results. 2016 closed with an overall performance in line with 2015 results," Colonna said, adding "Moreover, overall performance in the first half of 2017 appears to be in line with the same period the previous year."

He explained that part of this recent market fragility is due to a still stagnant domestic construction and building sector, for which the conditions for an adequate recovery still do not seem to exist: "This is evident in the construction products subsector, which accounts for about 50% of the entire paint and coatings market in Italy." Data from the Assovernici coatings trade association, whose main market of reference is the building and construction subsector, shows that market value of the subsector has dropped by 20% since 2010, the start of the Italian economic crisis, reaching €1.15bn in 2016.

Additionally, despite representing an important part of total market turnover, export volumes have not been robust enough in all subsectors to boost year-end performance results. "Only sectors that have a better propensity toward export, especially outside of the EU, such as the wood, car refinishing and decorative materials sectors, have been more encouraging, even boosting foreign trade numbers compared to the domestic market. The most receptive markets now appear to be in South America and Asia," Colonna explained. However, despite such a depressed market situation, it is worth noting how "the sector has shown signs of great vivacity over the last few months," Colonna said, with several acquisitions and divestments of companies or business units.

## SAN MARCO GROUP'S ACQUISITION OF EUROCOLORI

A recent acquisition was completed by leading manufacturer of professional paints and coatings for the building industry, the San Marco Group, which acquired the Padua-based EuroColori, tintometry and colorimetry producer of architectural coatings, in June 2017. EuroColori closed 2016 with €3.5M in turnover. "This is a strategic acquisition and an important investment for the future," said Federico Geremia, President of the San Marco Group's most important subsidiary, the Colorificio San Marco SpA "which will enable the Group to acquire specialised know-how in the area of colorimetry and colorimetric software for paints and coatings for the building industry."

The group, which this year [2017] celebrates 80 years in business, closed

2016 with a turnover of about €70M, up 1.5% yr-on-yr and contrary to the rest of the market, which contracted by 3%. Today, products of the San Marco Group are sold in 100 countries and exports represent 40% of overall sales, the Group reports.

Meanwhile, market leader in home and building paints in Italy and global leader in the yacht-naval segment, the publicly listed Genoa-based Boero Group, which has produced coatings, paints and protection cycles of extremely high quality since 1831, acquired for €1.8M two brands in 2016 through its subsidiary Brignola Srl: the Brignola and Torre brands. The transaction "intends to expand its commercial offer, having the same important tradition of reliability and expertise in the home paints sector," a company statement read. It said consolidated revenues for 2016 reached €85.4M (compared to €90.3M in 2015) and EBIT reached €1.9M (compared to €2.6M).

## INVESTMENT INTO SUSTAINABLE PRODUCTS

Worthy of note are the Boero Group's recent investments in the development of sustainable products. It has a line of sustainable, environmentally low-impact paints, called Boero Painting Natural and has invested considerably in a specialised research laboratory that is working on the creation of a paint comprised of natural ingredients, such as vegetable and plant waste from the food sector.

Indeed, according to Valentino Degani, Head of the technical and legislative division at Assovernici, most recent product novelties in the Italian sector have focused on paints for interiors, such as paints with a low environmental impact, waterproof and washable paints and anti-mould and condensation paints, as well as for exterior applications, like paints made with high hydrophobic siloxane polymers that are able to guarantee very high resistance to atmospheric agents and water and at the same time a high water vapour permeability. Degani said that it has been difficult for companies in a depressed market to introduce new, technologically advanced products due to the elevated costs compared to standard products. The situation producers face has also been aggravated by a constantly changing legislative landscape, he added. One of the most critical issues negatively impacting the market has been the ongoing updating of the [European Union's] CLP Regulation (EC) No 1272/2008 on the classification, labelling and packaging of substances and mixtures, which he claimed had been "often marked by unclear and contradictory decisions…" He also complained of continued EU-inspired restrictions on "the use of raw materials, which has led to increasingly heavy products labels, often without real justification and, in some cases, in direct contrast to the general criteria of the various regulations".



**From the archives: 1933 – Arson-Sisi leaflet of "Arsonia" paint for Teatro alla Scala (Milan). The company is celebrating its centenary this year**

## ARSONSISI CELEBRATES ITS CENTENARY

Arsonsisi, Italy's leading independent industrial paints and coatings producer, also celebrates its centennial of business activity this year [2017]. Over the past decade the company's strategy has focused on growth and diversification. In its most recent transaction, in 2015, it acquired Tecnocolor Srl, producer of high-performance specialist coatings, in addition to the acquisition of "a production licence from Beckers Industrial Coatings Italia to produce products for drums, tubes, tanks and cylinders," said Dr James Junghanns, Business Unit Manager of Arsonsisi.

The strategy has proven to be successful, with the company closing 2016 with great satisfaction, said Junghanns: "2016 was a turning point for the company … [as] it was a year of growth following the various reorganisations and acquisitions undertaken in 2015." Meanwhile, "2017 is turning out to be a year of stabilisation regarding the commercial structure and overall profit margins as a result of strong increases in raw materials," he added.

Currently the company has made considerable investments in research and innovation, especially in low or formaldehyde-free technologies, technologies eliminating bisphenol-A, and those reducing solvent content. "We are also investing heavily in UV-technology and, in collaboration with our partners, we have developed important technologies for replacing galvanic (which requires the use of hexavalent chromium) with a sputtering/plasma vapour deposition (PVD) cycle," confirmed Junghanns.

Among the major challenges the sector faces, Junghanns had this to add: "Certainly, the Italian powder coatings market is devastated by an excess of production capacity and a price-based competition model, thus bringing our products to commodity levels when, in reality, they are rather customised products. This, coupled with the national consumption crisis and the substantial non-competitiveness of the domestic manufacturing sector, has strongly affected demand. Increasing costs for raw materials is certainly another factor that further aggravates the current market situation." ■

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This year's *Egyptian Coatings Show*, held in Cairo in October, exceeded everybody's expectations, with both visitor and exhibitors more than happy, as *Chris Malthouse* reports

# Cairo show voted an outstanding success



With nearly 1300 attendees from 34 countries over the two-day event, the Cairo International Convention & Exhibition Centre was the place to be from October 11-12.

As the images on these two pages show, busy stands and crowded aisles brought a smile to everyone's face as the coatings industry met to do business, discuss products and services and make new contacts.

## PACKED STANDS

Following the outstanding success of the show in 2015, exhibitors I managed to speak to were, once again, more than happy, with many praising the quality of the visitors attending.

Dikran Kalayjian, Managing Director, Lanai Holdings, who along with CMP took two stands this year to make room for all the companies he represented was very pleased: "The stands are packed and next time we will have to take three stands to accommodate everyone!"

"Very happy and pleasantly surprised at the number of visitors," said Bartek Janas, Country Manager Middle East & Turkey, Fast & Fluid.

"Very happy, despite the smaller size I am very pleased with the calibre of visitors. We have talked with five or six CEOs of the top Egyptian companies in the industry.

"The exhibition has also given us a chance to meet people from both technical and commercial sides of the companies. The show has exceeded our expectations," said Michael Francis Shehata, Business Development Director, CBC Egypt.

"It's been a good show – got the kind of people we want to speak to. We set up targets before the show and have already met most of them. The show was well publicised with the paint industry in Egypt," noted Viren Sanghvi, Sauradip Chemical Industries Pvt Ltd.

Patrik Hutter, Country Cluster Manager Africa & Turkey, Covestro International SA reported that the stand had been "100% busy on the first day".

"Good show, lots of visitors," said Fabian Rossi, Sales Manager, MEA, Corob SpA.

Equally as busy were the Business Presentations held on both days, where visitors were keen to learn and discover


Egyptian Coatings Show 2017
The Middle East Coatings Show Cairo

more about the speakers' products and services. Companies taking part this year included: Fahmy Group; Egyptian British Co; Covestro International; Sauradip Chemical Industries; Nord Composites; and Ecore.

After a busy first day, exhibitors took time out to relax at the Gala Dinner, which as always, provided stunning entertainment and a real flavour of Egypt.


## ■ MECS 2018 DUBAI

We will return to Cairo in 2019 but in the meantime, we look forward to seeing everyone at the *Middle East Coatings Show* in Dubai in March 2018. So make sure you put the date in your diary to either exhibit or visit this key event in the coatings calendar, from March 19-21. For more information visit: www.coatingsgroup.com

**PPCJ**



*Vladimir G Kurbatov* and *Eugene A Indeikin*, Yaroslavl State Technical University, discuss the influence of polyaniline forms on the rate and depth of curing of epoxy oligomers

# Curing kinetic of epoxy oligomers in the presence of polyaniline

The influence of polyaniline forms on the rate and depth of curing of epoxy oligomers was determined. It is established that the use of the emeraldine form of polyaniline as a modifying agent of an amine hardener leads to the acceleration of the curing process, unlike the pernigraniline form. Studying the changes of the electronic absorption spectrum of the modified amine hardener shows the transition of the emeraldine form of polyaniline in the pernigraniline form over time.

## INTRODUCTION

It is known that polyaniline (PANi) is a polymer having a plurality of several various forms, which are capable of reversibly transforming into one another under the influence of external factors[1-2]. **Figure 1** shows a schematic diagram of mutual transformations of different forms of PANi.

As it was shown[1-2], the ability of polyaniline to transition into a reversible makes it possible to use it as a catalyst for certain reactions, for example hydrolysis of glycerol esters, etc.

In early works[6-8] it was shown that the amino cross-linking agent modified from the PANi emeraldine form produces epoxy coatings having highly complex physical and mechanical properties. It has been shown, that the use of the emeraldine form by PANi, in amounts up to about 0.4% by wt, leads to increased elastic modulus and tensile strength of the epoxy. A further increase in the content of PANi reduces the elastic-deformation properties. Introduction of the pernigraniline form by PANi reduces modulus epoxy material and slightly increases tensile strength. An amino cross-linking agent modified by PANi allows the production of epoxy coatings with high protection properties[9].

The possibility of the reversible transition forms of PANi, in a basic medium, may be such of a change of the properties of the modified amine crosslinking agent (ACA). Also, change of the properties created with this use of epoxy polymeric materials can be a consequence. It is interesting to study the stability of the modified ACA during this time because of the influence on the process of hardening of the epoxy oligomer.

## EXPERIMENT

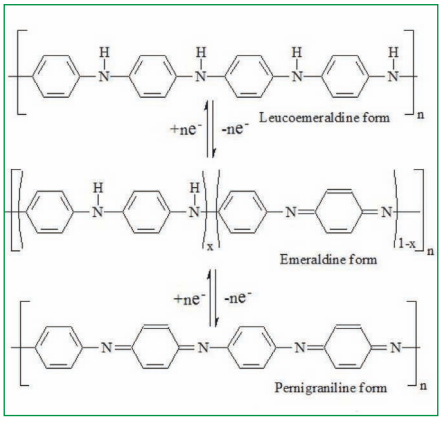
The epoxy oligomer (EO) with an epoxy equivalent of 205g/mol was used for the research. The 2-methylpentamethylene 1.5-diamine (MPMDA) with H-equivalent to 29g/mol (the main substance content is 99%) was used as ACA. N-methylpyrrolid-2-one (the main substance content is 99%) was used without further purification.

Undoped emeraldine and pernigraniline forms of PANi were used as the modifying additions for ACA. The undoped emeraldine form of polyaniline was prepared by oxidative polymerisation of hydrochloride aniline in an aqueous solution of hydrogen chloride in the presence of ammonium persulphate. The resulting green precipitate doped with hydrogen chloride emeraldine form PANi, was filtered and washed with 1M HCl and then with acetone to remove unreacted monomer and low-molecular oligomers. The washed precipitate was dried in air under vacuum at 60°C for 24hr. Dried doped PANi was treated with 1M aqueous ammonia for 12hr, then filtered and dried under vacuum at 60°C for 48hr. The pernigraniline form of polyaniline was obtained by treatment with a base in solution emeraldine form of N-methylpyrrolidium-2-on with a solution of 3-chloroperbenzoic acid in glacial acetic acid. The resulting dark purple solution was treated with triethylamine to form the base pernigraniline PANi precipitate. The resulting precipitate was filtered, washed with acetone and dried under vacuum at 20°C for 24hr.

Electronic absorption spectra modified PANi of MPMDA were recorded using a spectrophotometer Specord M-40[10]. The content of the epoxy groups was determined by infrared spectroscopy using a spectrophotometer Perkin Elmer RX-1. Kinetics of the curing of epoxy compositions using a sol-gel analysis[11] and by differential adiabatic calorimetry[12] were studied.

Calorimetric tests were carried out using a differential automatic micro calorimeter DAK-1-1 in the mode of direct detection rate dQ/dt at isothermal conditions. The composition was cured at a temperature of 60°C.

**Figure 1. The reversible inversion of different forms of PANi**

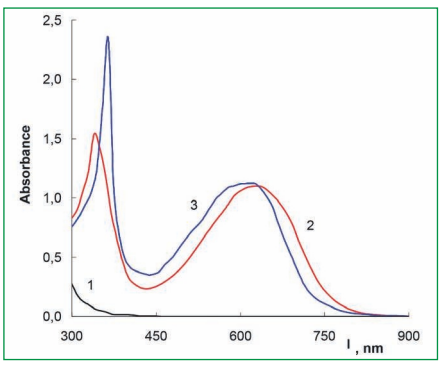



## RESULTS AND DISCUSSION

**Figure 2** shows the absorption spectra of PANi, MPMDA and MPMDA modified by PANi in the solution N-methylpyrrolid-2-on.

As the absorption spectra shown in **Figure 2** for the PANi solution observed two characteristic absorption peaks at

**Figure 2. Absorption spectra MPMDA (1), PANi (2), MPMDA modified by PANI (3) in the N-methylpyrrolidium-2-on**



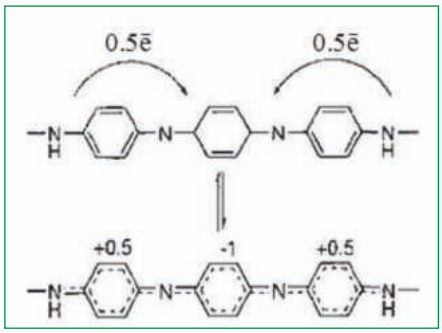



**Figure 3. The formation of molecular excitons with charge transfer in the quinoid ring of two adjacent benzene rings**

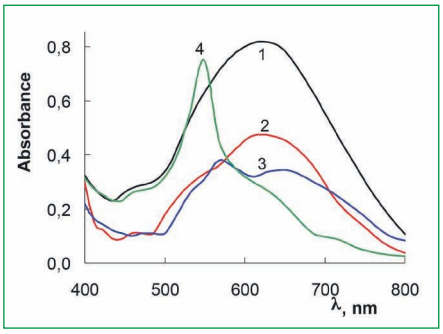



**Figure 4. Changes in the absorption spectrum of the MPMDA modified by PANi over time. Dwell time PANi modified MPMDA 1hr (1), 10 days (2), 25 days (3), 90 days (4)**

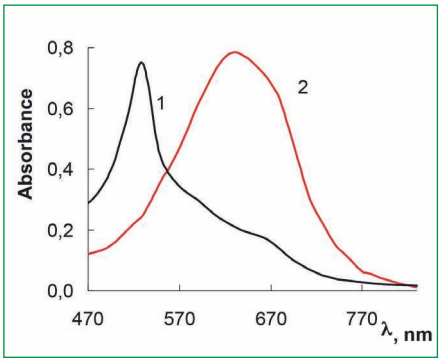



**Figure 5. The absorption spectra of MPMDA modified by PANi after 90 days of exposure (1), and after introduction of the reducing agent in it – TiCl3 (2)**

330nm and 630nm (curve 2, **Figure 2**). The maximum at ~330nm associated with the π-π * transition in benzene and quinoid structures. It has been found[13], a maximum absorption at ~630nm refers to the formation of molecular excitons qualitatively described as a charge transport in the quinoid ring of two adjacent benzene rings on the diagram (**Figure 3**).

A similar spectrum is observed for the ACA modified by PANi (curve 3, **Figure 2**), unlike ACA spectrum (curve 1, **Figure 2**) not having absorption maxima in the studied spectral region.

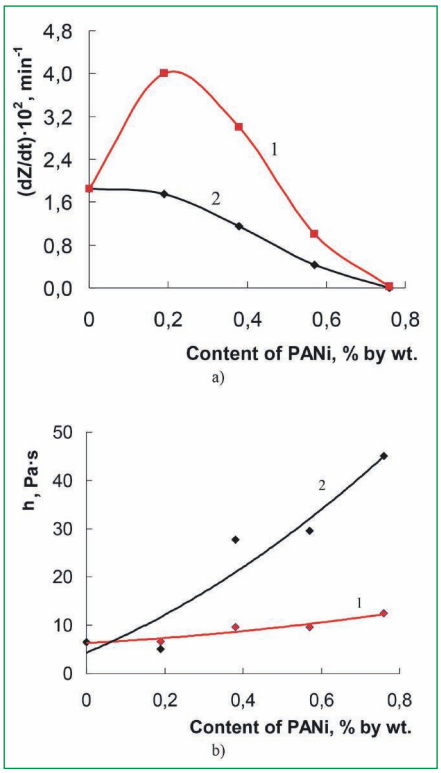



**Figure 6. Initial cure rate - dZ/dt (a) and the dynamic viscosity - Ð (b) vs the content of the emeraldine (1) and pernigraniline (2) form by PANi in the epoxy composition**

Electronic absorption spectra of the modified MPMDA change in time. Colour modified ACA at first becomes purple, then red-violet. These changes correspond to changes in the absorption spectrum of the MPMDA modified by PANi shown in **Figure 4.**

**Figure 4** shows that there is a shift of the absorption band previously located at 630nm to shorter wavelengths up to 550-560nm. The appearance of the absorption maximum at 550-560nm, is probably due to the transition emeraldine form of PANi to pernigraniline. However, the presence of 'shoulder' on the absorption spectrum at ~630nm at the same time, suggests the presence of several forms of PANi in the modified MPMDA, especially with a small storage time. The complete transition of PANi from emeraldine form to pernigraniline was observed with increasing storage time to 90 days, as evidenced by the disappearance of the 'shoulder' at 630nm at the absorption spectrum of the modified MPMDA solution.

The inverse process was observed when introducing reductant (as reductant was used titanium chloride (III)) for solution modified MPMDA in N-methylpyrrolidone. The shift absorption maximum in the range from 550nm to 670nm indicated for it (**Figure 5**).

Because of the established changes in forms of polyaniline, which is part of modified ACA, it is necessary to estimate the influence emeraldine and pernigraniline forms of PANI have on the curing process of epoxy oligomers.

**Figure 6** shows the dependences of the initial cure rate (**Figure 6a**) and the dynamic viscosity (**Figure 6b**) on the content of emeraldine and pernigraniline forms of PANi in epoxy composition. It can be seen that the dependence of the initial cure rate on the content of PANi is extreme, with a maximum of about 0.2% by weight. With increasing content of PANi the initial curing rate decreases. This can be explained by an increase in viscosity of the composition when increasing the content of PANi (**Figure 6b**), having a high molecular weight and addicted to associations and structuring due to the strong intermolecular interaction. In this case, limiting the content of gel-fraction in all compositions with the emeraldine form of PANi was comparable (95%). In addition, in determining the content of PANi probably violated limit compatibility system EO - ACA - PANi. As a result, part of the ACA can be adsorbed on the particles surface of PANi, drop down from the triple system and do not participate in the curing reaction.

Increasing the content of the pernigraniline form of PANi in the composition leads to a lowering of the initial cure rate. It should be noted, that the viscosity of compositions containing the pernigraniline form of PANi is significantly higher.

Apparently, the growth acceleration gel-fraction is observed even only after 30min of curing, even when using small amounts of the pernigraniline form of PANi (0.19wt%) in composition, whereas the use of ACA containing the emeraldine form of PANi achieved virtually the same time limit. When the content of the pernigraniline form of PANi is in excess of this amount, the content of gel-fraction in the coatings doesn't exceed the value achieved with original MPMDA, and at a content of 0.76% by wt in the composition, a strong delay of the hardening process was observed.

This is probably due to the fact that the pernigraniline form of PANi is an inhibitor of the curing reaction of epoxy oligomers of MPMDA.

**Figure 7** shows results of microcalorimetric tests for epoxy compositions containing the emeraldine form of PANi.

Introduction to the epoxy composition emeraldine form of PANi to 0.38% by wt leads to an increase of the rate of curing and conversion. When the content of the emeraldine form of PANi is more than 0.38wt% the conversion decreases. This is due to the fact that when increasing

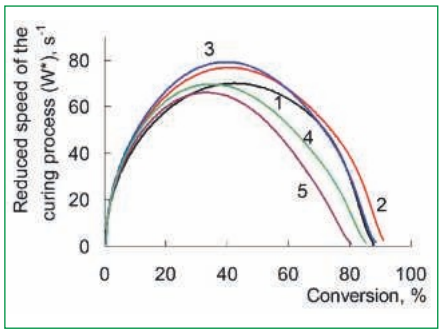



**Figure 7. Kinetics of epoxy compositions curing containing emeraldine form of PANi. The content of PANi in epoxy compositions, % by wt.: 0 - (1); 0.19 - (2); 0.38% - (3); 0.57 - (4); 0.76 - (5)**

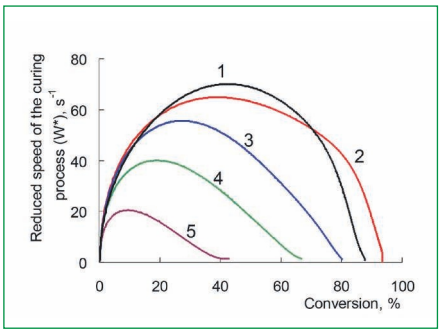



**Figure 8. Kinetics of epoxy compositions curing containing pernigraniline form of PANi. The content of PANi in epoxy compositions, % by wt.: 0 - (1); 0.19 - (2); 0.38% - (3); 0.57 - (4); 0.76 - (5)**

**Table 1. Influence structure of PANi on content of epoxy groups in epoxy polymeric materials**

| Content of PANi in epoxy coatings, % by wt | Content of epoxy groups*, % | |
|---|---|---|
| | Emeraldine form of PANi | Pernigraniline form of PANi |
| Uncured epoxy oligomer | 21.0 | |
| 0 | 2.6 | |
| 0.19 | 2.4 | 1.3 |
| 0.38 | 1.8 | 4.2 |
| 0.57 | 3.0 | 6.9 |
| 0.76 | 4.0 | 12 |

* The epoxy composition is cured at temperature 60°C within two hours

the content of the PANi over 0.38% by wt of the composition, the system becomes heterogeneous. It is caused by an excess of the limit of compatibility of components in the ternary system, PANi is released from the system and part of ACA is adsorbed on the surface of the particles of PANi.

**Figure 8** shows the results of microcalorimetric tests for epoxy compositions containing the pernigraniline form of PANi.

Increasing the content of the pernigraniline form of PANi in the epoxy composition leads to a monotonic decrease in the cure speed. Also, the pernigraniline form serves as an inhibitor of the curing process.

It is noteworthy that the conversion of the epoxy groups slightly increases in the presence of small amounts of the pernigraniline form of PANi (up to 0.19% by wt). Further increase of PANi reduces the amount of conversion of epoxy groups and reduces the rate of reaction (**Figure 8**). This is due to the fact that the compatibility of the violation in the ternary system occurs at a lower content pernigraniline form of PANi.

The results of the gel-sol analysis and microcalorimetric tests are consistent with the data of IR spectroscopy by the number of residual epoxy groups in the cured materials (**Table 1**).

The reduction of residual epoxy groups in polymer materials containing the emeraldine form of PANi to 0.38% by wt, confirms the assumption of the catalytic action of PANi in the curing reaction. The rise of residual epoxy groups is observed when the content of the emeraldine form of PANi is more than 0.38% by wt.

When the content of the pernigraniline form of PANi 0.19% by wt is observed, an acceleration of the curing process is seen, which was established by the gel-sol analysis. With an increase in content of the pernigraniline form of PANi in the material, the number of residual epoxy groups increases, thus indicating curing slowing.

## CONCLUSION

It is shown that the emeraldine form of PANi can be transformed into pernigraniline for a time in the modified MPMDA, as evidenced by the shift of the maximum in the absorption spectrum. The introduction of a reducing agent results in conversion back from a pernigraniline form of PANi to emeraldine. It is estimated that modified MPMDA containing the emeraldine form of PANi to 0.57% by wt do not lead to a slowing of curing and, consequently, the change of the complex performance properties of epoxy coatings. It was found that the use of the modified MPMDA by the pernigraniline form of PANi leads to inhibition of the curing process of epoxy compositions.

**PPCJ**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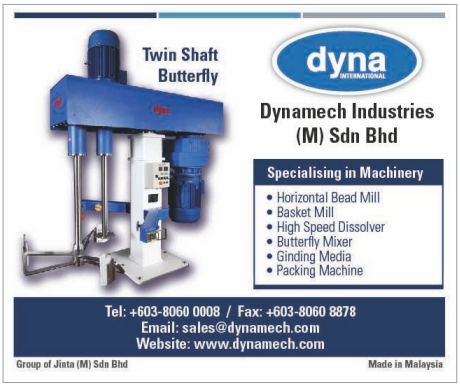


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