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2018

WOOD COATINGS

The best technical papers on wood coatings published in the European Coatings Journal within the past three years.

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Studying effects of different additives on bubble formation and dissipation.

88 CORE-SHELL EMULSIONS
Acrylic dispersions with oil-modified shell show versatile performance.

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FUNCTIONALITY AND AESTHETICS

These are the keywords associated with modern wood coatings. They must look pretty, have minimal impact on the natural appearance and be resistant to external influences. As a formulator, you are continually called on to be au fait with the latest advances in research and development. Such knowledge is rarely to be found in a single package. European Coatings Journal is about to change that. This thematic dossier is bursting with information on wood coatings that we have compiled for you. In it you will find all the relevant technical papers on wood coatings that have been published in European Coatings Journal over the last three years. Now there's a welcome development!

Sonja Schulte

ABOUT BYK

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BYK is one of the world's leading suppliers in the field of additives and measuring instruments. BYK formulates premium additives distinctively for wood coating systems, offering high quality performance characteristics like: easy to clean, scratch-resistance, UV resistance, excellent surface leveling; and, provide exceptional pigment stabilization within pigmented systems.

The requirements are particularly high for kitchen furnishings and flooring. It is important that the surfaces not only look outstanding but also feel great. They must be easy to clean and fulfill certain mechanical resistance properties. Different systems are used in different places of the world but the trend goes more and more from solvent-borne coatings to aqueous and UV systems.

BYK Additives do not only offer solutions for different problems but also a high level of quality improvement. Particularly BYK Additives with nanoparticles feature special property combinations such as transparency, scratch-resistance, UV-resistance and a long life cycle that the conventional materials simply cannot provide.

Testing and measuring instruments from BYK can effectively evaluate the quality of color, gloss and appearance as well as the physical properties of paint, plastic and paper products and are an important part of quality control.

As a globally operating specialty chemicals company, BYK has production sites in Wesel, Kempen, Moosburg, Schkopau and Geretsried (Germany), Deventer, Denekamp and Nijverdal (Netherlands), Widnes (UK), Wallingford, Chester, Gonzales, Louisville, Earth City and Rochester Hills (USA) as well as in Tongling (China).

Today the company employs around 2,200 people worldwide and forms part of the ALTANA Group.

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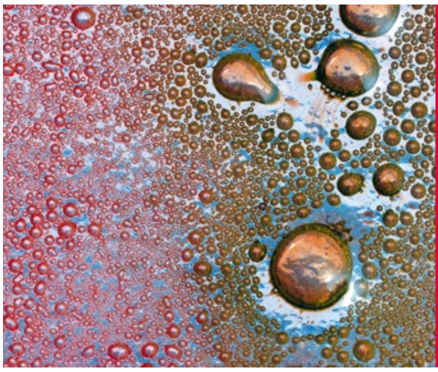

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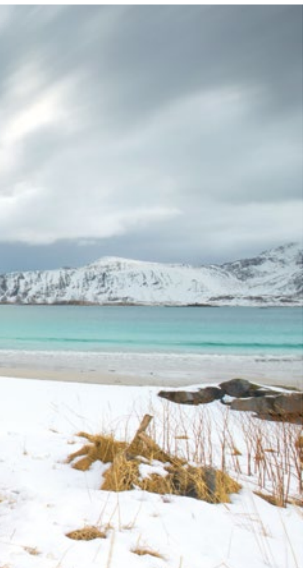

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REDEFINING LIMITS FOR THE WOOD COATING INDUSTRY

The Asia-Pacific region is the fastest-growing segment of the global wood coating market, in terms of volume. This growth is mainly attributed by heavy investment across building & construction industries and the durability and protection benefits offered by wood coating. The Asia-Pacific and RoW markets are estimated to grow at a high CAGR in the next five years. By Annirban Bhattacharya (published in ECJ 06/2016).

Wood is a substrate which has easy accessibility, has low weight-to-strength ratio, and high aesthetic quality, due to which it has been used as a building material. Wood is a paintable substrate and has many pros, but conditions such as moisture content, expansions, contraction of wood, and many other factors should be taken into consideration while developing wood coatings.

To resolve these conditions and also depending on the end application, the resin type and the curing chemistry can be varied accordingly. Major applications for the wood coatings include siding, decking, furniture finishes, flooring, and windows and door paneling. The top 3 applications i.e. siding, decking, and furniture consume for more than one-half of the global wood coatings produced.

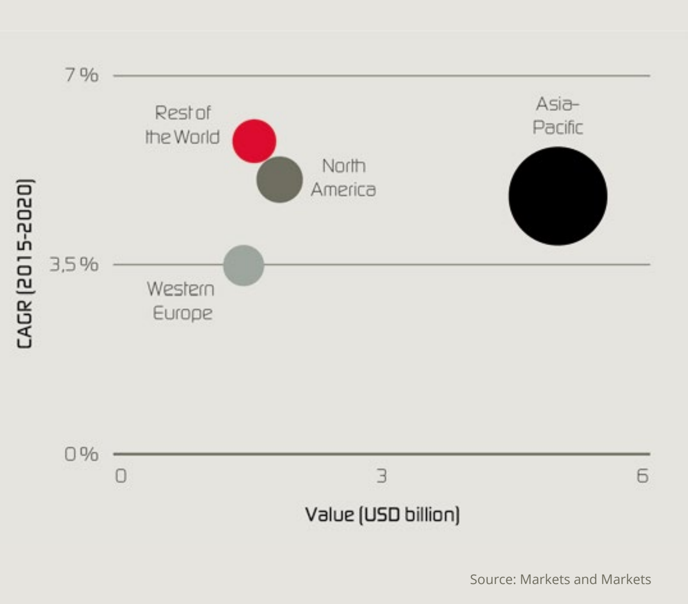
DEMAND FOR WOOD COATINGS IS MAJORLY FROM ASIA-PACIFIC

The increasing demand for housing and residential projects, because of the growing population, per-capita income, and improved life style made Asia-Pacific the major market for wood coatings. It is the largest market, both in terms of volume and value. The growing housing projects along with home remodeling and reconstruction are expected to drive the wood coatings market in the developing countries of Asia-Pacific. Rising cash-intensive non-residential construction and various government proposals to improve public infrastructure are fueling the waterborne wood coatings market. The consumption of wood coating is growing at a higher rate in Asia-Pacific region as compared to Europe.

The global market for wood coatings technology is projected to grow from USD 7.70 billion in 2015 to USD 9.72 billion by 2020, at a CAGR of 4.8%. In terms of volume, the radiation cure (UV/EB) wood coatings market is estimated to grow from 0.53 million metric tons in 2015 to 0.88 million metric tons by 2020, with the highest CAGR of 10.8%.

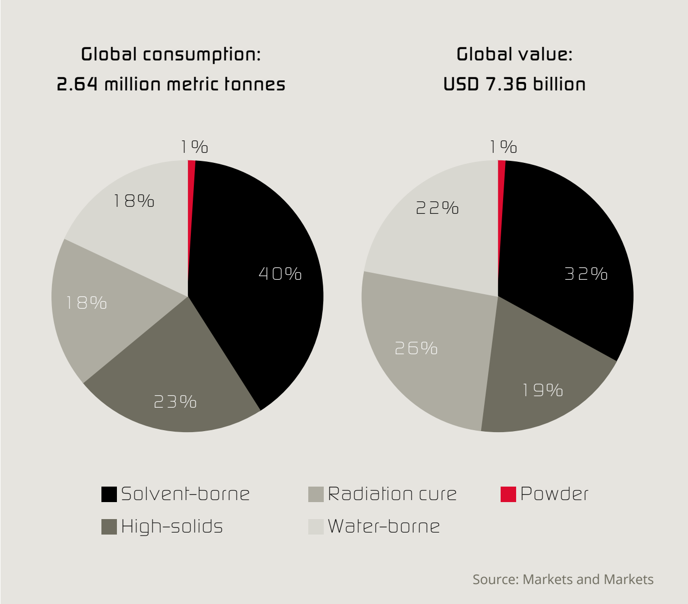
The current market size of the wood coating in terms of volume is es-

Fig. 1: Asia-Pacific is witness to grow at a high rate in the next five years.



Source: Markets and Markets

Fig. 2: Wood coatings market by technology in 2014.



Source: Markets and Markets

timated to be around 2.78 million metric tons in 2015 and is projected to grow at a CAGR of 5.30% between 2015 and 2020.

LIFECYCLE OF DIFFERENT WOOD COATINGS TECHNOLOGIES

Two forms of wood coating are available that are conventional and green. The conventional organic wood coatings technology uses dilute solutions of amino, polyurethane, acrylic, polyester, nitrocellulose, and other resins in a volatile organic solvent. In conventional coating formulations, the organic solvent performs the function of promoting desired flow characteristics, thereby facilitating the coating application. Primarily due to the EPA regulations, many new cleaner technologies in the wood coating industry have reformulated their coatings so as to reduce the VOC content and these are termed as green technologies. These technologies are waterborne, radiation cure, and powder.

For the past few years, there has been a shift in the demand for solvent borne toward waterborne wood coatings. Recent developments in the EU legislation regarding environmental and health issues have increased the demand in various applications of waterborne coatings in the wood segment. The increasing demand for green products has also created the need for supplies of green raw materials for coatings, most notably waterborne wood coatings.

It can be estimated that the growth of the wood coatings market is directly in proportion to the housing market. In the U.S., application of wood in building houses ranges from exterior siding, decks, and fences to the interior cabinetry, furniture, and flooring. Recently, due to the improved housing market in the U.S., there has been an overall impact on the wood coatings market.

RISE IN DEMAND FOR GREENER AND ADVANCED TECHNOLOGIES

The demand for environmentally friendly products has a major impact on the product value and innovation in the wood coatings market. Today, end users of wood coatings prefer water or UV/EB technology-based products that are green, easy to clean, and have durability as conventional high performance alkyd wood coatings available earlier in the market. This has led to an increase in demand for advanced technologies and innovations not only to meet consumer demand but also to exceed expectations.

In the wood coating industry, solvent borne and high-solids technologies account for more than one-half of the global market. Green technologies such as waterborne, radiation cure, and powder will be replacing these two conventional technologies rapidly by the next decade.

In the past few years, many of the wood coatings manufacturers developed several new products to meet various consumer demands. Some companies are also focusing on waterproofing properties in their wood coating products that provide multiple features, making it easier to choose and use the right deck stain. Some major companies are focusing on the elastomeric properties in coating technologies, which help the color expand and contract with the wood during temperature fluctuations over time, thus reducing cracking and peeling on the substrate. Wood coatings manufacturers are also focusing on research and development for advanced acrylic polymers, which can significantly improve the resistance to friction and damage with waterproofing properties exceeding the previous industry standards.

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Source: Nina Malyna/Fotolia.com

GROWTH IN STAGES

An overview of the global wood coatings market. By Damir Gagro (published in ECJ 07/08 2017).

Wood continues to be a popular material. Upbeat forecasts for housing and residential construction activity and increasing levels of urbanisation are boosting demand for wood coatings in particular. In this context, rising demand from the furniture industry is good news for wood coatings, because the furniture industry accounts for about 60% of their sales.

Compared with the global coatings market, which last year had a value of EUR 125 billion and a volume of over 40 billion litres, wood coatings are small fry. Market research company Orr & Boss estimates that they represent about 6 to 7% by both value and volume. That would make their contribution worth EUR 8.6 billion and imply a volume of around 2.6 billion litres.

WOOD COATINGS MARKET SET TO GROW TO USD 12 - 13 BILLION BY 2020

Prognostications about how the market will develop vary from study to study. But in view of the increasing levels of urbanisation in many parts of the world and the recovery in housing and residential construction activity, the prospects for the future look good. Markets and Markets (MaM), another market research company, estimated the size of the market in 2016 at almost EUR 9.95 billion. The company based this figure on demand for wood coating resins which it assessed as being worth EUR 2.98 billion. Given that resins account for about 30% of the value of wood coatings, this translates to a value of almost EUR 10 billion. MaM expects the market for these resins to grow by a CAGR of 5.4% through to 2021 by which estimate the resins market would then be worth EUR 3.83 billion. Applying the same figure of 30%, the wood coatings market would then be worth about EUR 12.6 billion.

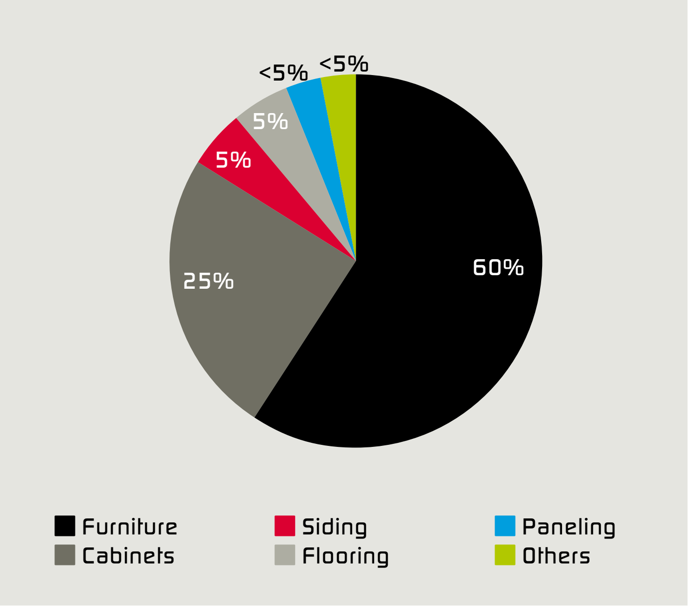
Different figures are being propagated in other studies. Yet these are clearly too high. One example is the estimate by Mordor Intelligence, a market research company. Its latest study of the global wood coatings market forecasts that the market will be worth EUR 18 billion by the year 2020. To be sure, demand for wood coatings will certainly rise, but these figures are far too optimistic. Historical data also need to be factored into the calculations.

Judging from past figures, a value of almost USD 20 billion is very unlikely to be reached. Historical data for 2008 provided by Orr & Boss valued the market a EUR 5 billion and estimated the volume at just over 1.6 billion litres. The published projection for 2013 was EUR 7.3 billion and a volume of 2.3 billion litres. The company's forecasts, which take 2013 as the base year, predicted a value for 2018 of around EUR 10 billion and a volume of 2.98 billion litres. Even though it might be argued that this is a cautious estimate, a more realistic gauge of the market value for 2020 and 2021 would be EUR 12 to 13 billion. Experience shows that a doubling of the market value within a period of five years is not feasible.

ASIA-PACIFIC REGION IS AND WILL REMAIN THE LARGEST MARKET BY VALUE AND VOLUME

Regionally, the market for wood coatings mirrors the entire coatings sector. By far the largest and therefore the most important market for wood coatings is Asia-Pacific. Market research companies are relatively unanimous in this respect, attributing 60% of the global wood coatings market to this region. Taking Orr & Boss' figures as a basis, the EUR 5.25 billion account for 61% of the total value of wood coatings, with the almost 1.7 billion litres corresponding to 65% of the total volume. Cautious estimates suggest that annual growth in this

Figure 01: Wood finishes by end use (on the basis of volume).



Source: Orr & Boss

Table 01: The global wood coatings market size by region in 2016.

	Volume (millions of litres)	Value (millions of EUR)
Asia Pacific	1,684	5,226
Europe	555	1,940
NAFTA	196	767
Africa	73	234
Latin America	62	225
Middle East	48	156
Total	2,618	8,548

Source: Orr & Boss

region will be about 13% by volume and just under 15% by value in the years ahead.

This high share and the positive prognoses are all down to the strong furniture industry in China. First, the furniture industry is the main buyer of wood coatings, with furniture production consuming some 60% of these systems. This figure has been a constant for several years and will in all likelihood remain at around 60% in the future. Second, China is the largest furniture maker in the world. According to the Chinese National Bureau of Statistics, China's 5,300 furniture makers produce 770 million items valued at EUR 79.4 billion. Data provided by the UNSD Comtrade Database show that furniture exports from China were worth EUR 52.5 billion. That puts China squarely on top. In second place but lagging far behind comes Germany, with exports worth EUR 10.5 billion.

EUROPE AND AMERICA FOLLOW IN SECOND AND THIRD PLACES

The second largest market for wood coatings after Asia-Pacific is Europe. Orr & Boss puts Europe's share of the overall wood coatings market at just over 20%. The 555 million litres equate to a share of 21% while the EUR 1.94 billion in value is equivalent to 23% (*Table 1*). Orr & Boss's data for the NAFTA region shows that the market is currently worth EUR 767 million (9%) and has a volume of 200 million litres (8%). These figures are clearly at odds with the data from the market researchers at The Freedonia Group, a US company with a particular focus on the paint and coatings market in the region. Freedonia estimates demand in 2015 at 875 million litres (231 million US gallons), worth EUR 3.16 billion. Even though the construction industry has recovered faster and more strongly in the US than was expected a few years ago, these figures are likely to be too high. However, one explanation for the discrepancy could be the different data basis. The Freedonia Group's data includes all coating systems for the protection of substrates made of wood – not just coatings.

SOLVENT-BORNE SYSTEMS WILL CONTINUE TO DOMINATE THE MARKET

The majority of all wood coatings continue to be solvent-borne. The market researchers are relatively unanimous here, estimating the solvent-borne fraction at 60 to 70% of the total volume. Conventional solvent-borne systems lead the rankings with over 40%. High-solids solvent-borne paints account for a good 25%. Water-borne systems and radiation-curable coatings together make up almost 30%. There will be little change in this breakdown in the coming years. There will be marginal changes in favour of water-borne and UV systems as a result of a shift towards more eco-friendly products. This is a process which is mostly evident in Europe and North America, as these regions have a higher proportion of eco-friendly paint systems than Asia-Pacific. However, given that the latter is the largest in terms of wood coatings, the share of solvent-borne systems has the greater impact on the overall market.

There are several factors that have an impact on sales of wood coatings. Among the most important are the general economic situation and residential construction activity. The second of these, residential construction, plays a significant role. First-time buyers or occupiers of new houses or apartments, be they owner-occupiers or tenants, tend to purchase new furniture. In the coming years, construction activity in apartments and houses is expected to enjoy annual average growth of between 1 and 7%. China and the US head up this forecast, with the remaining spaces in the top 5 being filled by Western Europe, India and Indonesia. But it is not just construction activity in itself which is boosting demand for wood coatings. The type of house or apartment is also crucial. More expensive residential units usually also have a higher proportion of coated wooden surfaces. The less expensive segment tends to rely more on chipboard. Likewise, higher-quality and high-priced furniture leads to higher paint consumption. Ready-made furniture, on the other hand, tends to be finished with fewer wood coatings.

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CEN STANDARDISATION FOR EXTERIOR WOOD COATINGS

CEN/TC 139/WG2 – coatings for exterior wood – prepares European standards, mainly on various test methods for coatings on exterior wood. This may seem straightforward, but there are quite contradictory interests. Standards are written by industrial participants, not by end users. In addition, national certification schemes may profit from international standardization, but national tests also compete with international methods. By Peter Svane, Coating Consultancy Copenhagen, and Bernd Reinmüller, DIN (published in ECJ 03/2016).

The CEN/TC 139/WG2 standardization was inaugurated in 1989 and so far five European standards on coating systems for exterior wood have been completed.

These finished five standards include:

- EN 927-1, Classification and selection
- EN 927-2, Performance specification
- EN 927-3, Natural weathering test
- EN 927-5, Assessment of liquid water permeability
- EN 927-6, Artificial weathering test

The working group however has much more on its agenda (see Table 1). Since 2009, WG2 has made a long list of test methods – that eventually may combine into one or more performance profiles e.g. for cladding and for timber windows. One important tool in this process is the so called "CEN Technical Specification" (CEN/TS). The name is misleading, because it simply is a description written like a real EN standard but under less strict conditions. A technical specification (TS) should be transformed into an EN after some years. So the actual CEN Technical Specifications on wood coatings may become parts of the EN 927 standards series at their next revision.

CEN TEST METHODS AND NATIONAL GUIDELINES

The idea of having common European test methods is to ease testing, reduce costs, and remove barriers to trade. Ideally, this is to the benefit of manufacturers as well as end users. CEN standards are, however, written by industry (as well as institutes) – not by consumers. Many countries have national test schemes for timber windows, including specifications for coating systems. One example is the guiding document No. 14 by the German paint industry association (VdL) entitled "Requirements on coating systems for factory-made applications on wood window frames, wood-metal window frames and wood doors" (see box above). The document takes EN 927-documents as a starting point, but deviates considerably from the standards and adds substantial testing.

THE DUTCH GUIDELINE FOR WINDOWS AND JOINERY

The Dutch guideline for windows and joinery is even farther away from the EN-standards. The Dutch have their own unique procedures. One of them a special cross-cut tape test. It uses two parallel cross-cuts instead of one (see Figure 1). CEN/TC 139/WG2 found this idea so attractive that they adopted it on European level and described it as a CEN/TS.

Summing up, there may be competition between the work of CEN/TC 139/WG2 and national control schemes – but also a synergy. The players are consumers, paint manufacturers, test institutes, certification and standardization bodies; some of these – particularly the "consumers" are clearly underrepresented in the ongoing standardization process. Standardization work is time consuming, and the coating making up just 80 µm to 100 µm on top of a solid wooden construction several centimetres thick may not be given the highest priority.

EXAMPLE: GUIDING DOCUMENT NO. 14 BY THE GERMAN PAINT INDUSTRY ASSOCIATION (VDL)

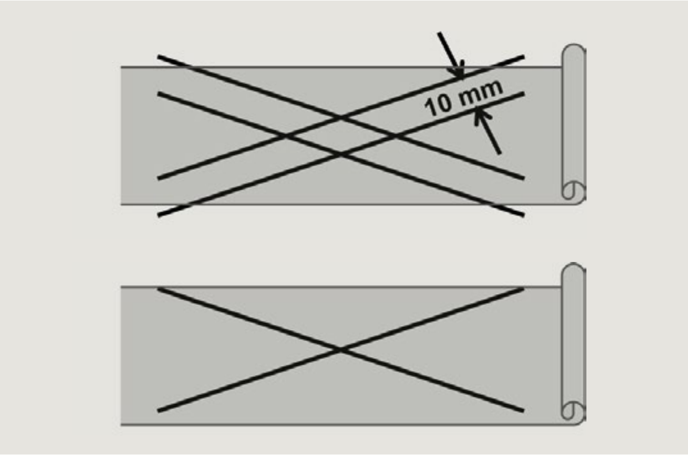
“Requirements on coating systems for factory-made applications on wood window frames, wood-metal window frames and wood doors”

This guideline is about the state of the art of wood window coatings, their suitability of use and the conduct of test methods as well as the evaluation of their results for factory-made wood window applications. The goal is to set up uniform test methods that give reproducible and repeatable results. The test and evaluation of wood coatings according to EN 927-3 only indicates the basic suitability of a wood coating system but is insufficient to give an overall view. Therefore, additional test methods and test criteria are requested.

CEN /TC 139/WG2 - THE NEXT 20 YEARS

WG 2’s main task is to write standards. But WG 2 has been the starting point of much more than that: several EU-funded research projects, many round robin trials, and a series of smaller or larger development projects within the group. WG 2 can now offer a portfolio of ten test methods for exterior wood coatings to the market, three of them EN-standards, seven CEN/TS; finally, EN 927-1 – Guide to classification and selection of and EN 927-2 Performance specifications.
Individual countries may still prefer other or additional tests, but as time goes by more and more CEN/TS-methods will turn into EN-standards, and it is compulsory for the CEN-member states to implement them as national standards. After some decades there will probably still be national schemes, but their contents will be based on the EN 927-series – provided that WG 2 does a proper job and that new enthusiastic members will join this qualified forum.

Figure 01: Traditional cross-cut test (top) and the Dutch “double cross” below.



Tab 01: Work plan & achievements of CEN/TC 139/WG2, 2010 - 2016.

No	Property / Topic	2010 WI*	2010 TS**	2010 EN***	2016 WI*	2016 TS**	2016 EN***
1	Classification and selection			X			X
2	Performance specification			X			X
3	Natural weathering test			X			X
4	Water vapour permeability test				X		
5	Liquid water permeability test			X			X
6	Artificial weathering test			X			X
7	Microfoam test	X				X	
8	Knot staining test	X				X	
9	Film extensibility test	X				X	
10	Tannin staining test	X				X	
11	Blocking test	X				X	
12	Impact resistance test	X				X	
13	End grain sealing test					X	
14	Wet adhesion, dolly test	X			X		
15	Wet adhesion, X-cut test	X			X		
16	UV-transmission test	X			X		
17	Mould and algae assessment				X		
18	Tensile properties of a coating film ****						
19	Testing on different wood species ****						
20	Specification for window coatings ****						
21	Dry film thickness determination ****						
22	Leaching ****						
23	Emissions ****						
24	Paint film thickness measurement ****						
25	Heat build-up ****						
	Sum total	9	0	5	5	7	5

*) WI – Working Item **) TS – CEN Technical specification ***) EN – European standard ****) Ideas for future projects

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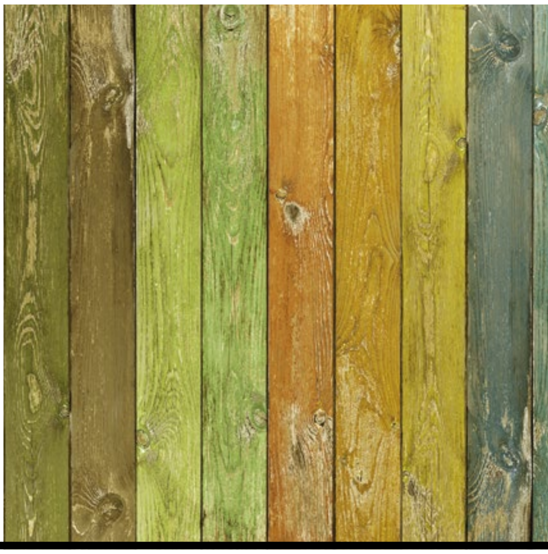
Two questions, two answers:

1 In your opinion, what are the key parameters to enhance the durability of exterior wood coatings?

2 Aside from durability, which new developments will influence the wood coatings industry in the next 5 to 10 years?

(published in ECJ 07-08/2017)



Source: Andrey Kuzmin - Fotolia

1 With more than 25 years of experience gained in both outdoor-exposure and accelerated-weathering tests, we recognised at an early stage that using a wood which was stable to solar radiation could significantly extend the lifecycle of a transparent coating. For this reason we often act as consultants, advising on the proper wood to select for a given application – as not all timber is able to meet customer expectations. It's my belief, however, that, if we ignore the different species of wood and just consider coating performance, we will find that the glass transition temperature of the coating film is a crucial factor in exterior durability. You see, if the paint film manages to retain its glass transition temperature as it ages, it will perform better outdoors, e.g. in terms of gloss retention and cracking. For this reason, the right choice of resin is crucial, and so too is working closely with reliable, forward-thinking resin suppliers. All that a formulator like myself can do to further improve the outdoor resistance of coatings is to find the best-possible combination of fillers, pigments, HALS and UV filters that will shield the resin from UV radiation and limit the change in glass transition temperature over time.

2 People all over the world are now paying more and more attention to the issues of air pollution and global warming. The decision by the US government to hobble the Environmental Protection Agency and to exit the so-called Paris Agreement COP21 has spawned a huge debate in all the other signatory countries, which miraculously have managed to stay committed to the agreement. Simply relying on greater efficiency to reduce carbon emissions is not the way to pursue such ambitious goals. Instead, we need to re-invent industrial processes in a truly sustainable way. That is why we recently developed – in conjunction with DSM Coating Resins – the first bio-based high-performance acrylic coatings for industrial wood finishing. This technology allows up to 40% of the resin solids content to come from biomass, without competing with the human food chain. We realise that this is just a first step, but we believe that industrial coatings will become more and more sustainable in the years ahead and less dependent on oil-based materials. Unfortunately, manufacture and application of coatings will make only a small contribution here, because it is electricity, transportation and heat generation which have the biggest impact on carbon emissions. Nevertheless, it is significant that the coatings industry, which is often wrongly accused of being a highly polluting business, has set itself such green standards and to transition from solvent-borne to water-borne and then to renewable coatings. I believe that our customers will appreciate this development of new sustainable paints for outdoor wood protection and that resin producers will see it become one of the dominant trends in the market.

> "Up to 40% of the resin solid content coming from biomass is not competing with the human food chain."

Claudio Grandoni
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Book tip

Coatings Formulation
Bodo Müller and Ulrich Poth, March 2017, 312 pages
ISBN: 9783866301269
www.european-coatings.com/books


Source: papinou - Fotolia

1 As in many application areas, we still see room for using more polyurethane dispersions in order to achieve longer lasting finishes. The durability of an exterior finish will benefit from the low Tg of a polyurethane which also offers high water vapour permeability, low water absorption and low to no dirt pick-up. This does not mean that one would need a product based on PUD only – even smaller quantities of PUD will help to improve current acrylic-based coatings.

We are working on polyurethane dispersion-based coating systems which can offer superior colour stability in pigmented systems with a minimum of dirt pick-up over time. Such coating systems could be more sustainable as the paint could have a much longer time in service compared to today's systems. On top of that, polyurethane-based coatings can be much easier to renovate after time, as they tend to chalk and not to crack like acrylics.

Recent work has also proven that inherent matt polyurethane dispersions can be used in exterior coatings to obtain highly transparent clear finishes with low gloss surface that are offering a more hydrophilic structure that leads to a more "clean" surface in time. The matt surface remains while the coating is aged and looks more homogenous compared to classical matting agent based products. Needless to say that the "standard" glossy PUDs also offer a very long gloss retention over time.

Durability is not just linked to having the best and most fancy topcoat, it is a result of all layers of the coating and the substrate working jointly together to obtain the best results. Since some years we are propagating the use of polymers which will help to stabilize the lignin of the wood in order to form a more UV/weather resistant derivative of wood & polymer – that way helps boosting the properties in clear finishes as the wood is the "weak link" in our whole process. Further work is done to help making even more efficient systems using the same technology. In pigmented coatings, we also notice that pigmented primers are very often "underrated" in their design and function – a poor primer may destroy all weathering properties while a "smart" primer can react with the topcoat to form a crosslinked layer system with ideal intercoat adhesion.

In simple words we can state that a "matched chemistry" approach in the different coating layers can sometimes boost properties more than just one layer which has been optimized in its properties.

> "Durability is not just linked to having the best and most fancy topcoat, it's a result of all layers of the coating."

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2 Certainly, new development will be based around lower emission systems and renewable resource materials – that is already seen in certain areas of the market. We would appreciate if the discussion would focus on "sustainable coatings", that would favor polyurethanes in general as they are very long lasting materials.

Book tip

Understanding Coatings Raw Materials
Vijay Mannari and Chitankumar J. Patel, April 2015, 287 pages
ISBN: 9783866308831
www.european-coatings.com/books

NOT JUST FOR WOOD


Source: didecs - Fotolia

Radiation-curable coating systems are considered to be a niche application, but have become firmly established in several application areas, such as the furniture industry. As our overview of current binders shows, radiation-curable systems are characterised by great diversity and can be used in many industries (published in ECJ 05/2017).

Radiation-curable coatings enjoy a good reputation. They need little or no solvent, which benefits their environmental record, and they harden extremely quickly, thereby enabling high throughput rates. For all of this to occur smoothly, the components of the radiation-curable coatings must do their job well. We have already seen that photoinitiators are important (see ECJ 9/2016, p.16-17) – but binders are just as crucial.

Here, users can choose from a wide range of materials to create the right properties. For example, epoxy acrylates are attractive on ac-

Company	Product	Chemistry	Viscosity (mPa·s)	Non-volatile compounds	Density (g/cm³)	Acid number (mg KOH/g)	Colour
Alberdingk Boley	Alberdingk Lux 572	Polyurethan acrylate	10 - 200	-	-	-	-
	Alberdingk Lux 2411 VP	Acrylate copolymer	1,500	-	-	-	-
Allnex	Ebecryl 1290K	Hexafunctionale urethanacrylate	2,000 (Höppler, 60 °C)	100%	1.15	-	< 1 (Gardner)
	Ebecryl 525	Polyesteracrylate	40,000	60%	1.21	25	< 200 Apha
BASF	Laromer LR 8800	Polyesteracrylate	4,000 - 8,000	-	1.12	< 5	< 10 (Iodin)
	Laromer LR 9005	Aromatic urethanacylate dispersion	20 - 250 (23 °C, 250 s^{-1})	38 - 42%	1.1	-	-
Covestro	Bayhydrol UV 2282	Polyurethane dispersion		38 - 40%	1.06 (20 °C)	-	-
	Roskydal 850 W	Unsaturated polyester	9,000 - 15,000	100%	1.11 (20°C)	12 - 22	-
IGM Resins	Photomer 3015	Funcionale epoxy acrylate	30,000 - 100,000 (25 °C)	-	-	< 3	< 2 (Gardener)
	Photomer 3016-40T	Functionale acrylate ester	6,000 - 9,000 (25 °C)	60%	1,14	< 4	< 2 (Gardener)
Synthopol	Syntholux 1014 W	Polyurethane dispersion	10 - 300	40%	1.04	-	-
	Syntholux 1160 PA	Polyether acrylate	300 - 800	-	1.07	< 10	< 1 (Gardner)

count of their low price and high reactivity. They generally have a high viscosity thanks to a high molecular weight and the formation of a large number of hydrogen bonds in solution. They cure to form very hard layers that offer good protection against corrosion. However, epoxy acrylate films have a tendency to turn yellow.

Urethane acrylates have thoroughly good properties too, but these come at a price. They are reputed to offer the best compromise of hardness, resilience, chemical resistance and abrasion resistance on one hand and flexibility and elasticity on the other. Like the epoxy acrylates, they have a high viscosity, which again is due to hydrogen bond formation. By comparison, e.g., polyester acrylates are relatively low-viscosity products and can sometimes be employed without the need to add monomers. Moreover, one of their salient features is that they can be easily adapted to all kinds of application areas. As the table shows, a number of other binders also find application, with the choice here being dependent on price and application area. You will also find dispersions in the overview. These are suitable, e.g., for applying radiation-curable coatings by spray gun.

Area of application	**Properties**
Parquet, varnish, furniture and primer	No VOC content Gute Anfeuerung Good overpaintability
Wood, plastics, furniture and kitchen coatings	Gute Anfeuerung High gloss
Wood coatings and fillers, scratch resistant plastic coatings	Very fast curing Good surface hardness Good scratch and abrasion resistance
Screen print, industral coatings, primers for metal coatings	Good adhesion on metal, paper and plastics Good interlayer adhesion
Wood, paper	Compatible with most acrylic binders Good chemical resistance
Wood, paper, cardboard, plastics	Good resistance against houshold chemicals Good scratch resistance Generates tack-free films
water-based UV coatings for wood substrates	Good chemical resistance Gute Anfeuerung
Clear and cloloured coatings for wood and furniture	Freoo of any monomer content Good resistance agains houhold chemicals High luminosity
Lithography, screen printing, metal decoration, clear coats, paper, cardboard, wood and plastic	Fast curing High gloss Good resistance against solvents
Lithography, screen printing, metal decoration, clear coats, paper, cardboard, wood and plastic	Low odor Very high scratch resistance Good resistance against solvents
Wood and plastics coatings	Good elasticity Good chemical resistance Free of emulsifiers and co-solvents
Low viscoity coatings	Free of monomers and organic solvents

> “The European furniture industry generates an estimated annual turnover of EUR 96 billion.“

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STEP-GROWTH THIOL–THIOL PHOTOPOLYMERIZATION AS RADIATION CURING TECHNOLOGY

The paper introduces a novel UV-curing technology based on thiol–thiol coupling for polydisulfide network formation. By varying thiol functionality and structure, oligomer chain length and monomer/oligomer ratio, the network architecture can be finely tuned. The molecular mobility of the polydisulfide network is crucial to high thiol conversion rates and yields. Ultimately, spatial control enables the formation of a photopatterned poly(disulfide) film, used as next-generation high refractive index photoresist.

Noémi Feillée et al., Journal of Polymer Science Part A: Polymer Chemistry, Vol. 55, Issue 1, 2017, pages 117 - 128

ANTI-AGEING FOR WOOD


Source: fotoknips - Fotolia

Wood is a beautiful material. However, it is also a natural product, and this means it has the occasional drawback. Prolonged exposure to UV radiation, for example, can cause undesirable changes in its colour. In addition to UV absorbers in paint, HALS can also help to prevent this. We provide an overview (published 07-08/2017).

Trendy materials come and go. Wood, which can be used to build a table or even an entire house, has outlasted them all. Humans seem to have a genetic affinity for this beautiful natural product. But natural products change over time, and wood is no exception. One significant and often undesirable characteristic is the change in colour often caused by UV radiation. The lignin in the wood has maximum absorption at approximately 280 nm, and that is right in the middle of the UV-A range. The UV radiation causes chemical changes, and these, in turn, cause the changes in colour. This mainly affects wooden materials used outdoors. But the slightly longer-wave UV-B radiation, which is not filtered out by windows, can also cause slight colour changes indoors. In addition to changes in colour, it can also cause cracks to appear.

Company	Product	Chemistry	Active content	Density in g/cm³	Colour	Viscosity in mPa·s
BASF	Tinuvin 123-DW (N)	Aminoether substituted Tetramethylpiperidin-derivate	ca. 30 % (KB-205206)	1.01 - 1.05 20 °C, DIN 51757)	-	9 (20 °C, 150 s^{-1}, DIN 53018)
	Tinuvin 249	Piperidin -derivate	-	0.9469 (20 °C)	Slightly yellowish liquid	626 (20 °C, OECD 114)
Clariant	Hostavin 3070 Disp	Polymeric HALS	52%	1.07	-	-
	Hostavin TB-03 liq	1:1 solution of Triazen + non-substituted HALS	85%	1.01	-	-
Everlight	Eversorb 95	Sebacinacid, bis(2,2,6,6-tetramethyl-1-(octyloxy)-4-piperidinyl)ester, reaction product wih 1,1-dimethylethyl-hydroperoxide and octane	-	0.97 (20 °C)	Slightly yellowish liquid	2,700 - 3,300 (20° C)
	Eversorb AQ5	Steric hindered amin NOR-Type	-	-	Orange liquid	1,800 - 2,400 (25 °C)
Songwon	Songsorb CS 292	Bis (1,2,2,2,6,6-pentamethyl-4-piperidinyl)-sebacetate and 1-(methyl)-8-(1,2,2,2,6,6-pentamethyl-4-piperidinyl)-sebacetate	-	-	Slightly yellowish liquid	-
	Songsorb CS AQ01	POE (n) 2,2,6,6-tetramethyl-4-piperidinole	-	-	Clear, slightly yellowish liquid	-

Aside from standard UV absorbers such as iron oxide or nanoscale titanium dioxide, high-quality paints also use HALS (Hindered Amine Light Stabilisers), which are sterically hindered amines. Even though they do not absorb UV light themselves, they do delay the radical degradation of the lignin caused by photooxidation. They function as hydrogen donors that deliver a hydrogen atom to a peroxide radical. This reaction allows them to form stable nitroxyl radicals and thus function as free radical scavengers. Antioxidants use a comparable mechanism.

HALS REMAIN EFFECTIVE FOR A LONG TIME

HALS are often substitutes of 2,2,6,6-tetramethylpiperidine, which can be manufactured, for example, by the conjugate addition of ammonia to phoron. The stabilisers are able to regenerate and therefore remain effective over a very long period of time. Clear paints, however, already contain UV absorbers that filter out at least 95% of the UV radiation. Additional HALS help to neutralise the effect of the residual radiation. In contrast to UV absorbers, their effectiveness is not dependent on the layer thickness of the paint film, and they also have a satisfactory effect even at comparatively low concentrations. Depending on the type of paint and the formulations, amounts between 1 and 5 percent by weight are generally used.

Molecular weight	Properties
-	No interaction with acetous ingridiends High thermal stability Easy to use with a large viariety of water-based systems
-	No interaction with acetous ingridiends Good colour stability Good compatibility with solvents of different polarity
-	No VOC Low migration and release of HALS Compatible with eco-labels
-	For high quality water-based or solvent-based wood coatings
737 g/mol	No influence on the colour of the substrate Good solubility in many solvents High synergy with UV-absorbers Low alkalinity
-	Specifically desined for water-based coatings No obligation for labeling Reduces ckracking
509 + 370 g/mol	Minimises cracking and loss of gloss Recomended for automotive, wodd, industrial and radiation-cured coatings
-	Enviroment friendly due to enhanced bio-degradability Designed for water-based systems Can co-polymerise into PUR-systems to minimise VOC and fogging issues

> "Birch wood contains 19-20% lignin. Coniferous wood sometimes has up to 32%."

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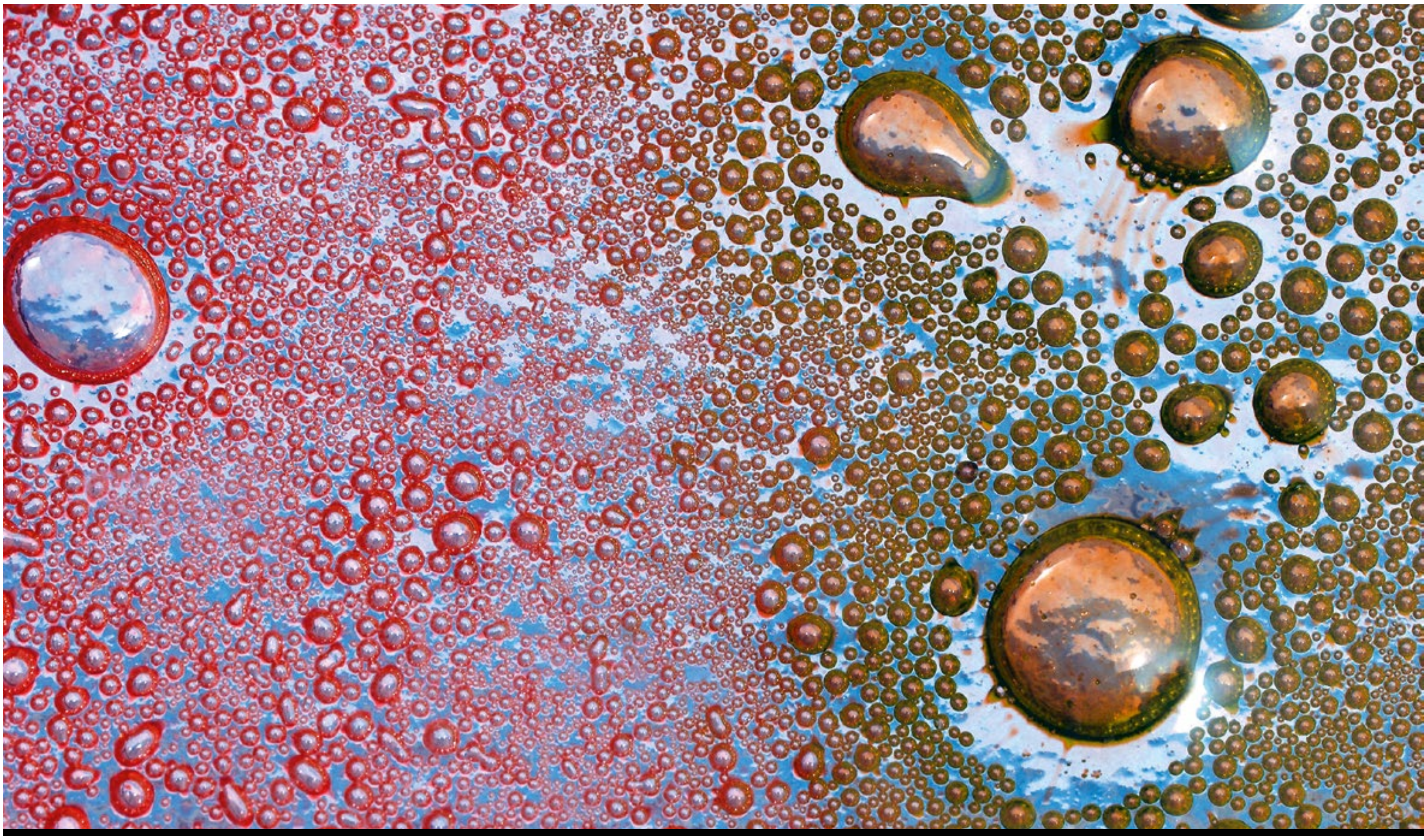
www.european-coatings.com/raw-material-databases

RAPID DETERMINATION OF OLIGOMERIC HINDERED AMINE LIGHT STABILIZERS IN POLYMERIC MATERIALS

A fast and simple liquid chromatographic method for the quantitative determination of oligomeric hindered amine light stabilizers is presented. A key aspect is the completely different retention behavior depending on the pH, enabling a single peak elution by a pH gradient. This allows a quantitation with simple UV detection independent of the oligomeric composition

Georg Kreisberger et al., Journal of separation science, Volume 40, Issue 11, June 2017, Pages 2366–2373

Source: fotoknips - Fotolia



CAUGHT ON CAMERA

Defoamer performance measured by evaluation of coating film appearance. By Mojgan Nejad, Maryam Arefmanesh, Katie Henderson, Javad Esmaeelpanah, Sanjeev Chandra, and Javad Mostaghimi (published in ECJ 10/2015).

To prevent air entrapment and foaming, defoamers are usually added to water-borne coating formulations. Defoamer performance was studied by capturing high resolution images of a coating sprayed on glass substrates. Image analysis provided a quantitative measure of the efficacy of additives. Surprisingly, the most effective product was a non-ionic wetting agent rather than a defoamer.

In addition to decorative purposes, coatings are applied on wood surfaces to improve their performance [1]. Of the various coating formulations, polyurethanes (PU) have the highest abrasion and chemical resistance [2]. Until recently, PU solvent-based coatings were dominant in the wood coating market. However, due to environmental legislations and consumer preference, the market is shifting to water-based formulations [1].

One of the main challenges in this technology shift is how to reduce the surface tension of water-based coatings closer to the surface ten-

Figure 1: The camera set-up (left) and the experimental set-up for bubble measurement study (right)

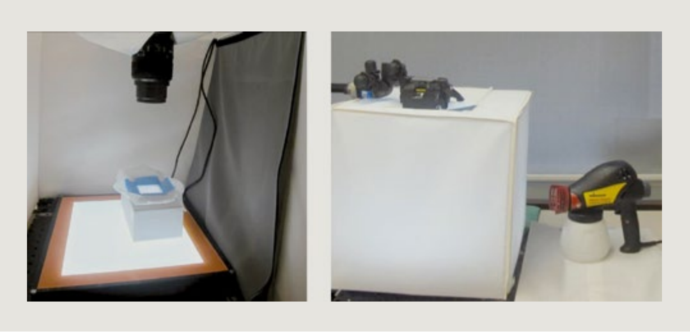
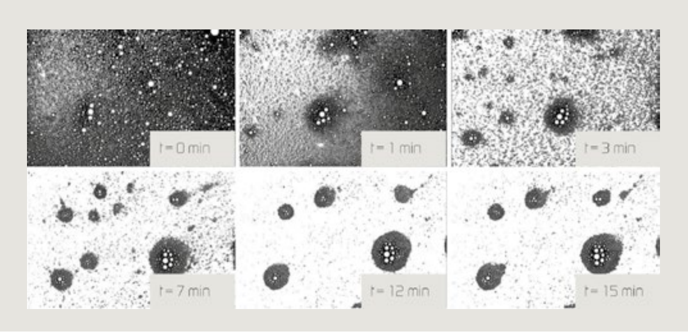


Figure 2: Pure PUD resin images after processing (area under observation is 33 x 21 mm)



RESULTS AT A GLANCE

→ The low evaporation rate and high surface tension of water makes water-based formulations prone to bubble entrapment and blistering defects. Air bubbles can form during manufacturing, packaging and application. To prevent foam problems, defoamers are usually added.

→ The effects of different additives on bubble formation and dissipation were studied by capturing high resolution images of a water-based polyurethane resin coating sprayed on glass substrate.

→ Image analysis shows that certain additives reduce the number of both bubbles formed initially and the number that remain after 15 minutes in the wet film. The quantitative analysis gives accurate comparisons of the efficacy of the defoamers tested.

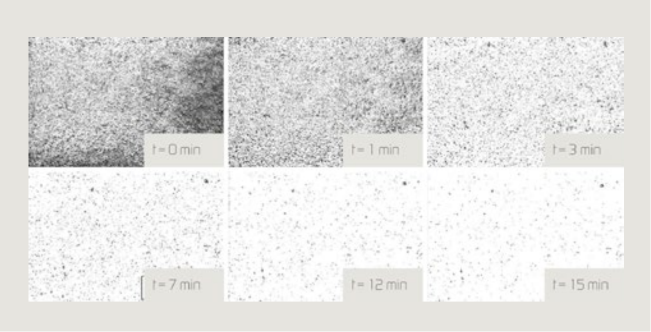
→ The addition of a non-ionic wetting agent resulted in almost no bubble formation, which was surprisingly better than all the defoamers evaluated in the study.

sion of solvent-based coatings, which is around 25 mN/m [3]. In order to have good wetting and adhesion, the surface tension of any formulated coating should be significantly lower than the surface energy of the substrate it is to be applied to [4].

For instance the surface energy of wood is around 44 mN/m [5] while water has a surface tension of 72 mN/m; therefore, different additives are used in water-based coating formulations to reduce the surface tension towards that of the coating itself, which is around 30 mN/m [3]. During drying, if the surface viscosity of the applied film becomes too high the bubbles formed cannot escape from the surface and will become entrapped in the coating film. In addition, the formation of CO_2 due to the reaction of isocyanate with water can also cause bubble formation problems in water-based polyurethane coatings [2, 6].

Defoamer additives are used to prevent air entrapment and foaming. Defoamers are low surface tension liquids that can enter the foam lamella [7], or act as a carrier medium to transport hydrophobic particles into the foam lamella; both will cause the foam lamella to collapse [7].

Figure 3: Byk-346 (0.35 wt%) surfactant + resin images after processing (area under observation is 33 x 21 mm)



Block-copolymer defoamers are commonly used in new water-borne formulations [8]. Although it is relatively simple to predict which type of additives will break down the bubble lamella, detailed predictions are very difficult because there are a variety of components that could potentially end up at the foam interface [6].

To deal with foaming of a new coating formulation, it is critical to look at the combination of surfactants, wetting agents, water-soluble polymers and antifoams [6]. The main objective of the current study was to design an accurate quantitative study that measures the effects of different additives on bubble formation and dissipation in water-borne polyurethane resin formulations.

SURFACE TENSION MEASUREMENT PROCEDURE

A two-component water-based aliphatic polyurethane resin (from Daotan) designed for formulation of clear topcoat wood coating was used as the base resin in this study. A number of commercially available defoamers and general additives usually recommended for wood coating formulations were also obtained from different manufacturers. The surface tension of pure resin was measured and compared to that of resin after being mixed with various additives at different concentrations. These measurements were performed using a “Sigma 70” tensiometer with the Wilhelmy plate (22 x 50 x 0.15 mm) method with an average of ten readings for each sample.

In all bubble studies, the additives were mixed with the resin following the exact ratio as recommended by the manufacturer for the formulation of the wood coating. Experimental analysis was conducted to quantitatively and qualitatively determine the effects of different additives used in the coating formulation on bubble count, bubble size and their changes in the 15 minutes immediately after spraying. For this study, the effects of each additive were tested individually. Each formulation thus contained two components: pure resin and one of the additives of interest. The names of all additives and the concentrations used in the study are shown in the first two columns of *Table 1*. These combinations were completely mixed using a wooden stirrer and then sprayed on the glass using a hand-held compressed air spray gun.

APPLICATION AND IMAGING PROCEDURE

The number of spray passes was adjusted based on the density of resin and surface area of glass so that that the final film would have a wet film thickness of around 150 µm. The glass substrates used were heat-resistant borosilicate squares (5 x 5 x 0.3 cm by McMaster-Carr). Once the spraying was complete, the coated-glass substrates were placed under the digital SLR camera (Nikon “D90”) for imaging, as can be seen in *Figure 1* (left).

In order to better control the accuracy of still-shot timing, a timer system (TC-N3, JYC Technology) was used. An LED light panel (from Porta-Trace) with work surface dimensions of 22 cm by 27 cm and a bright white LED was used as the light source. A light box was also placed around the setting to shield the camera from external light sources.

An image of the complete experimental set up can be seen in *Figure 1* (right). Images were taken every 5 seconds for 15 minutes. The images were then processed using “ImageJ” software, utilising a macro that provided a summary including bubble count and average bubble size for each image analysed.

IMPACT OF VARYING ADDITION RATES IS CHECKED

The results of the surface tension measurements are summarised in *Table 1*. Measurements were taken for each additive at a fixed concentration of 0.1 % and then compared to that of the surface tension resulting from the concentrations currently recommended for the formulation of the wood coatings.

Two factors should be considered when determining the benefits of an additive with respect to surface tension: the magnitude of the decrease in surface tension between the pure resin and the additive/resin formulation, and the difference in surface tension when comparing the two concentrations studied.

In addition to this, the data provides an indication of the concentration needed to reduce the surface tension. If the surface tension of a 0.1% formulation is similar to that of a higher concentration, that means there is no need to use a higher amount.

For instance, the micro-defoamer ("Surfynol MD 20") had an even lower surface tension when only 0.1% was added. That means not only is a higher concentration unnecessary, but a higher amount even gives slightly negative effects on surface tension.

Another example is "Byk-346" surfactant, which is a polyether-modified polysiloxane additive recommended for the reduction of surface tension. The addition of 0.1% to the resin reduced the surface tension to 25.8 mN/m which is very close to the surface tension result after the addition of 0.3% (25.0 mN/m). The higher addition is therefore of little benefit.

RESULTS OF BUBBLE ENTRAPMENT STUDY

Initial and final bubble count and size varied for different additives. In each case, the bubble count decreased with time until a final bubble count was reached during the 15 minute image analysis study. *Figures 2-6* show snapshots of processed images taken at t = 0, 1, 3, 7, 12 and 15 minutes for different additives. The resolution of each image was 4288 x 2848 pixels. *Table 2* shows a summary including initial and final bubble count and bubble size for each additive tested.

The pure resin started with the complete surface covered with bubbles in different sizes. The bubbles then started moving around, colliding with each other and coalescing to form a few large bubbles, an effect due to the surface tension gradient created around the bubbles (*Figure 2*). Gradually some of those bubbles popped, reducing the number on the surface, but still many of the bubbles remained on the surface even after complete air-drying of the resin (after 24 hours). The addition of a silicone-based surfactant ("Byk-346") eliminated the formation of large bubbles, yet the initial number of small bubbles was high and some still remained after 15 minutes of observation time (*Figure 3*).

Figures 4 and *5* show images taken from the addition of two defoamers produced by the same company. The new formulation called "Foamex 822" is clearly much more effective than "Foamex 800". The first is indeed recommended as a more effective formulation than the latter by the producer.

As can be seen from *Figure 6*, the non-ionic surfactant used as a wetting agent ("Hydropalat") was the most effective additive in reducing the initial foam formation in the resin, also resulting in fast dissipation of the few small bubbles formed.

Figure 4: Foamex 800 (0.39 wt%) + resin images after processing (area under observation is 33 x 21 mm)

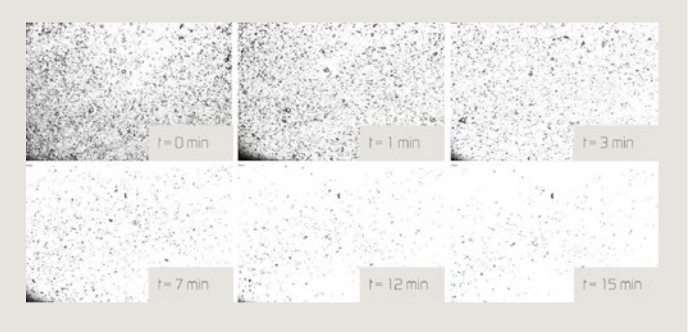


Figure 5: "Foamex 822" (0.39 wt%) + Resin images after processing (area under observation is 33 x 21 mm)

Figure 6: "Hydropalat WE3322" (0.95 wt%) + resin images after processing (area under observation is 33 x 21 mm)

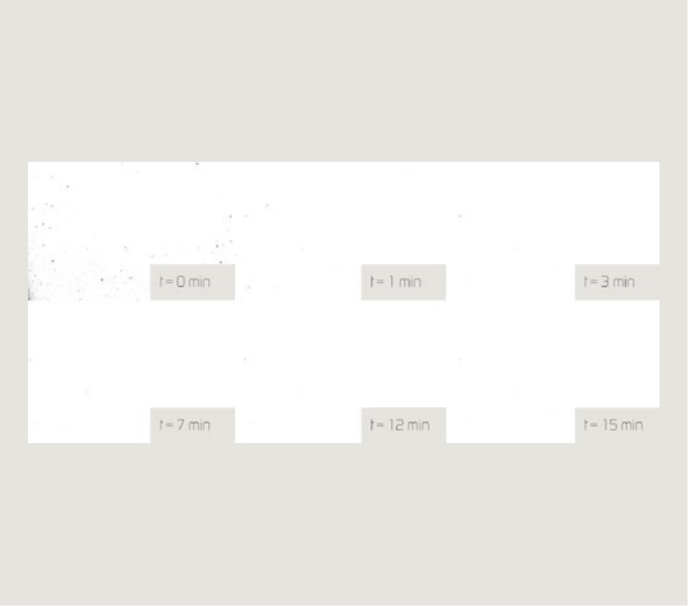
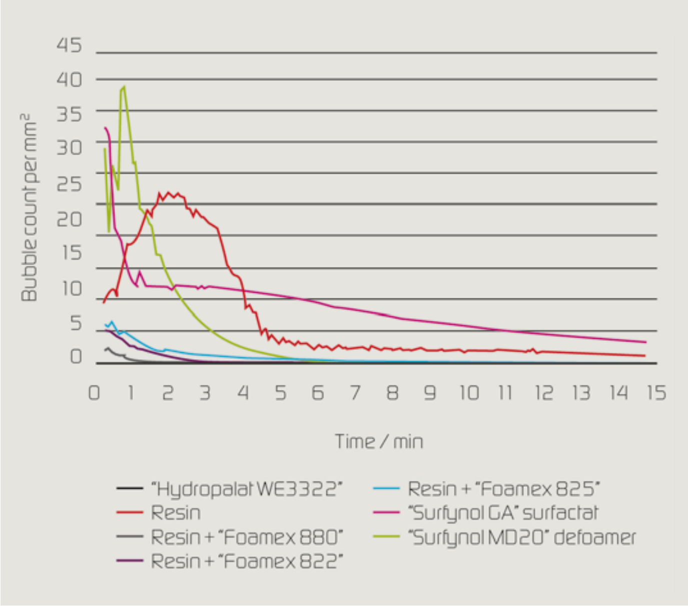


Figure 7: Bubble count per mm^2 vs. time for pure resin and mixture of some additives with resin



Trends showing the reduction in bubble count over give an indication of the potential benefits of each additive. *Figure 7* shows in detail the bubble count of a number of additives and resin over time. In some cases like the pure resin as shown in *Figure 7*, there is an increase in the number of bubbles in the first few minutes which could be explained by movement of dissolved bubbles in the film to the surface and then a gradual decrease in number of bubbles is seen as they escape from the surface.

PROCEDURE OFFERS POTENTIAL FOR MORE DETAILED STUDIES

The unique design of this study allowed accurate comparisons of the efficacy of a number of defoamers, surfactants and wetting agents in foam reduction when added to a water-based poly-urethane resin formulation. Detailed studies showing the number of initial bubble formations and their dissipation with time will help producers of defoamers to have a better view of existing issues.

These results along with surface tension analysis will also help the paint formulator to choose the best possible defoamer and know the exact amount needed for formulation. Among all additives tested in this study, a non-ionic surfactant showed the most promising results with the lowest initial bubble formation and an almost completely bubble-free wet film after 15 minutes observation time.

More in-depth study in close collaboration with the paint raw material producer is needed to explain these observation effects, based on the chemistry of surfactants or defoamers and how it can be utilised for a wide range of resin types and formulations.

Understanding the mechanisms which reduce the formation of bubbles and their faster dissipation in the liquid film of water-borne coatings will be a breakthrough study for major producers of coatings additives and coating industries. More work is needed to confirm the effect of the combination of additives and the optimal order of their addition in the bubble entrapment study.

Bubble movement in paint during drying or curing time and the mechanisms that would either hold them to the substrate or push them to the surface to pop is the emphasis of ongoing research at the Centre for Advanced Coating Technologies at the University of Toronto.

Table 2: Surface tension of pure resin and mixtures with additive at recommended rate to wood coating formulation and also at 0.1% for uniform comparison

Raw materials	% additives as recommended	Surface tension (mN/m) 0.1 %	Surface tension (mN/m) % as recommended
Pure resin (Daotan)	83	44.7	44.7
"Foamex 800" (Defoamer)	0.4	37.1	31.8
"Foamex 822" (Defoamer)	0.4	35.2	32.5
"Foamex 825" (Defoamer)	0.4	31.5	30.7
"Airex 902 W" (Defoamer)	0.4	38.8	37.5
"Surfynol MD 20" (Micro defoamer)	0.2	28.7	29.3
"Hydropalat WE 3322" (Wetting agent)	0.9	28.9	28.7
"Rheovis" (Thickener)	0.1	39.9	39.9
"BYK-346" (Surfactant, silicone)	0.3	25.8	25
"Surfynol GA" (Surfactant, non-ionic)	0.3	41.5	40.3
"Michem" (PE wax emulsion)	4	44.8	22.5
"Twin 4100" (Surfactant)	0.9	20.9	21.2
"EnviroGem" (Surfactant)	0.3	30.7	30.7
"Dynol 960"(Superwetting siloxane surfactant)	0.3	23.8	23.9
"Acematt" (Matting agent)	0.8	45.3	46.9

Table 3: Initial and final bubble counts and bubble size of pure resin and mixture of resin with each additive

Additive	Initial bubble count (per mm^2)	Final bubble count (per mm^2)	Initial average bubble size (mm^2)	Final averagebubble size (mm^2)
Pure resin	19.6	1.19	0.04	0.11
"Acematt"	61.7	18.7	0.05	0.08
"BYK-346"	50.0	0.82	0.06	0.08
"Foamex 800"	48.8	0.66	0.05	0.07
"Foamex 822"	6.21	0.04	0.04	0.07
"Foamex 825"	6.91	0.23	0.04	0.08
"Surfynol MD20"	34.4	0.09	0.03	0.07
"Hydropalat WE3322"	0.41	0.09	0.03	0.06
"Michem" Emulsion	35.1	3.83	0.06	0.08
"Rheovis"	21.0	4.31	0.05	0.10
"Surfynol GA"	37.9	2.90	0.05	0.09

> “Addition of a very small amount of the non-ionic wetting agent significantly reduced the surface tension of the resin.“

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Three questions to Mojgan Nejad

How do you explain the good performance of the non-ionic wetting agent? *The nonionic wetting agent ("Hydropalat WE3322") which was used in this study in addition to its wetting properties had a defoaming capability by destabilising foams. The good performance of this additive might be partially explained by the fact that the addition of a very small amount (0.1%) resulted in a significant reduction of the resin's surface tension (from 44.7 mN/m to 28.9 mN/m). However, further in-depth study is needed to look at the chemistry of the resin and defoamers in order to explain the exact mechanism by which this additive performs in comparison with other additives*

To what extent is bubble formation tolerable in water-borne coatings? *The amount and also the average size of the bubbles that can be tolerated in any formulation depend on the final application of the coatings. For instance, if the formulation is designed for high-end custom-designed wooden cabinets, then having even a small number of bubbles, which are usually trapped at the corners or edges of the cabinet doors, will negatively affect the gloss and the general appearance of the products. Thus, for these applications, the coating has almost zero tolerance for bubbles. While, for other applications like exterior decks, fences and sidings to have some small entrapped bubbles would not create any visible defect on the coating's appearance.*

Can bubble formation only be avoided by using an additive? *It depends on the size, number of bubbles and the stage that they form. Some resin formulations might have fewer bubbles to start with which may pop-up before drying of the film and would require no additives for adjusting the formulations. Additionally, it may depend on the stage that bubbles form for instance during application (spray or brush), in spray coatings droplet size and velocity play an important role in bubble entrapment. Bubbles are created when droplets approach a substrate and the air pressure in the gap separating the two increases, creating a depression in the droplet surface in which air is entrapped. Reducing droplet diameter and impact velocity both diminish the likelihood of air bubbles being formed, solving the issue without the use of additives.*

ACKNOWLEDGEMENTS

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HIGH PERFORMANCE ENABLED BY NATURE

New polyurethane crosslinker with significant bio-based content. By Gesa Behnken, Andreas Hecking, Berta Vega Sánchez. (published in ECJ 01/2016).

Seventy percent of the carbon content of a new hardener for polyurethane coatings and adhesives is provided by biomass. The bio-based crosslinking agent matches the high performance and quality level of conventional petrochemical-based isocyanates, even meeting the very high demands of the automotive industry.

The ecological compatibility of products is becoming a critical factor for businesses that want to defend their position and grow in the market, because consumers are increasingly deciding in favour of sustainable goods and making sure they incorporate renewable materials. Environmental labels help them to identify relevant products more effectively. Examples include the "Vincotte OK Biobased", "DIN CERTCO Biobased" and "USDA Certified Biobased Product" labels.

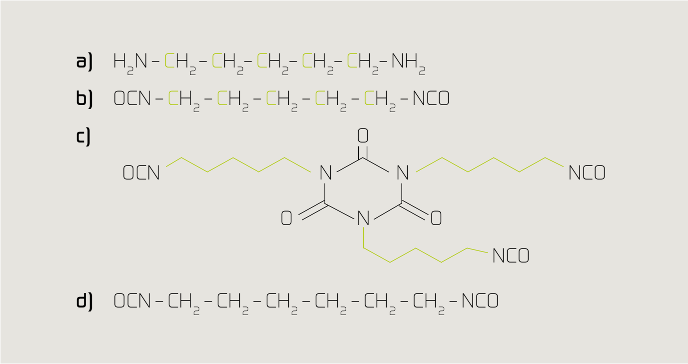
A number of U.S. states are supporting this trend. For example, the "BioPreferred" programme from the U.S. Department of Agriculture (USDA) compels public institutions to buy the material with the highest proportion of renewable raw materials for purchases over 10,000 US dollars [1].

In striving to fulfil these consumer demands, brand owners are in search of bio-based sustainable materials. This applies to the automotive industry, but also to others including the Ikea furniture stores and the Coca-Cola Company, which developed the "plant bottle" made partially from plants [2].

COATINGS INDUSTRY COMMITS TO 'GREEN PRODUCT' TREND

The coatings and adhesives industry has recognised this trend towards eco-friendly products, too. "Sustainability has become a key part of the growth and marketing strategies of a number of coating

Figure 1: Structural formulas of (a) Pentamethylene diamine (PDA), (b) Pentamethylene diisocyanate (PDI), (c) PDI trimer and (d) Hexamethylene diisocyanate (HDI); the carbon atoms from biomass are shown in green.



RESULTS AT A GLANCE

→ A new bio-based, high-performance hardener for polyurethane (PU) coatings and adhesives was developed. It is the first product of a new platform based on pentamethylene diisocyanate (PDI). Five of the seven carbon atoms in the material are bio-based.

→ Tests have shown that the bio-based hardener can create coatings that are just as weather-, chemical- and scratch-resistant and easy to apply as conventional coatings made exclusively with petrochemical inputs. The innovative hardener can offer greater freedom in formulation and faster drying.

→ Good results have been obtained in tests of automotive OEM and refinish formulations, anticorrosive and wood coatings. Chemical modification of the hardener allows an even wider range of PU systems to be crosslinked.

companies," reported the *Coatings World* European correspondent *Sean Milmo* in October 2014 [3].

This is backed up by statements such as that by *Peter Nieuwenhuizen*, former Director of Innovation and Partnerships at AkzoNobel [4]: "Given the challenges the world is facing in terms of resource scarcity, we are actively looking for bio-based alternatives for our chemicals." Henkel has also committed itself to a sustainability strategy and issued a guideline [5]: "Our products deliver greater value with a reduced environmental footprint."

The right starting materials can make a key contribution to meeting sustainability demands in the coatings and adhesives industry. Covestro (formerly Bayer MaterialScience) has launched a new high-performance hardener made from renewable raw materials. It is the perfect reaction partner to the bio-based polyols already used in polyurethane coatings and adhesives. Now these coatings can be formulated almost entirely from bio-based components.

At the 8th International Conference on Bio-based Materials in April in Cologne, Germany, the new hardener was honoured with the Bio-based Material of the Year 2015 innovation award [6]. With this new hardener, users and manufacturers in various industries can position themselves as pioneers of more sustainable materials.

PRODUCTION SHOWS GREATLY REDUCED CO_2 FOOTPRINT

The new hardener "Desmodur eco N 7300" is a trimer of pentamethylene diisocyanate (PDI) (*Figures 1b*, *1c*). PDI is manufactured from pentamethylene diamine (PDA) using innovative gas-phase technology which consumes significantly less energy and solvent than conventional processes.

The PDA suppliers use biotechnology – specifically fermentation – to manufacture PDA (*Figure 1a*) from biomass. PDI is therefore synthesised in just two steps, as opposed to the four required for the petrochemical synthesis of the corresponding petrochemical substance hexamethylene diisocyanate (HDI, *Figure 1d*), a conventional diisocyanate raw material. The internal evaluation showed a significant double-digit improvement in percentage of the CO_2 footprint of bio-based PDI in comparison to HDI. The energy efficiency of PDI cradle-to-gate is significantly better.

PDA is produced from the starch of field corn (maize), which is converted enzymatically by specially developed microorganisms in a highly efficient process. Field corn comprises varieties of maize which are not suitable for human consumption, meaning that PDA manufacturing does not compete directly with the food chain. Field corn is already used in the production of bio-fuels and numerous other products, such as paper, cosmetics, cleaners and textiles.

It has been estimated that only 80 square kilometres of arable land – an area slightly larger than the city of Leverkusen in Germany – are required to produce 20,000 tonnes of the new hardener, enough to

Figure 2: Viscosity of the conventional (red curve) and bio-based hardener (black curve), dissolved in butyl acetate. Common solvents behave in the same way.

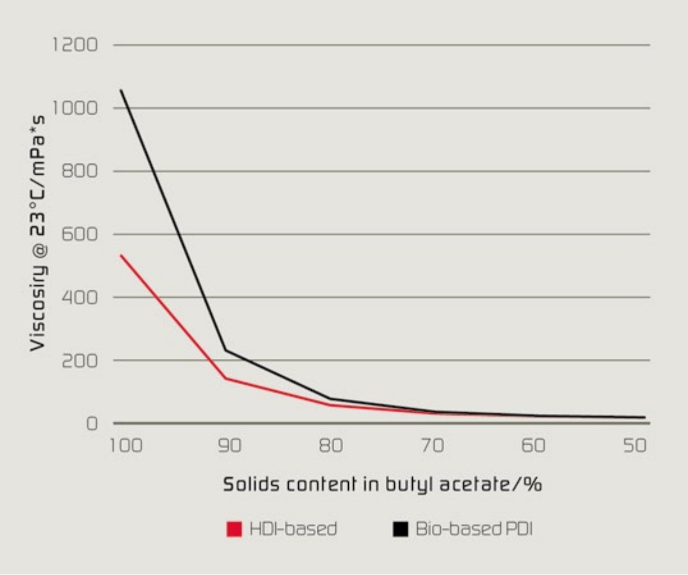
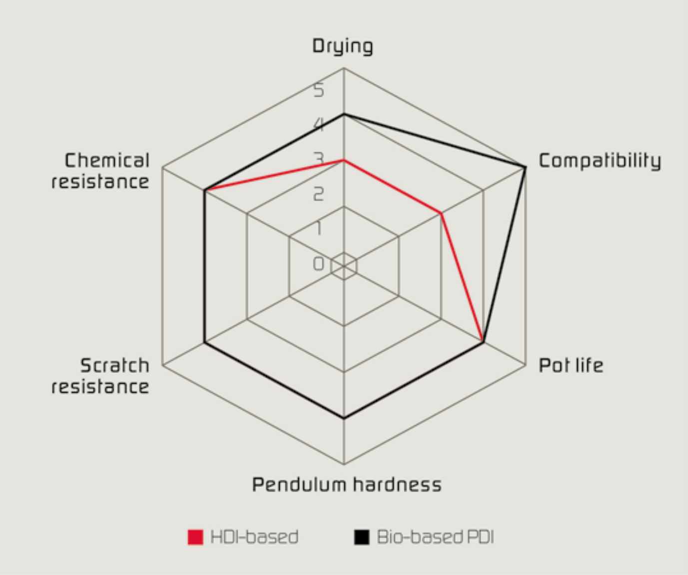


Figure 3: Property profile of coatings based on the new PDI hardener (black curve), compared with those containing the conventional HDI hardener (red curve).



apply three coats of paint to 30 million cars.

To make production even more sustainable, PDA suppliers are working intensively on ways to use bio-waste or cellulose instead of field corn. The development of this second generation feedstock is expected to take several years to be fully integrated into PDA production.

RADIOCARBON TESTING CONFIRMS BIO-BASED CONTENT

Field corn is the carbon source for all five of the non-functionalised carbon atoms in PDI. In other words, of the total of seven carbon atoms in the monomer, five - or 71% - are plant-based, as confirmed by ^{14}C radiocarbon testing in accordance with the ASTM D8666 standard [7].

The method is based on the following phenomenon: the dead organisms from which petroleum and natural gas deposits have formed contain only low percentages of ^{14}C isotopes of carbon due to radioactive decay. In contrast, living organisms constantly acquire new carbon from the environment, which translates into a higher percentage of ^{14}C isotopes. Despite the slow continuous decay, this higher percentage remains virtually constant because ^{14}C is constantly being created in the upper atmosphere.

PERFORMANCE MATCHES PETROCHEMICAL STANDARDS

The new hardener can be used for the same applications as the HDI-based hardener “Desmodur N 3300”. This is a long-established product for automotive OEM coatings, automotive refinish, industrial coatings including anti-corrosive and wood coatings, as well as adhesives for flexible packaging.

The viscosity of the solvent-free, bio-based hardener is 9,200mPa•s, meaning it is higher than that of the conventional hardener (3,000mPa•s). This, however, is of no significance in practice, as illustrated in *Figure 2*, because the viscosities of the conventional hardener and the new bio-based alternative equalise for formulations containing common solvents and at solids content below 75%.

The reason for this behaviour is that in the solvent-free state, the stacked PDI trimers attract one another more strongly than the HDI trimers because the PDI-based materials have higher polarity. However, just a small amount of solvent is sufficient to break down the stacking. As soon as this happens, the inter-molecular forces of PDI and HDI trimers do not differ significantly.

Figure 3 gives an overview of the bio-based hardener’s properties. Coatings formulated with this component are not inferior to those with a conventional hardener in terms of weathering, scratch and chemical resistance, hardness or processing (pot-life). They even dry slightly faster. The bio-based hardener offers major advantages when it comes to compatibility, particularly with highly functionalised polyols.

Figure 4 illustrates this, using the example of coatings formulated with highly branched polyesters “Desmophen 650 MPA”: because of the lack of compatibility between the hardener and the polyester, the gloss of the HDI-based coating is measurably and visibly lower than that of the bio-based coating. For coatings manufacturers, the better compatibility of the new hardener means greater freedom in formulation.

Figure 5: Gloss and yellowing levels after weathering: comparison of automotive coatings with the new PDI hardener (black curves) and conventional HDI hardener (red curves).

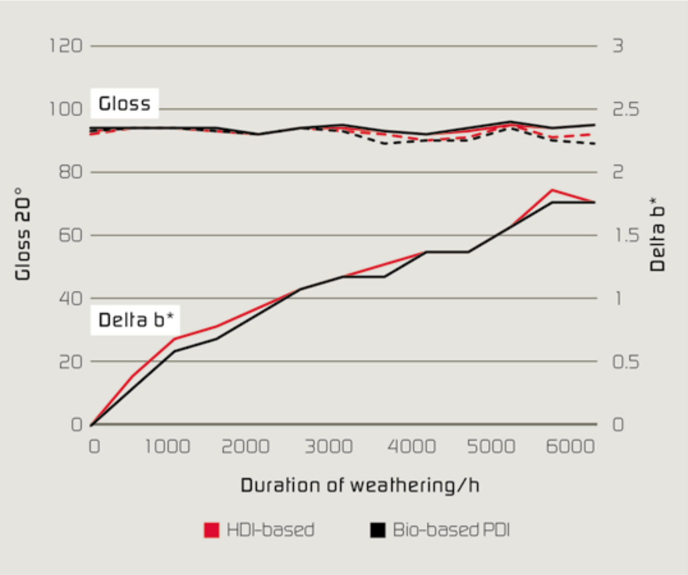


Figure 4: Gloss levels of coatings in which the bio-based hardener (left) and the conventional hardener (right) were combined with a branched polyester.

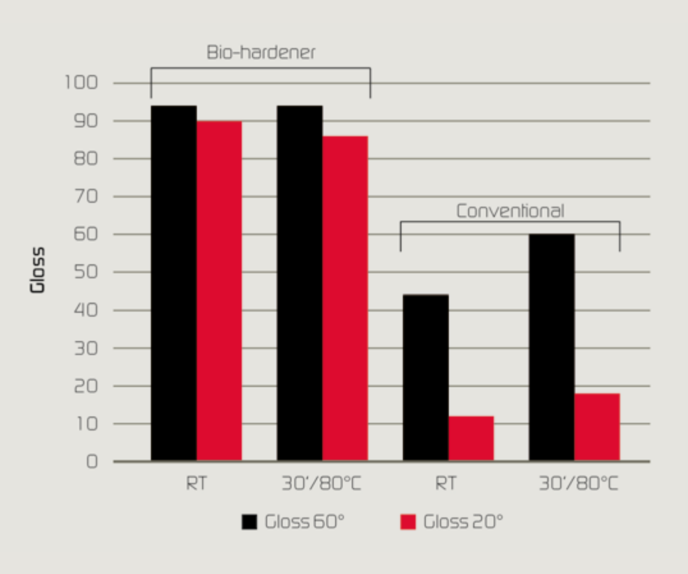
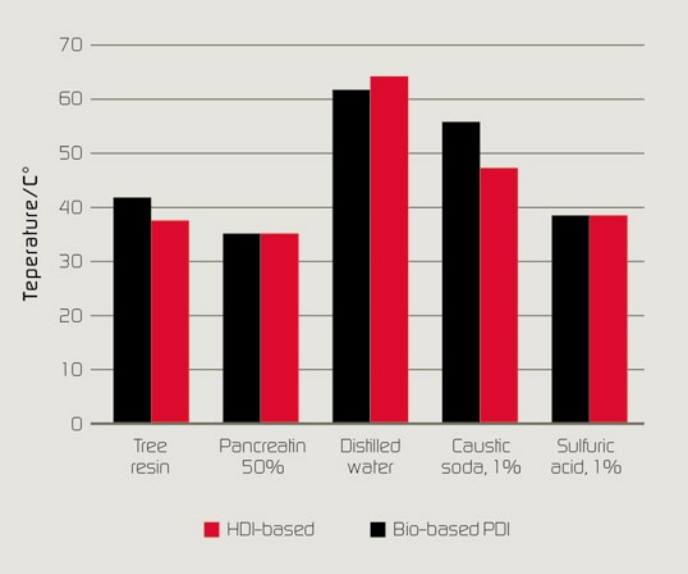


Figure 6: Chemical resistance of automotive coatings with the new PDI hardener (black) and the conventional HDI hardener (red) expressed as failure temperature in a gradient oven.



HIGH PERFORMANCE IN AUTOMOTIVE OEM FORMULATION

In automotive OEM coatings, the new hardener allows auto manufacturers in particular to further increase their percentage of bio-based materials. The current Mercedes C class, for instance, incorporates 76 components made from renewable raw materials with a total weight of 26.3 kilograms, an increase of 55% over the previous model range [8]. However, until now car manufacturers have used renewable raw materials primarily in the automotive interior. But now these raw materials can start taking over a vehicle's exterior as well, which carries very high emotional value. Tests with sample formulations have confirmed that coatings with the new hardener meet the high demands of automotive manufactures just as well as those made from established petro-based hardeners.

Figure 7: Dry scratch resistance and self-healing effect of automotive coatings with the new PDI hardener (left) and the conventional HDI hardener

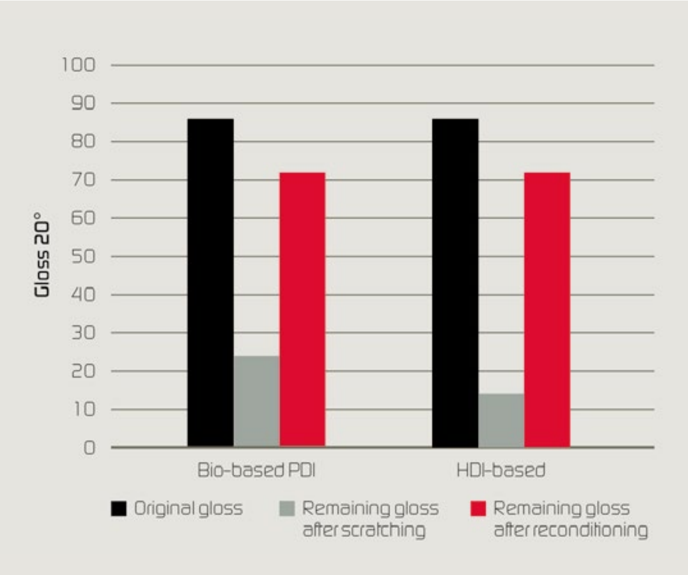


Figure 5 shows that both coatings deliver virtually identical results in weathering tests: Even after 6,000hours of weather exposure, the gloss does not deteriorate and only slight yellowing is detectable.

GOOD CHEMICAL AND PHYSICAL RESISTANCE

Chemical resistance was tested in a gradient oven at temperatures between 36 and 68°C. The sample substances – resin, pancreatin, demineralised water, 1% sodium hydroxide solution and 1% sulfuric acid solution – were applied to the coatings and the samples exposed to heat for 30minutes. The results were assessed after 1 hour and 24hours in storage under standard climate conditions.
The temperature at which each sample substance displays the first signs of damage was recorded to obtain the test results (*Figure 6*). No significant differences were determined between the coatings made from petrochemical products and those containing the bio-based hardener.
Dry scratch resistance was determined using the hammer test: The flat side of a hammer was wrapped in a layer of steel wool or sandpaper. The hammer is placed at right angles to the coating and pulled evenly in a line over it, without using the edge or applying any additional physical force.
The residual gloss was then measured on the damaged areas. After storing the coated sheets for 2 hours at 60 °C in a laboratory drying cabinet, gloss levels were measured again to test self-healing (reflow). The results are shown in *Figure 7*. The coating based on the new hardener also compared very favourably in this category.

A WIDE RANGE OF LOWER CURE TEMPERATURE APPLICATIONS

Automotive refinish coatings are applied at lower temperatures (40-70 °C) than automotive OEM coatings, and are therefore formulated differently. In this application too, coatings made with the bio-based hardener are comparable with the properties of conventional PU coatings, for example in terms of dry and wet scratch resistance, weathering resistance and processing.
Figure 8 shows that coatings incorporating the bio-based hardener reach drying stage 4 (DIN 53150) even faster than the conventional ones. This improved drying also comes into play in protective coatings

Figure 8: Drying time of automotive refinish coatings with the new PDI hardener (black) and the conventional HDI hardener (red).

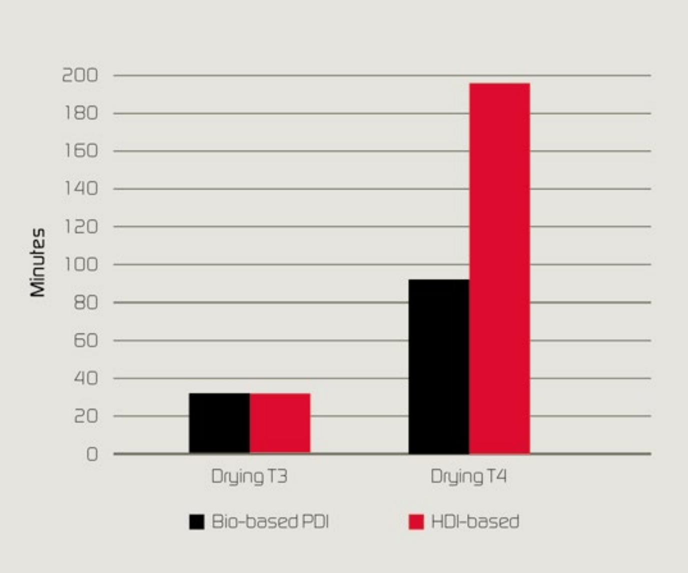
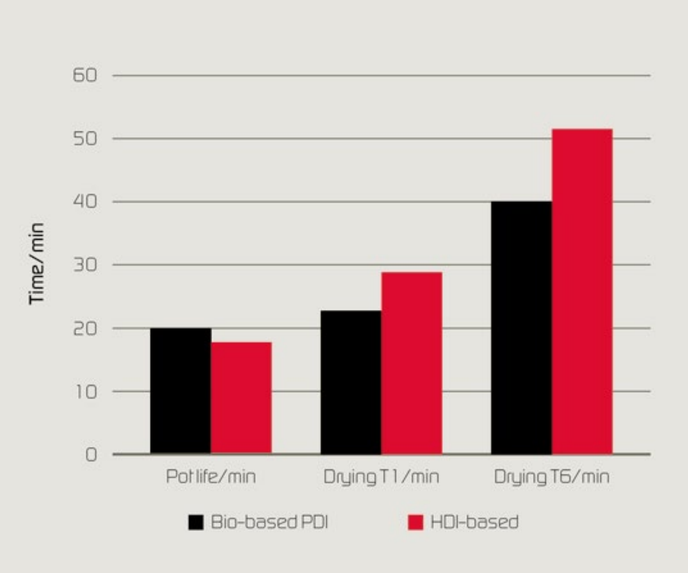


Figure 9: Pot-life and drying time of anti-corrosive coatings with the new PDI hardener (black) and the conventional HDI hardener (red).



such as anti-corrosive formulations: *Figure 9* illustrates an improvement in drying behaviour with only a slight influence in shortening of the processing time (pot-life).

The new bio-based hardener is also suitable for 2K PU wood clearcoats in both matt and gloss formulations. With regard to chemical resistance, scratch resistance and gloss, it demonstrates the same high performance as conventional hardeners, but shows slight advantages when it comes to the drying time of the coatings.

The new hardener is just as reactive in adhesive formulations (for example, in flexible packaging applications) as the established product.

BUILDUNG BLOCK FOR A BROAD TECHNOLOGY PLATFORM

It is not planned to commercialise the PDI monomer itself but instead wants to use it as the foundation for a new technology platform. Blocked, hydrophilic, silanised and water-borne polyurethane dispersions (PUDs) have already been produced and tested during development of the new hardener.

As with the bio-based hardener, the properties of the modified systems are very similar to those of the established HDI products. Unexpected and advantageous properties have also been found in these systems.

Examples here include coatings where the bio-based hardener has been modified with silane groups. They have a higher residual gloss after mechanical loading and thus scratch less easily than coatings based on similarly structured silanised HDI polyisocyanates. Coating films manufactured with PDI polyisocyanate show much better solvent and chemical resistance with the same proportion of silane groups.

Systems hydrophilised using internal and external emulsifiers and based on the PDI product have been crosslinked with standard waterborne hydroxy-functional polyacrylate dispersions. In terms of their coating properties, these products are at least comparable to the similarly structured hydrophilic HDI polyisocyanates and exhibit much faster drying.

In tests with standard blocking agents, the new hardener blocked with diethyl malonate showed a much lower tendency to crystallise than a product similarly based on HDI polyisocyanate. For the first time, a purely diethyl malonate blocked, linear aliphatic polyisocyanate thus seems possible.

The other blocked versions of the new hardener behaved in testing in a way that is at least comparable to similarly manufactured HDI polyisocyanates.

Substituting conventional hardeners with bio-based crosslinking agents in various water-borne systems showed that the conventional hardeners in water-reducible, lightfast single-component polyurethane baking coatings and in waterborne urethane acrylate dispersions, for example, can be replaced without compromising performance.

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Dr Gesa Behnken
Covestro

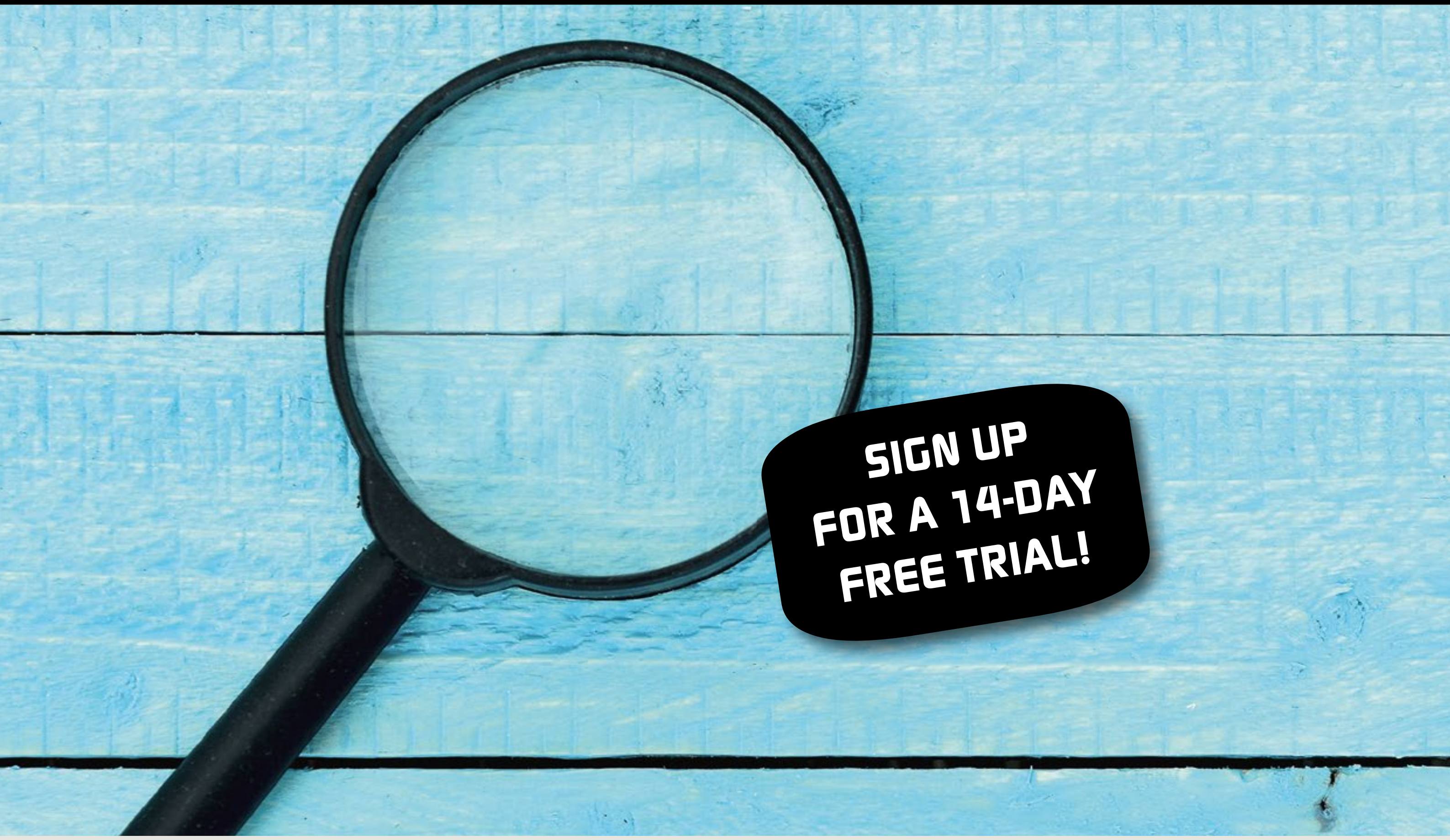
> “Faster curing and greater compatibility.“

Three questions to Gesa Behnken

Is the hardener already on the market? Has there been any initial feedback? *“Desmodur eco N 7300” was launched on the market at the European Coatings Show in April 2015. Samples have been sent out on a wide scale since 1 August 2015, while the commercial rollout will be taking place next year with an annual capacity of up to 20,000 metric tons. We worked with selected partners to develop this new hardener in the run-up to the market launch. The positive feedback from these customers was a key factor in deciding to commercialise it.*

You’re only taking into account the CO_2 footprint from manufacturing the new PDI. What about the full environmental assessment? *The new hardener was also superior to standard products in other categories, such as the overall energy balance. Yet there are also challenges, as with the vast majority of bio-based products, since agricultural land is needed to produce biomass.*

What weaknesses does the hardener have that can/must still be optimised? *Compared to standard HDI trimers, the hardener has even better properties, such as faster curing and greater compatibility with high hydroxyl containing polyols. However, there are areas of application that we cannot cover with it. We’re looking to establish a new technology platform based on PDI that enables applications to be used on a widespread basis. For instance, we’re working with selected partners on further potential products in the area of waterborne polyurethane coatings.*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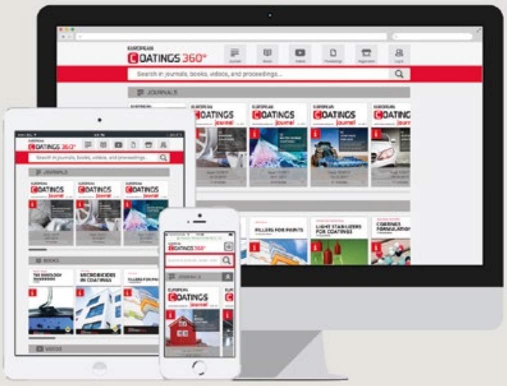

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CREATING THE RIGHT FINISH

New UV/EB curable binder for matte formulations. By Guido Vanmeulder and Marie-Astrid Goes, Allnex (published in ECJ 04/2016).

Reducing the level of matting agent makes it possible to formulate finishes with improved rheology, transparency, and stain and scratch resistance on wood, resilient flooring, plastics and paper foil substrates. A new matte extender creates highly versatile, stable coating systems that are easy to formulate.

The popularity of matte and ultra-matte finishes in applications from high-end electronics to luxury packaging, cosmetic packaging and furniture, has increased in recent years. To help manufacturers of industrial products more easily meet this growing market need, a new UV/EB curable polyester acrylate binder has been developed that requires less matting agent to achieve long-lasting, (ultra-low) matte finishes on wood, resilient flooring, plastics and paper foil substrates. Reduced matting agent levels provide improved rheology, transparency, and stain and scratch resistance. Importantly, the new matting agent is monomer- and solvent-free and requires no diluents to achieve excellent performance in both clear and pigmented systems intended for use as

Figure 1: Milky-white appearance of the matte extender emulsion.

RESULTS AT A GLANCE

→ A new solvent-free polyester acrylate matte extender makes it possible to formulate ultra-low and low gloss 100% solids UV curable coatings without sacrificing mechanical properties.

→ The matte extender reduces the need for matting agents, resulting in improved rheology, transparency, and stain and scratch resistance properties

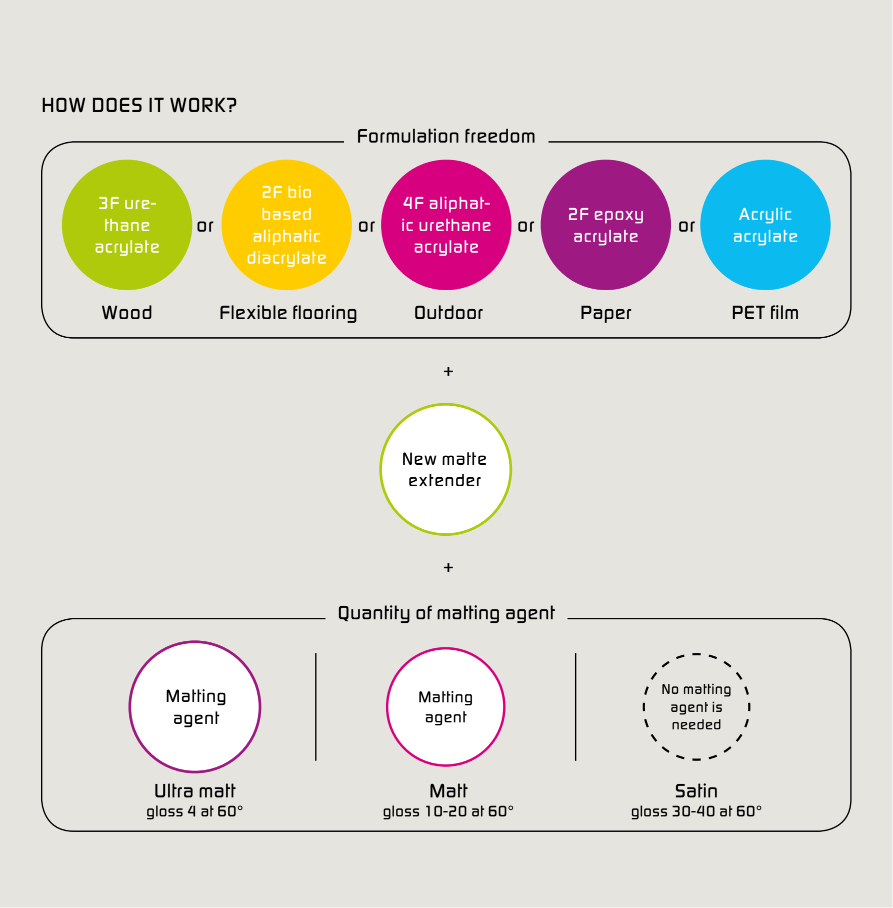
→ By adjusting the content of the new resin system, it is possible to achieve 100% solids UV curable coatings with gloss levels ranging from ultra-matte to satin.

→ The matte extender can be easily incorporated into formulations and provides a stable, matte appearance in clear and pigmented topcoats and sealers of varying thicknesses.

→ As there is no need to add solvents or monofunctional monomers when using the new matte extender, it is easy to formulate regulatory-compliant, matte coatings.

→ Coatings formulated with the new matte extender can be cured over the full spectrum of UV light or using LED or electron-beam radiation.

Figure 2: Schematic showing the formulation flexibility made possible with the new matte extender.



topcoats or self-sealing coatings. Coatings formulated with the new binder can also be cured using the full spectrum of UV light and LED and electron-beam radiation.

MATTE EXTENDER FOR LOW GLOSS REQUIREMENTS

From cosmetic packaging to cars, smartphones and snack food packaging, consumer interest in matte finishes is growing. Younger consumers in particular are used to the matte finishes on their smartphones and tablets and are attracted to other products with a similar appearance. In the automotive industry, for instance, matte finishes first appeared on trim pieces, then customisers began offering the all-over matte look. More recently these coatings have been offered on several luxury vehicles, and most car makers are now exploring the wider possibilities of using matte finishes. Demand for low gloss coatings is increasing for wood surfaces, including furniture, parquet, kitchen cabinets and construction, plastics and metal substrates used in consumer products (electronics, automotive, etc), concrete protection, and in the graphic arts industry.

For many of these applications, radiation-curable coatings offer many advantages over conventional coatings. In addition to improved coating properties, which include increased durability, scratch and stain resistance and clarity, radiation curing processes consume less energy and produce less waste. Coating formulations also cure very rapidly and contain very low levels of volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) or none at all.

Unlike conventional solvent-borne and water-based resin systems that are easy to formulate as low gloss coatings, 100% solids UV curable resins are difficult to matte. There is no solvent or other diluent to evaporate and help transport the matting agents to the surface, so typically twice as much matting agent is required. The use of such high quantities of matting agents negatively affects the rheology, appearance and resistance of the coatings. In addition, to achieve ultra-matte (dead matte) systems, it is generally necessary to add solvents and monofunctional diluents.

Table 1: Physical properties of the new polyester acrylate matte extender.

Typical values	
Viscosity CP-shear rate 20 (s-1) at 25 °C, MPa.s	±3500
Colour, Gardner	white milky
Physical properties	
Density, g/cm^3	0.8
Molecular weight, theoretical	1,000
Functionality, theoretical	4
Polymer solids, % by weight	85
Typical cured properties	
Young's modulus, MPa(1)	842
Tensile strengths, MPa(1)	8.6
Tensile elongation, %(1)	1.4
Glas transition temperature, °C	65

(1) Measured on a 120 μm EB cured film.

Table 2: Reference and new starting point formulations for a parquet topcoat.

Ingredient	**Reference formulation**	**New starting point formulation**
Aliphatic urethane acrylate	30	30
Conventional polyester acrylate	20	0
New polyester acrylate	0	20
Monomer	42	42
Curing agent	5	5
Silica matting agent	10	10
Wax agent	2	2

Table 3: Gloss results for parquet coatings.

Gloss	**Reference formulation**	**New starting point formulation**
60°		
Length/cross direction	17/14	2/4
85°		
Length/cross direction	45/23	23/24

Table 4: Performance comparison for topcoats based on "Ebecryl 898": the best balance of haze and gloss was achieved with the added matte extender.

	Haze, Gardner	**Gloss 60° coat on Lenata**
Glass plate	0	-
Standard topcoat	24	12
New topcoat with new matte extender	28	4
Standard topcoat + 10 pbw 1-functional monomer	27	6
Standard topcoat + 20 pbw 1-functional monomer	36	3

Table 5: Stain resistance of the reference and new starting point formulations.

18 hours spot test	**Ref. benchmark, gloss 60° : 17**	**New with new matte extender, gloss 60° : 5**
2% Eosine	2	2
Coffee	5	5
Mustard	2	2
Red wine	5	5
EtOH/ water 1/1	5	5
Bleach water (7%)	5	5

Consequently there is a significant market need for 100% solids radiation-curable resin systems that can be readily formulated as ultra-low and low gloss coatings without comprising coating quality. To address this need, a solvent-free, matte extender has been developed that, when combined with low levels of matting agents, allows the formulation of 100% energy curable coatings with low gloss values without losing formulation flexibility or performance.

REDUCING MATTING AGENT IMPROVES COATING PERFORMANCE

The new matte extender is based on polyester acrylate chemistry and acts as a wetting agent, transporting matting agents to the surface where they are most effective. As a result, less matting agent is required to reduce gloss. Even an ultra-matte appearance is possible without any loss in coating performance.

The physical properties of the matt extender are presented in *Table 1*. The 100% solids, energy curable binder is monomer- and solvent-free, has a viscosity of approximately 3,500 mPa.s at 25 °C, and exhibits Newtonian behaviour. Though it is milky-white in appearance (*Figure 1*), it is transparent when fully cured.

The chemistry of the matte extender makes it possible to achieve a wide range of lower gloss levels, including ultra-low ("dead matte") gloss values of < 5 at 60°, without the need to add any solvents or monofunctional diluents. Importantly, these gloss levels are stable and do not increase over time. The resin also does not yellow over time and provides stable formulations in which there is no sedimentation of the matting agent.

In recognition of the needs of coating formulators for formulating freedom and flexibility and to minimise their inventory and carrying costs, the new matte extender was designed as an ideal blending partner that is effective in a wide range of coating systems (see *Figure 2*): coatings designed for curing over the full spectrum of UV light; LED and electron-beam radiation, as well as conventional UV curing systems;

- coatings containing many other 100% solids, radiation-cured resin systems, allowing the formulation of low-gloss finishes with tailored properties for a wide range of substrates, including wood, resilient flooring, plastics and paper foil substrates;
- coatings formulated with commonly used matting agents;
- ultra-low and low gloss finishes applied in a wide range of dry film thicknesses (6 to 120 µm);
- both clear and pigmented matte formulations;
- formulations applied by spray, curtain or roller coating;
- ultra-low and low gloss coatings that are compliant with the most stringent regulatory requirements because there is no need to add monomers or solvents.

When the new matte extender is used in these coating formulations, significantly less matting agent is required to achieve the same low gloss level as conventional 100% UV curable resins. The need for less matting agent translates into improved rheology characteristics, better transparency, deeper curing, and stain and scratch resistance similar to that of high gloss systems. Coatings containing the new binder also tend to have a better soft feel, and those designed for wood substrates exhibit enhanced transparency. In addition, the new binder does not negatively influence the flexibility or hardness of coatings. As a result, the matte extender is ideal for use in topcoats and self-sealing coatings.

EASY FORMULATION

The new binder has been designed to be easy to use in all of the above-specified coating systems. Its low viscosity makes it very easy to incorporate into coating formulations. The resin system is also compatible with polymers and matting agents commonly used in 100% solids radiation-cured coatings, making it an ideal blending partner.

By varying the choice of other resins systems used in a formulation along with the new matte extender and by adjusting the quantity of matting agent, it is possible for coatings manufacturers to develop solutions for the wood, paper, plastics, and graphics arts applications that cover the full range of gloss values from ultra-matt to satin. Even formulations with no added matting agents can benefit from incorporating the new resin system. As a result, the new matte extender provides both formulation efficiency and flexibility when preparing 100% radiation-curable coatings.

PROVEN PERFORMANCE

To confirm the ability to achieve enhanced matting effects with the new matte extender, reference coatings for various substrates with low matting agent levels were prepared. Their properties were compared with those of coatings based on similar formulations, but with a portion of the conventional resin replaced with the new binder.

The following examples are for a coating formulated for wood and paper substrates. The reference and new starting point formulations are presented in *Table 2*.

Gloss

First, the gloss performance of the starting point formulation at different thicknesses was investigated. The coating was applied at dry film thicknesses (DFTs) of 6–120 µm on black Leneta paper and UV cured at 10 m/min using 2x 80 W Hg lamps. The 60° gloss values for the coatings with DFTs of 6, 4, 80, and 120 were 5.1, 4.4, 4.0 and 3.2, respectively, clearly indicating that the variation in gloss was limited, regardless of the coating thickness.

The standard and new coating formulations were then each applied at a wet film thickness of 25 µm to wood panels previously sealed with 3 coats of an aromatic urethane acrylate resin. UV curing was performed at 10 m/min using two 80W Hg lamps. The gloss of each wood panel was measured along its length and in the cross direction, and the results are shown in *Table 3*.

The results confirm that the new matte extender significantly decreased the gloss of the parquet coating in both angles and directions. In fact, the gloss values were reduced by greater than a factor of 3 along the length and in the cross direction at 60°, and a "dead matte" appearance was achieved.

Transparency

Next, the haze of the reference and new starting point formulations was determined to evaluate the effect of the new matte extender on transparency. Each coating was applied at a wet film thickness of 30 µm on glass plates and Leneta paper and then cured at 7 m/min using an 80 W Hg lamp. The haze of each coating on glass was measured using an XL-211 Hazegard system, and the gloss values at 60° were determined for each coating on paper. The results are presented in *Table 4*.

The haze value of the coating formulated with the matte extender was only slightly higher than that for the standard topcoat on glass (28 vs. 24), while the gloss of the coating when applied to Leneta paper was reduced by a factor of 3 (4 vs. 12). In addition, when a similar level of gloss was achieved for the standard formulation by adding 20 pbw of a monofunctional monomer, the haze of the standard coating increased to 36. The new matte extender clearly provides ultra-low gloss coatings with levels of transparency similar to those observed for conventional 100% radiation-curable systems with much higher gloss values.

Resistance

The stain, scratch, and abrasion resistance characteristics of radiation-cured coatings have been key factors in their adoption for consumer electronics and other industrial OEM applications. Any new matte extender for 100% solids radiation-cured coatings must provide the desired reduction in gloss without impacting their resistance.

“100% UV matt coatings are in high demand because of their environmental footprint.“

Guido Vanmeulder
ATG Engineer Radcure
Allnex Belgium SA/NV
Guido.Vanmeulder@allnex.com

3 questions to Guido Vanmeulder

How easy is it to incorporate the new extender into existing formulations? *Depending upon the gloss levels that need to be achieved, the new matt extender reduces the required level of matting agents. A slight modification and fine-tuning of existing formulations is required in order to obtain the best results with “Ebecryl 898”.*

Do you think stricter regulations will push UV/EB technology even further? *Yes, growth is expected especially in solvent-free 100% UV formulations. The new matt extender was designed to be solvent-free, monomer-free and BPA-free.*

Will the demand for matte finishes continue? What are the benefits? *100% UV matt coatings are in high demand because of their environmental footprint compared to conventional solvent- and/or water-based coating systems. Matt coatings are still requested in different types of markets.*

The resistance of coatings based on the reference and new starting formulation were thus subjected to the 18 hour spot test. Each coating was applied on white Leneta paper at a wet film thickness of 25 µm and UV cured at 10 m/min using two 80 W Hg lamps. As can be seen in *Table 5*, the resistance behaviour of the two coatings was identical even though the coating with the matte extender provided a dead matte finish and the gloss of the reference coating was more than three times higher.

Versatile binder

The new matte extender makes it possible to formulate 100% radiation-curable coatings with ultra-low to low gloss values while retaining key performance properties such as stain resistance and transparency.

The monomer- and solvent-free, 100% solids polyester acrylate resin does not require any special handling, is stable upon storage, and can easily replace conventional resins in formulations intended for use on a wide variety of substrates. Low gloss levels are maintained even under high-speed curing conditions, and the gloss level is not affected by coating thickness over a wider range. In addition, both pigmented and clear topcoats/sealers can be formulated with the new matte extender for both interior and exterior applications. With no added solvents or monomers, the new binder system readily meets regulatory requirements for low-VOC formulations.

Because of these features, the new matte extender is a highly versatile binder that addresses the key market need for a solution that enables the formulation of low and ultra-low gloss 100% solids UV curable coatings (no addition of solvents or diluents) that have desirable rheology, transparency and stain and scratch resistance properties.


Jorge Prieto + Jürgen Kiene
WOOD COATINGS
EUROPEAN
COATINGS library
VINCENTZ


Source: Nefetova - Fotolia.com

GROWING PERFORMANCE

High quality water-borne crosslinking resins incorporate vegetable oil. By Anthony Pajerski, Jonathan Bird, George Ahrens and Naser Pourahmady, Lubrizol Advanced Materials Inc (ECJ 04/2016).

The development of crosslinkable water-based polyurethane dispersions (PUDs) with renewable content is outlined. The first products contained up to 25% vegetable oil. Later developments allowed the vegetable oil content to be raised to 50%. Modified acrylic dispersions are available with similar oil content. Coatings show good general properties, weathering performance and economy.

With diminishing oil reserves and customers' increasing environmental consciousness, the conversion of biomass and bio-based ingredients into useful products for coatings and binders offers a considerable and sustainable growth potential for chemical companies. Recent advances in genetic engineering and enzyme catalysis make the production of new bio-based building blocks possible and economically attractive.

At the same time, a major move toward greener, safer products by market-leading customers mandates chemical manufacturers to come up with suitable products to help customers with 'green' initiatives or risk losing their business. Many new products from plant-based raw materials have been introduced by suppliers to coating industry in recent decades. A recent review of products made from bio-based raw materials is available in the ACS Symposium series [1].

RANGE OF BIO-BASED PRODUCTS IS CONSTANTLY EXPANDING

In addition to the production of several commodity raw materials from renewable resources, an increasing number of new bio-based raw materials are becoming available which can be used to develop new products for coatings applications. Some are derived from the major by-product of bio-refineries, glycerol. Several other building blocks such as levulinic acid and itaconic acid are being derived from biomass.

Some companies are developing new building blocks from combinations of these raw materials. A new hydroxy-acid from a combination of levulinic acid and glycerol has recently been commercialised. Several oligomeric derivatives and polymeric products are also becoming available from similar resources [1]. In addition to the industrially developed products, several research groups in academic institutions have reported interesting results. The group in the University of Delaware led by Dr Richard Wool have shown promising results in making composite materials from combining vegetable oil with maleic anhydride [2]. Zoran Petrovic's group in Kansas Polymer Research has discovered a method of making a bio-based-petrochemical hybrid polyol, reacting a cyclic ether with a vegetable oil-based polyol in the presence of a cationic or coordinative catalyst [3]. The hybrid polyol is then reacted with isocyanates to create polyurethanes that have good hydrolytic resistance.

Despite the great demand for more environmentally friendly products, it is hard to justify a premium price for coating products based solely on their renewable content. There is a general belief in the industry that products from bio-based raw materials will be inferior to petroleum-based products in cost/performance balance. Lubrizol has developed several technology platforms in recent decades to progressively improve the environmental portfolio of its products, using higher levels of renewable raw materials.

These technologies allow products to be offered with considerably higher renewable content at equal or superior cost/performance balance to petroleum based products. The composition of products based on these technologies is described in patents and publication [4-7].

In this paper, the general properties of representative examples from each of these technologies will be discussed in comparison to standard water-borne acrylic and urethane coating polymers. The reader may become satisfied that it is possible to generate coating products with a 'greener' portfolio using bio-based raw materials without having to sac-

RESULTS AT A GLANCE

- → The range of renewable-based chemical building blocks available to create raw materials for coatings has increased, offering scope to formulate materials with enhanced performance and/or reduced cost.

- → The development of water-based polyurethane dispersions (PUDs) with renewable content is outlined. The first products had up to 25% vegetable oil content and crosslinked by oxidation. The development of improved self-crosslinking chemistry allowed the vegetable oil content to be increased to up to 50%. It is now also possible to produce modified acrylic dispersions with similar oil content.

- → Tests of coatings formulated on these materials have shown increased hydrophobicity, good general performance and high resistance to weathering. They are compatible with standard dispersion resins and allow coatings to be formulated with lower VOC content.

rifice the performance relative to similar products made of conventional petroleum based raw materials.

EVOLUTION OF URETHANE DISPERSIONS WITH VEGETABLE OIL

In 2005 the company introduced the first series of polyurethane dispersion (PUD) products which contained up to 25% components derived from vegetable oil [4]. Examples of this technology are referred to below as low-oil urethane (LOU). This technology uses the unsaturation present in the oil components of the polymer for latent crosslinking by an oxidation mechanism. A few years later, another technology for water-borne PUD coatings was introduced, using a self-crosslinking chemistry [5]. This technology allowed the vegetable oil component of the urethane resins to be increased to as high as 50%. This technology will be referred to as high-oil urethane or HOU. This technology has now been extended to water-borne acrylic and other vinyl polymers [6]. It is now possible to produce oil-modified acrylic resins with as high as 50% components derived from vegetable oil. This technology is referred to as high-oil acrylic, HOA. Some of the properties with representative examples from each of these technologies are discussed here.

EXPERIMENTAL TEST PROCEDURES SUMMARISED

All polymers were prepared according to the procedures described in previous publications [4-7]. Particle size analysis was done on a Malvern "ZEN1690". Glass transitions were determined by DSC analysis on a TA Instruments model "Q2000". Melt onset of the polymers was determined by thermo-mechanical analysis (TMA) on a TA Instruments model "Q400". Transmission Electron Microscopy (TEM) characterisations were performed on a 120 KV Philips "CM12" instrument. All samples were either microtomed or solution deposited onto coated support grids prior to the analysis.
Viscosity measurements were done using a Brookfield viscometer. Dynamic mechanical analysis (DMA) was done using an ARES Rheometer with a dynamic temperature ramp from -100 to 200 °C at 4 °C/min. Samples were prepared from drawn down films of polymer dispersions without formulation.

LOW-OIL URETHANE DRIES SLOWLY BUT PERFORMS WELL

In *Figure 1* the dynamic mechanical behaviour of a sample of low-oil urethane (LOU) is compared with a standard 2K water-borne PUD. It is obvious from the G' curve that the crosslinking mechanism of the 2K standard PUD sample is more efficient. The oxidative crosslinking mechanism in LOU is slower, but it provides sufficient crosslinking after a complete cure to give good mechanical and chemical properties for various applications. The application performance of these two samples was compared in a clear wood finish for flooring application. This offers a good comparison of resin performance, since the application requires minimum formulation. The effects of external additives such as pigments, fillers, coalescent, etc. are minimised. *Figure 2* shows the wear properties of the LOU compared to a standard PUD and also an alkyd resin as the retention of gloss after several months of testing on a finished wood floor.
Like any conventional water-borne PUD, the oil-modified urethane LOU polymers are an anionic stable, white dispersion in water, with typical pH around 7.5 to 8.5. Their viscosities are 300-600 cP at 45% solids and 20-40 cP at 33% solids. Many other properties are comparable to standard PUD and they process and cure similarly to conventional PUD products. Interestingly, these polymers display excellent colour stability and seem to be suitable for a variety of indoor and outdoor applications.

IMPROVED CROSSLINKING ALLOWS HIGHER OIL CONTENT

With the encouraging results from the LOU technology platform, the possibility of incorporating more vegetable oil into the composition of the polymer was studied. Although various vegetable oils had been studied (linseed, sunflower/safflower, soybean), due to the availability of various soy oils and derivatives it was decided to use this type of oil in the development of new technologies.
A shortcoming in the first series of oil-modified products was thought to be in the crosslinking mechanism. The oxidative coupling mechanism

Table 1: Typical properties of oil-urethane and oil-acrylic dispersions.

Property	HOU	HOA
Particle Size (nm)	100	50
Dispersion viscosity (cP)	110	40
Glass transitions (°C)	-21 & 66	-14 & 52
Melt onset (from TMA)	266	300
Dispersion solids content (%)	40	40

Table 2: Comparison of application properties of oil-modified polymers.

Property	LOU	HOU	HOA
Renewable Content (% weight)	25	50	50
VOC capability	<250	<50	<50
Gloss 60°	92	88	96
König hardness (14 days)	66	14	35
Chemical resistance*	8.7	9.2	8.8
Taber abrasion, mg loss	165	200	150

*Average of 12 chemicals tested, rated 10 with being best.

seemed slow and in some cases insufficient for maximum performance. Therefore, considerable effort was devoted to the development of a self-crosslinking mechanism to enable:

- More oil-based components to be incorporated in water-borne urethane and acrylic polymers;
- Elimination of external crosslinkers which are usually not considered to be environmentally friendly and are inconvenient to use (2K system vs 1K self-crosslinking).

Details of the self-crosslinking system and its advantages are discussed in other publications [5, 7].

In 2010 a new water-borne soy-urethane dispersion technology was introduced with polymers containing as much as 50% raw material derived from soybean oil, HOU (high-oil urethane). In addition to having a higher renewable content, this also offered lower VOC than traditional petroleum based products and a convenient self-crosslinking system, therefore being useful as 1K coating in various applications.

More recently, the scope of this technology was extended to acrylic and other vinyl copolymers, referred to as HOA (high-oil-acrylic).

ELECTRON MICROSCOPY REVEALS PHASE SEPARATION

It is important to note that all these technologies are water-borne dispersions, anionic-stabilised by functionalisation of the oil-polymer backbone, and neutralised by a counter ion. Details of the synthesis process and composition of the resulting polymers are discussed elsewhere [4-7]. Transmission electron micrography (TEM) of these polymers indicates some level of phase separation and non-uniformity along with some homogeneous particles of urethane, acrylic, or functionalised oil (*Figure 3*). The unstained sample of HOU (*Figure 3a*) indicates composite particles with distorted boundaries. The ruthenium stained material (*Figure 3b*) depicts two particle size ranges, the larger particles (80 to 100 nm) appear to be the urethane component and the smaller particles (30 nm) are most likely soybean oil. In the case of soy-acrylic HOA polymers the particles seem to have more defined boundaries and more uniform morphology. TEM of both stained and unstained samples of HOA (*Figure 3c* and *3d*) indicates acrylate-rich particles (dark colour) and soy-rich particles (lighter colour). The majority of particles are about 30 nm. Particle size measurement by a light-scattering method showed average particle size of 100 nm for HOU and 50 nm for HOA. The difference in the particle size between the two methods may be due to the drying effect in the TEM method.

RESINS ARE IDEAL FOR LOW VOC WOOD COATINGS

Some general properties of HOU and HOA are shown in *Table 1*. Both oil-urethane and oil-acrylic polymer dispersions have the characteristics of conventional water-borne urethane and acrylic dispersions. General physical and chemical properties of these polymers are very similar to the products made solely of petrochemical based raw materials.

These oil modified polymers show excellent processing characteristics, film formation and compatibility with a variety of formulation additives. Despite the non-uniformity of particles in the dispersion of HOA and HOU, as discussed above, they form clear films and they have good adhesion to a variety of substrates.

Due to their high oil content, they present a more hydrophobic character than conventional polymers. Their flexible backbone and ability to be absorbed into the wood substrates make them very suitable for wood coating applications.

Some application properties of coatings prepared from LOU, HOU, and HOA without any formulation are compared in *Table 2*. As expected, the acrylic and urethane polymers with higher oil content are softer than the LOU with lower oil content. However, with further crosslinking and other additives these polymers can be formulated to give the desired hardness.

An advantage of HOU and HOA polymers is that they can be formulated to form lower VOC coatings than traditional petrochemical based polymers. All three polymers exhibit good chemical resistance and good wear properties when applied to wood. These polymers are easy to formulate and compatible with most other acrylic and urethane dispersion resins.

The oil-modified polymers are also compatible with conventional anionic-stabilised water-borne urethane dispersions and acrylic emulsions. Therefore, these polymers can be blended with standard PUD or acrylic emulsions to improve hydrophobicity, increase renewable content or lower the VOC of the coating system.

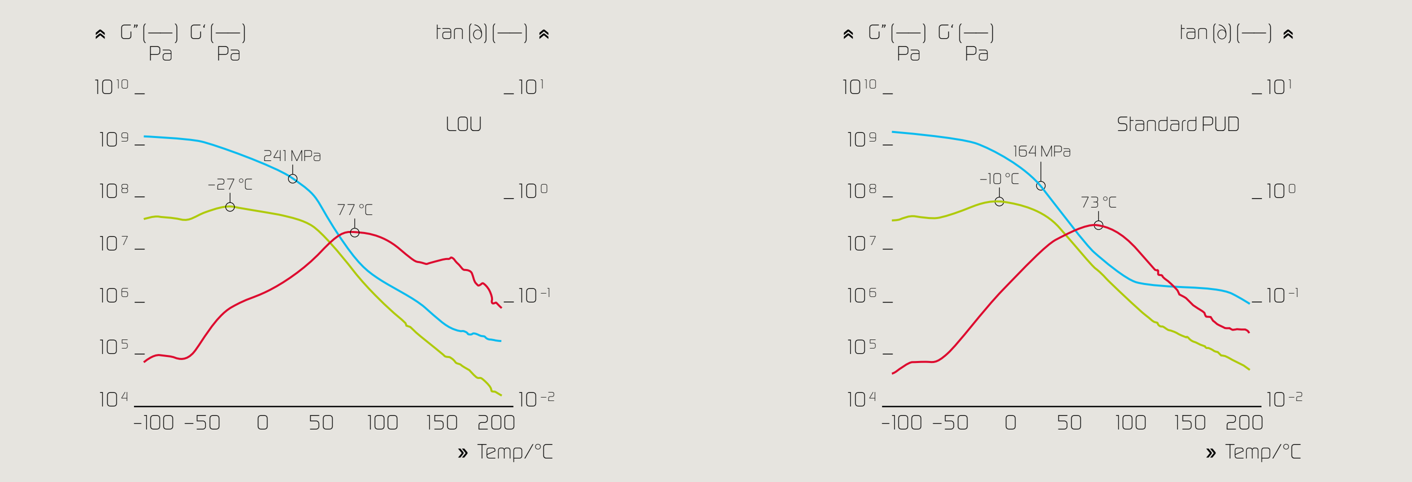
The durability of several coating systems (their capability to retain the original gloss on wood substrates after outdoor exposure for six months) is shown in *Figure 4*. All oil-modified samples show better durability than a conventional PUD clear woodfinish product. Furthermore, all the oil-modified polymers described here are compatible with conventional acrylic emulsions and urethane dispersion resins. The scope of compatibility and their usefulness in new applications are under investigation.

ADVANTAGES OF BIO-BASED PRODUCTS SUMMARISED

Water-borne dispersions of several oil-modified urethane and acrylic polymers containing as much as 50% of components derived from vegetable oil are discussed. Incorporation of the renewable components in these polymers imparts better hydrophobicity, improved mechanical properties, outdoor durability and lower VOC to the final coating systems formulated from these polymers.

No basic physical or chemical properties are sacrificed by modifying the

Figure 1: Dynamic mechanical analysis of LOU and standard PUDs.



polymer backbone with incorporation of a high level of renewable material into the resin system. Polymers made by the technologies described here are compatible with conventional water-borne acrylic emulsions and urethane dispersions. Extension of these technologies to higher renewable content and their benefits in new applications are under further investigation.

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Figure 2: Gloss retention of LOU compared with standard PUD (applied as floor coatings).

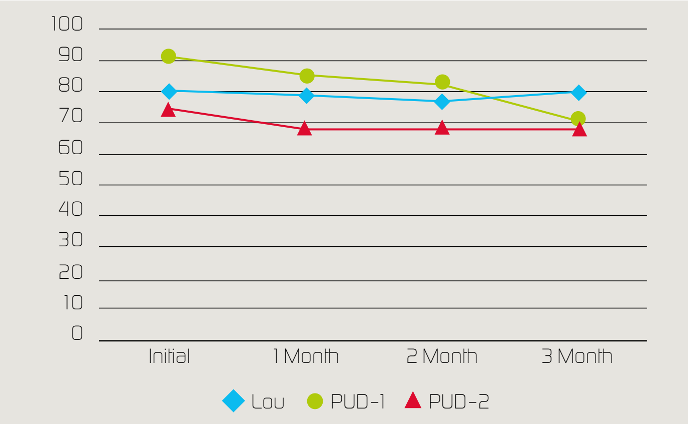
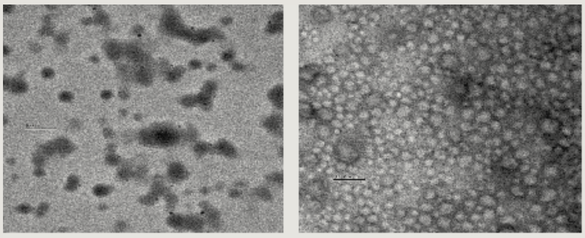
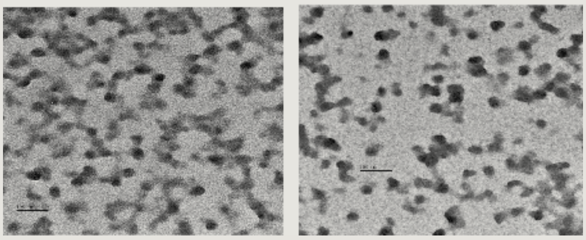


Figure 3: TEM photographs of soy-urethane and soy-acrylic polymers.



(a) HOU unstained

(b) HOU uruthenium-stained



(c) HOA unstained

(d) HOA uruthenium-stained

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> "The resins behave very much like self-crosslinking water-borne urethanes."
>
> Naser Pourahmady

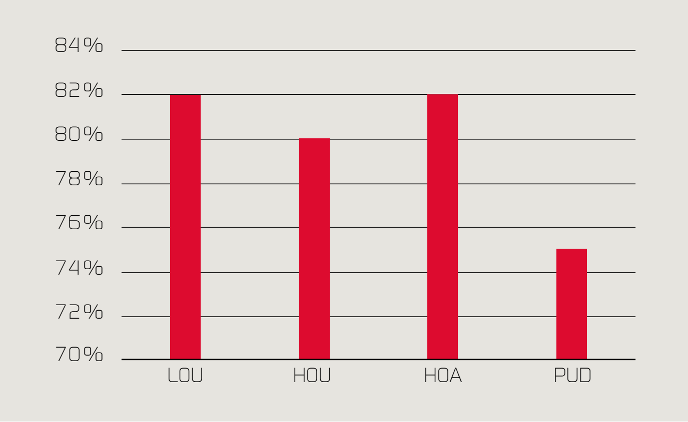
3 questions to Naser Pourahmady

To what extent does a formulation need to be adjusted when using water-borne crosslinking resins based on vegetable oil? *These self-crosslinking dispersion polymers are designed to be used as a drop-in for conventional acrylic emulsions or polyurethane dispersions. Some minor adjustments to formulation are always needed when a resin in formulation is changed, but our vegetable oil based dispersion resins behave very much like self-crosslinking water-borne urethanes.*

The share of vegetable oil in PUDs was increased from 25% to 50%. Where do you see the limit for a further increase? *The limitation is more in the performance side rather than the synthesis. The vegetable oil is considered to be the soft hydrophobic portion of the entire polymer system. The higher the level of oil, the better the hydrophobicity and softness, but you lose other mechanical properties. So, the limitation is in maintaining a balance of useful physical properties.*

According to your results, the resins are ideal for low VOC wood coatings. For which further applications do you see potential for these resins? *This technology is very suitable for textile binder and coatings, graphic arts, adhesives, and various industrial coatings. We are currently modifying the resin backbone to make them more useful for some of these applications.*

Figure 4: Gloss retention of bio-based and standard PUD coatings (formulated as clear wood finishes) after exterior exposure on wood panels for six months.



Source: Jenny Sturm - Fotolia.com

A CURE FOR WOOD PROTECTION

Water-based UV PUD finishes offer enhanced resistance properties. By Laurie Morris, Alberdingk Boley USA (ECJ 09/2016).

Factory-applied exterior woodfinishes are often based on acrylic emulsions or polyurethane dispersions. UV curable PUDs were evaluated as alternatives. The best showed the required high flexibility combined with high surface hardness. Retention of wood colour in QUV testing was much better than that of the commercial clear coatings used as controls.

Water-borne (WB) UV curable chemistry has shown significant growth in interior industrial wood markets because the technology provides excellent performance, low solvent emissions and increased production efficiency. These same advantages can be beneficial for factory-applied exterior applications including window and door frames, cladding and other mill-finished work.

These market segments conventionally use acrylic emulsions and polyurethane dispersions because they have excellent gloss and colour retention and demonstrate superior durability. In this study, polyurethane-acrylic resins with UV functionality have been evaluated in accordance with industry specifications for this market.

BENEFITS AND CHOICE OF UV CURED COATINGS

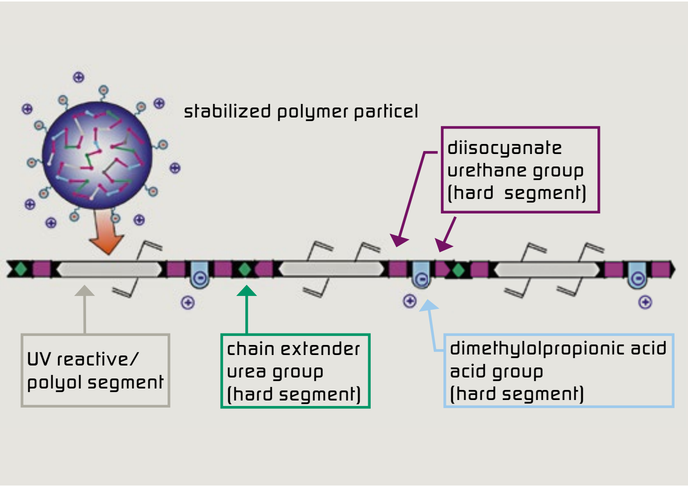
UV coatings offer the end user the benefits of outstanding chemical and scratch resistance, excellent block resistance, very low VOCs and a small equipment footprint with reductions in storage space. The properties of these systems compare favourably with two-component urethane systems without the complications of hazardous cross linkers and potlife concerns. The overall system is cost-effective because of increased production speeds and lower energy costs [1].

Water-borne (WB) UV coatings have many inherent advantages. While 100% solids UV oligomers are typically high in viscosity and must be thinned with reactive diluents, WB UV PUDs (polyurethane dispersions) have a low viscosity that can be adjusted with traditional WB rheology modifiers.

WB UV PUDs have an initially high molecular weight and do not build molecular weight during cure as dramatically as 100% solids UV coatings. Partly because they have little or no shrinkage during cure, WB UV PUDs offer excellent adhesion to many substrates.

The gloss of these coatings is easily controlled with traditional matting agents. These polymers can be very hard but also extremely flexible, making them ideal candidates for exterior wood coatings.

Figure 1: Chemistry of WB UV PUDs.



RESULTS AT A GLANCE

→ Factory-applied woodfinishes for exterior use are commonly based on acrylic emulsions or polyurethane dispersions. Both offer good gloss, colour retention and durability but with the acrylics there is a compromise between flexibility and hardness.

→ UV curable coatings offer significant advantages in terms of producing hard, low VOC coatings without the hazardous crosslinkers required for 2K polyurethane systems.

→ UV curable PUDs are especially advantageous in terms of obtaining finishes with sufficient flexibility for exterior wood applications yet a hard finish without difficulties in gloss control.

→ A number of UV PUDs were evaluated in clear exterior woodfinishes. The best of these showed the required flexibility combined with high surface hardness. Initial QUV tests showed that these clear coatings offered much better retention of the wood colour than the commercial 1K and 2K clear coatings used as controls.

CHEMISTRY OF WB UV PUDS

Water-borne (WB) UV PUDs are made by incorporating UV functionality into the backbone of a PUD. A pre-polymer is produced by reacting a polyol and a UV acrylate with a stoichiometric excess of an aliphatic isocyanate (*see Figure 1*).

Dimethylolpropionic acid, an anionic stabilising agent, is used to build functionality into the polymer chain. An amine is used for neutralisation. Then the pre-polymer is dispersed in water and chain extension is carried out to increase molecular weight.

These UV PUDs can be polyether, polyester and/or polycarbonate based. There is a large selection of UV acrylates available with varying backbones and functionalities. The choice and amount of the UV functional material used affects the final crosslink density of the coating. There are also several processing options that affect the final polymer performance.

Modifications to WB UV PUDs are made for various reasons. Acrylic dispersions can be added to improve exterior durability and reduce costs. Surfactants can be added to improve shelf stability. Emulsified UV acrylates can be added to adjust drying properties. Because different types of WB UV resins can provide different performance parameters, technologies can be combined to optimise the properties needed.

Unlike 100% solids UV coatings, WB UV coatings are stable dispersions of colloidal particles that must coalesce to form a continuous film before UV cure can take place. This process of film formation takes place in several stages beginning with water evaporation. The schematic in *Figure 2* provides further details of this process.

LIMITATIONS OF TRADITIONAL EXTERIOR WOOD COATINGS

Environmentally friendly exterior wood coatings are traditionally made from water-borne acrylic dispersions and polyurethane dispersions. Both one-component (1K) and two-component (2K) urethane coatings are used, with the 2K coatings providing the best performance properties.

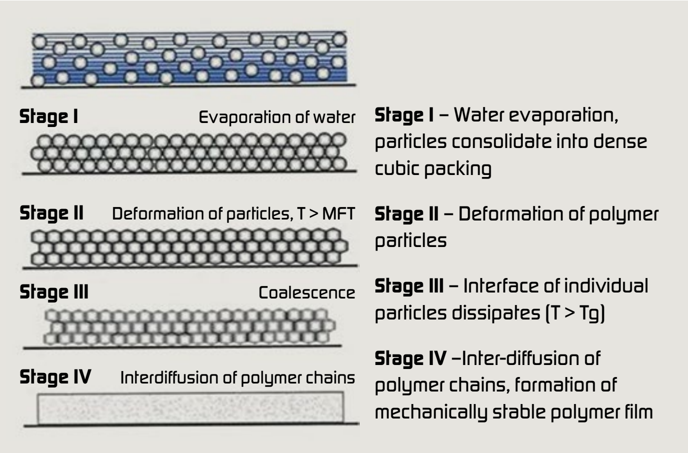
WB acrylic dispersions have excellent UV stability and very good weathering resistance. However, they can have the disadvantage of poor flexibility [2]. Flexibility is essential for an exterior wood coating because wood is a dimensionally unstable substrate.

Flexibility can be improved by lowering the glass transition temperature of the acrylic dispersion but this can have an adverse effect on block resistance [2], scratch resistance, mar resistance and dirt pick-up resistance. Modification of the acrylic dispersion with a PUD will increase flexibility yet improve the scratch and mar resistance.

INITIAL EVALUATION OF UV RESIN BLENDS

The first phase of this project was to identify the best UV technology in combination with other resin technologies with excellent exterior performance for exterior industrial wood applications. The resin blends were evaluated for hardness development, blocking resistance, water resistance, cure response and QUV resistance. The resins tested are described in *Table 1*. Coatings were formulated using both UV absorber and hindered amine light stabiliser (HALS). All coatings were tested using two different photoinitiator combinations, as shown in *Table 2*. In this phase of testing all coatings were cured at 800 mJ/cm^2. The coatings with only alpha hydroxy ketone photoinitiator were cured using a mercury lamp. Coatings with both alpha hydroxy ketone and acyl phosphine oxide photoinitiator were cured using both a mercury lamp and a gallium lamp.

Figure 2: Stages in initial drying (before UV cure) of UV-PUD dispersions.



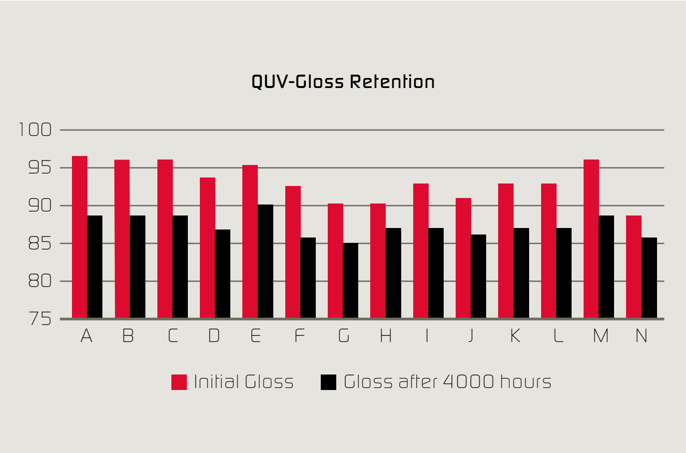
Stage I – Water evaporation, particles consolidate into dense cubic packing

Stage II – Deformation of polymer particles

Stage III – Interface of individual particles dissipates (T > Tg)

Stage IV –Inter-diffusion of polymer chains, formation of mechanically stable polymer film

Figure 3: Gloss retention in QUV testing of initial formulations over white ceramic substrate.



PHYSICAL TEST METHODS SUMMARISED

Hardness development was tested by making a 150 micrometre (µm) draw down on a glass panel. Air drying was for 10 minutes followed by force drying for 10 minutes at 50 °C. Koenig hardness was measured before cure then one hour and three days after cure.

Block resistance was tested by making a drawdown on a "3B-H" Leneta chart using a 3 mil (75 µm) solid bar applicator, with drying as above before UV curing.

Two strips were cut off 1" x 4.25" (2.5 x 11 cm approx.) perpendicular to the draw down direction. They were placed face to face (i.e., coatings touching) and a 1000 gram weight was put on top of duplicate samples. Samples placed on a glass plate were put in a 50 °C oven for one hour. Block resistance was rated from 0 to 10 after removal from the oven (0: Pieces are 100% completely sealed; 10: Pieces fall apart with little or no effort upon shaking).

The same drawdown and curing procedure was used for the water resistance tests. After 24 hours, a small glass vial of water was inverted on the surface of the coating over the black section of the card.

After 24 hours the water was removed and the surface wiped dry. Blushing and blistering were checked visually and rated on a scale of 0 to 5 with 5 being no effect and 0 being complete destruction of the film.

HOW CURING RESPONSE WAS EVALUATED

The cure response is measured by comparing the FTIR absorbance peaks of the C=C bond (810 cm^{-1}) and C=O bond (1730 cm^{-1}) before and after curing. The C=C bond reacts during UV exposure; the C=O bond does not react [3].

Make a 3 mil drawdown on a "3B-H" Leneta chart. Air dry for 10 minutes then force dry for 10 minutes at 50 °C. Using FTIR, measure and record the IR absorbance at 810 cm^{-1} and 1730 cm^{-1}. Cure the charts and then re-measure and record the IR absorbance at 810 cm^{-1} and 1730 cm^{-1}. Calculate the percent cure:

The relative concentration of UV cured group (%) is determined by the following equation:

$$\frac{[A]^{UV}_{810} / [A]^{UV}_{1730}}{[A]^{\circ}_{810} / [A]^{\circ}_{1730}} \text{-X } 100$$

Figure 4: Colour change after QUV testing of initial formulations over white ceramic substrate.

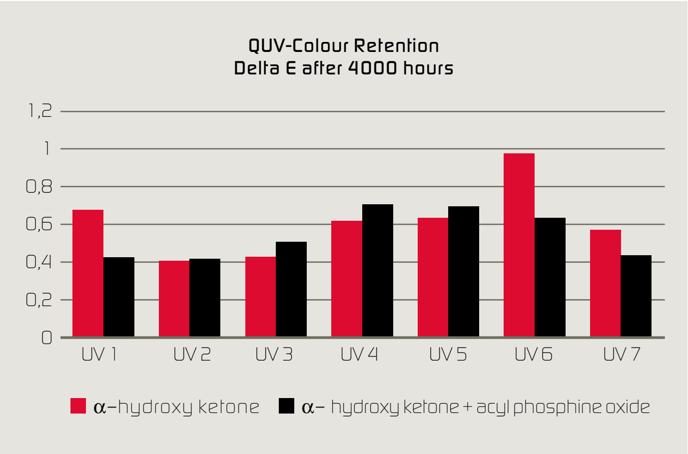


Table 1: Description of the different resins tested.

Reference	**UV Type**	**Modification Type**
UV 1	UV PUD Hybrid 1	Self X-linking resin with low MVTR*
UV 2	UV PUD Hybrid 2	Self X-linking resin with low MVTR
UV 3	Emulsified UV acrylate	Self X-linking resin with low MVTR
UV 4	UV PUD Hybrid 1	Self X-linking resin with high MVTR
UV 5	UV PUD Hybrid 2	Self X-linking resin with high MVTR
UV 6	Emulsified UV acrylate	Self X-linking resin with high MVTR
UV 7	UV PUD	n/a

* MVTR = Moisture Vapour Transmission Rate

Figure 5: Initial gloss loss evaluation after 4000 hours of QUV exposure (second phase, coatings tested on poplar panels).

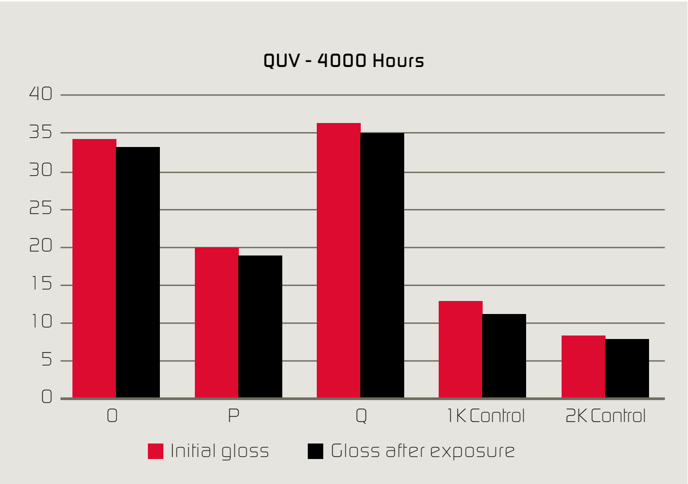
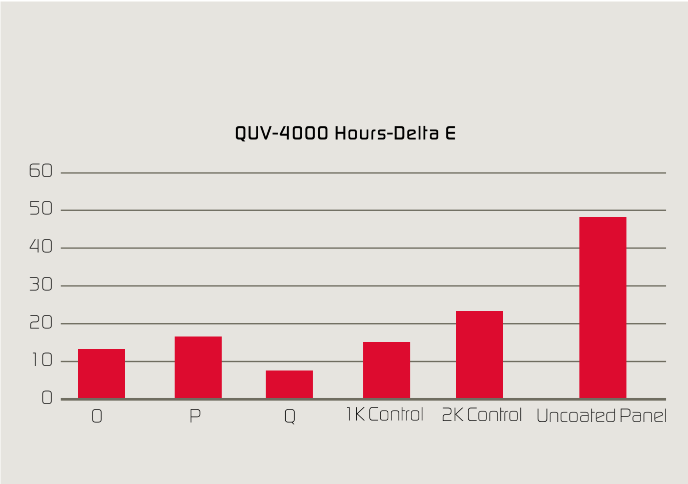


Figure 6: Initial colour change evaluation after 4000 hours QUV exposure (second phase, coatings tested on poplar panels).



Where $[A]^{\circ}_{810}$ is the IR absorbance at 810 cm^{-1} before UV irradiation, $[A]^{\circ}_{1730}$ the IR absorbance at 1730 cm^{-1} before UV irradiation, $[A]^{UV}_{810}$ the IR absorbance at 810 cm^{-1} after UV irradiation, and $[A]^{UV}_{1730}$ the IR absorbance at 1730 cm^{-1} after irradiation [3].

ARTIFICIAL WEATHERING TEST PROCEDURE

Make a 4 mil (100 µm) drawdown on a white ceramic tile. Air dry for 10 minutes then force dry for 10 minutes at 50 °C. Cure. Wait seven days before testing. Record the CIELab colour data for each tile using a BYK Gardner "Color-guide" sphere. Record the 60° gloss for each tile using a BYK Gardner "micro-TRI-gloss" meter.

Tiles were placed in the QUV cabinet with type 340 UVA bulbs and the cabinet was set for four hours of UV light followed by four hours of condensation. Cycles were run for 4000 hours then colour change (delta E) and gloss loss were determined.

RESULTS OF INITIAL EVALUATION SUMMARISED

- Block resistance and water resistance were excellent on all samples. However, significant differences were found in Koenig hardness and cure response, as shown in *Table 2*.
- All samples also showed excellent QUV results with minimal gloss and colour changes after 4000 hours of exposure (see *Figures 3* and *4*).
- The addition of acyl phosphine oxide photoinitiator did not significantly affect the properties of the coatings (see *Table 2*). Consequently, alpha hydroxy ketone photoinitiator alone was used in the later tests.
- UV 3 was eliminated from the study due to production difficulty, and UV 4, UV 5 and UV 6 due to low cure response and hardness.
- UV 1, UV 2 and UV 7 were thus included in Phase 2 testing.

PHASE 2 TESTS CARRIED OUT TO INDUSTRY STANDARDS

In Phase 2, coatings were evaluated according to the specifications outlined in the American Architectural Manufacturers Association AAMA 653-14, Voluntary Performance Requirements and Test Procedures for Organic Coatings on Wood and Cellulose Composite Substrates.

This specification covers factory-applied coatings intended for service in exterior environments [4]. QUV resistance testing was repeated on a poplar wood substrate. Coatings were formulated using traditional defoamers, surface tension modifiers, wax emulsion and rheology modifiers. The solids by weight of the coatings was controlled with water. Details are summarised in *Table 3*.

PANEL PREPARATION AND TEST PROCEDURES SUMMARISED

Unless otherwise stated in the AAMA 653-14 specification, all panels were prepared by the following procedure:

- Spray approximately 4 wet mils (100 µm) of coating over a 4 x 6 inch (10 x 15 cm) unstained Southern yellow pine panel.
- Air dry for 10 minutes.
- Force dry for 10 minutes at 50 °C.
- Cure with a mercury lamp at 800 mJ/cm^2.
- Sand with a 3M "Superfine Sanding Sponge".
- Repeat all steps except final sanding.

Unless otherwise stated in the AAMA 653-14 specification, all panels had the cut edges sealed with a 2K 100% solids urethane sealer. All sides of the panels were coated. All panels were aged for seven days before testing was performed.

Wet adhesion, dry adhesion, impact resistance and four environmental resistance tests were carried out (hydrochloric acid, mortar, detergent and humidity). All properties were rated on a scale of 0 – 5 with 0 being complete film destruction and 5 being no effect on the film. All three coatings obtained the maximum rating of 5.

Fifteen cycles of a cyclic humidity chamber/freezer test were performed, and all three coatings also passed this test.

Panels for the QUV testing were prepared in the same way as the AAMA panels except that the substrate was 2 x 4 inch (5 x 10 cm) poplar panels. QUV cycles were performed as in Phase 1. A commercially available 1K and 2K control and an uncoated panel were included for reference.

INITIAL TESTS SHOW VERY GOOD RESULTS

The three experimental samples passed the testing indicated in AAMA 653-14. This is a good indication that these coatings will perform well in an exterior environment.

Table 2: Summary of formulations; formulation pairs differ only in the absence or presence of the second PI.

Ingredients	**A/B**	**C/D**	**E/F**	**G/H**	**I/J**	**K/L**	**M/N**
UV 1	133.57	0	0	0	0	0	0
UV 2	0	129.37	0	0	146.87	0	0
UV 3	0	0	117.18	0	0	134.68	0
UV 4	0	0	0	151.07	0	0	167.86
UV absorber	0.84	0.84	0.84	0.84	0.84	0.84	0.84
HALS	0.84	0.84	0.84	0.84	0.84	0.84	0.84
PI - Alpha hydroxy ketone	1	1	1	1	1	1	1
PI - Acyl phosphine oxide	0/1	0/1	0/1	0/1	0/1	0/1	0/1
Water	34.5	38.4	55.89	17	21.2	33.39	0.21
Test results							
Koenig hardness (after 3 days)	117/115	17/116	115/121	74/83	87/101	86/64	190/192
Cure response (% C=C bond cure)	98.6/98.2	98.6/99.2	100.0/99.6	88.3/83.7	87.8/86.5	94.6/96.9	95.3/98.0

“Because they cure in seconds they offer the manufacturer a faster production time.“

3 questions to Laurie Morris

What are the main advantages of the newly developed WB UV PUD wood finish? *WB UV PUDs provide excellent gloss retention, hardness and flexibility. They have superior adhesion due to their low shrinkage. Because they cure in seconds they offer the manufacturer a faster production time and the ability to package and ship their products immediately after cure.*

Why have WB UV PUD little or no shrinkage during cure? *Waterbased UV PUDs have an initially high molecular weight and do not build molecular weight as they cure as much as 100% solid UV coatings which are made from monomers and oligomers.*

Can these systems be cured by using LEDs? *Because LED lamps emit radiation in the UV A range, 315 – 400 nm, they provide excellent through cure but lack surface cure. To achieve surface cure, radiation in the UV C range (200 – 280 nm) is needed. LED lamps that emit in the UV C range are being developed but are not yet commercially available.*

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The cold crack cycle test and the humidity test are extreme environments for wood and wood coatings. Wood swells during periods of high humidity and shrinks during periods of low humidity. This instability puts extreme stress on the coating. Coatings that do not have the flexibility needed to move with the substrate can show whitening or cracking when exposed to this punishing environment.

The Phase 1 QUV testing over white ceramic substrate was completed to determine the yellowing properties and gloss retention of the coatings. The Phase 2 QUV testing over unstained poplar substrate was completed to determine the ability of the coatings to protect against the degradation of the wood substrate.

The wood panels coated with the WB UV products show much less color change than the commercial controls but all of the panels show significant color change after 4000 hours of QUV exposure. In exterior industrial wood applications it is typical that the wood is first coated with a stain or an opaque base coat. Formulation Q had the best performance in this study and it is expected that this formulation will do well over a stain in the exterior exposures. It is not recommended that any clear coating should be applied without a stain or base coat for an exterior wood application.

EXPOSURE TESTS ON-GOING TO CONFIRM GOOD PERFORMANCE

Water-based UV coatings have become the industry standard for interior industrial wood applications. The excellent hardness, flexibility and chemical resistance of these coatings make them good candidates for exterior industrial wood applications.

The coatings tested show excellent humidity and cold crack resistance. They have very good gloss retention and are non-yellowing when exposed to UVA radiation. This technology can help to increase productivity and comply with VOC restrictions. Future work will focus on exterior exposures in South Florida, Arizona and North Carolina according to AAMA 653-14 specifications.

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Table 3: Formulations used in phase 2.

Ingredients	**O**	**P**	**Q**
UV 1	312.5	0	0
UV 2	0	302.7	0
UV 7	0	0	392.5
UV Absorber	2	2	2
HALS	2	2	2
Surfactant	1.4	1.4	1.4
Wax	12.1	12.1	12.1
Defoamer	1.4	1.4	1.4
Photoinitiator	2.3	2.3	2.3
Water	80.7	68.7	0.5
Rheology modifier	0.8	0.7	1
Total	**415.2**	**393.3**	**415.20**

LIKE CLOCKWORK

Big factories can coat up to 100,000 pencils a day. The pencils are pushed in a pipe-like case with paint. Surplus coating is then wiped off when they are extruded from the container. The process is repeated up to seven times.

Source: phanuwatnandee - Fotolia.com

LESS IS MORE

Only small amounts of coating are needed to coat a pencil – less than one gram is used apiece. The pencil has a long history – its first precusors were produced in 1565 in England.

Source: Deutsches Lackinstitut


Source: zhu difeng - Fotolia.com

BETTER THAN BLENDING

NMP-free acrylic polyurethane hybrid dispersion shows high performance. By Jennifer Long-Susewitz, BASF Corporation (published in ECJ 12/2016).

Polyurethane dispersions and acrylic emulsions are often blended to achieve the performance desired for furniture and floor finishes. However, poor compatibility may impair performance. A new NMP-free acrylic polyurethane hybrid dispersion provides excellent physical and chemical resistance for interior wood finishes.

Government regulations and consumer concern are major drivers for the reduction of volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) in coatings, particularly those used over wood substrates where these materials can leach out over time.

Two technologies remain dominant for wood coatings in North America. The most widely used technology for higher end furniture is that of solvent-based nitrocellulose lacquers and acid-catalysed conversion varnishes. Due to the regulations and concerns already mentioned, UV and water-based coatings are on the rise in the North American market [1].

ADVANTAGES AND LIMITATIONS OF TWO WATER-BORNE SYSTEMS

Acrylic emulsions and polyurethane dispersions (PUDs) are two of the technologies competing with conventional solvent-based coatings, especially in furniture and flooring applications where emissions into consumers' homes can occur. There are advantages and disadvantages with both acrylic emulsions and PUDs. Acrylic resins are lower in price than PUDs due to processing and raw material costs. However, many acrylics contain surfactants which have the potential to bloom to the surface, so reducing the gloss of the coating. PUDs offer superior abrasion resistance because of intermolecular hydrogen bonding and can be produced without surfactants, allowing the coating to reach a high gloss level.

Also, because of the chemical bonding of hydrogen to water, which is considered to be a plasticising effect, PUDs have a relatively low minimum film forming temperature (MFFT) in relation to their glass transition temperature (Tg), so less cosolvent is required for proper coalescence and final film hardness is not reduced, as it would be within an acrylic system [2].

Unfortunately, many PUDs contain N-methyl pyrrolidone (NMP), a solvent attracting increasing attention from environmental regulators in California and the European Union for its inhalation hazards. NMP is used in the production process to assist the incorporation of dimethylol propionic acid (DMPA), a crystalline carboxylic acid polyol, into the backbone of the polymer.

Due to NMP's high boiling point (202 to 204 °C), the hazardous solvent cannot be removed from the polyurethane dispersion. Typically, the level of NMP present in PUDs is between 10% and 15% [4].

HYBRID SYSTEM RESOLVES PROBLEMS WITH BLENDS

To improve the properties of the individual acrylic and PUD systems and also to reduce the cost of a pure PUD system, it is common practice to blend the two. However, the results are not what one would expect. The properties are actually of lower quality than predicted from the 'rule of mixtures' due to incomplete compatibility between acrylic and PUD systems [3].

The incompatibility results in phase separation of the polymers, which can cause internal strains resulting in inadequate coalescence. This leads to a coating with higher than desired permeability and reduced cohesive strength [2]. New technology has been developed to address regulatory concerns associated with NMP and the unpredictable performance of blending conventional acrylics with PUDs. Hybrid acrylic and

Table 1: Calculated VOCs of prepared coatings.

Coating type	Calculated VOC
Hybrid	270 g/l
Acrylic	214 g/l
Blend	211 g/l

RESULTS AT A GLANCE

→ Polyurethane dispersions have been widely used in the furniture and flooring industry and are often blended with an acrylic resin to achieve the desired coatings performance properties. However, problems with compatibility between the two components often result in performance which is not as good as expected.

→ There are increasing regulatory concerns regarding the use of NMP (N-methyl pyrrolidone) in the production of polyurethane dispersions.

→ Tests are reported on a new NMP-free acrylic polyurethane hybrid dispersion which achieves the excellent abrasion resistance, high hardness and chemical resistance desirable for coatings used on flooring and higher quality furniture.

PUD polymers have been processed without the use of NMP; instead, acrylic monomers are used as the solvent. These monomers contain functional groups which react with the available groups on the urethane, so allowing covalent grafting of the acrylic onto the urethane [5].
To address market trends and consumer and regulatory demands, BASF has developed an NMP-free acrylic polyurethane hybrid. The performance strengths of this product for use in furniture and flooring coatings will be examined and compared with a self-crosslinking acrylic resin and a physical blend of a self-crosslinking acrylic resin with a PUD.

TEST COATINGS AND SUBSTRATES

Three different coating systems were tested in clear coat formulations. They are the hybrid, acrylic, and blend (1:1 blend on a solids basis of the acrylic and a PUD). The calculated VOC of each coating is presented in *Table 1*. For all tests other than hardness development, after wet application the coating was allowed to dry for seven days in ambient laboratory conditions prior to evaluation.

For chemical resistance and adhesion to wood tests, the coatings were brush applied to sanded Hard Maple veneer at an application rate of 100 g/m^2. For adhesion to metal as well as flexibility, the coatings were drawn down to obtain a dry film thickness in the range of 1.8 – 2.0 mils (45 - 50 µm) on cold rolled steel treated with "Bonderite 1000" conversion coating.
Hardness was tested on glass with the coatings drawn down at 120 wet µm. Abrasion resistance, also tested on glass, was drawn down at a wet film thickness of 200 µm.

TEST PROCEDURES SUMMARISED

The polymers were evaluated for performance properties relevant to coatings that would be applied to furniture and flooring applications.
Adhesion was tested by using a razor blade to cut an X scribe into the coating. Wet and dry adhesion were tested by the tape pull method, ASTM D 3359, using a standard tape. Wet adhesion was performed after a one hour water spot test over the X scribe. Ratings are 0A – 5A, where 5A is no loss of adhesion and 0A is complete adhesion loss.
Chemical resistance was evaluated as a spot test where the chemical saturates a filter paper which is then covered with a watch glass to prevent evaporation. Exposure times are eight hours to coffee, water, and mustard; one hour to 70% isopropyl alcohol (IPA), 100% ethyl alcohol, "Formula 409" cleaner, 5% "Palmolive" brand dish detergent solution, and "Betadine" (povidone-iodine). Hardness on glass was measured by pendulum at one and seven days and reported in number of oscillations. Measurements made in triplicate were averaged. Pencil hardness was also performed on the same wood panels as used for chemical resistance.
Flexibility was evaluated on cold rolled steel by carrying out both direct and reverse impact resistance tests. The impact ratings are reported in pounds when there is no damage or adhesion loss of the coating. Conical mandrel bend was also performed, fast and slow, according to ASTM D 522 – 93a.
Abrasion resistance was tested by "Taber Abrader" using 1000 gram weights and CS-17 rotating stones. The stones were reconditioned every 250 cycles. Measurements were taken at 500 and 1000 cycles and reported as milligrams of coating lost.

Figure 1: Hardness development measured by the König pendulum hardness test.

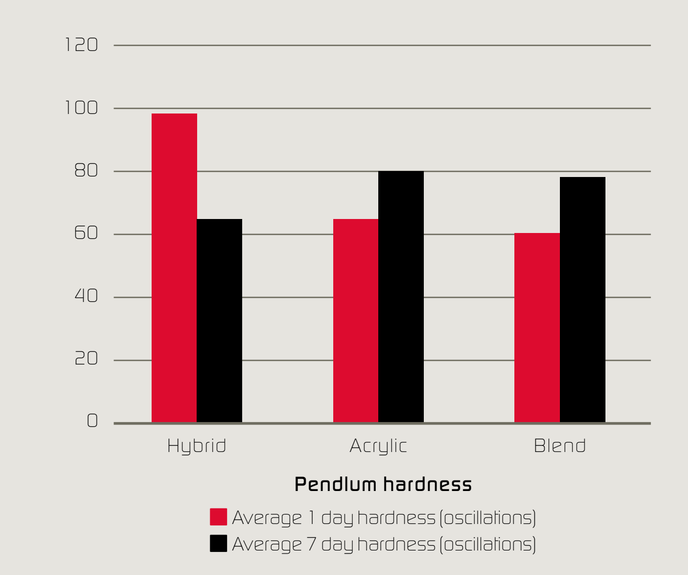
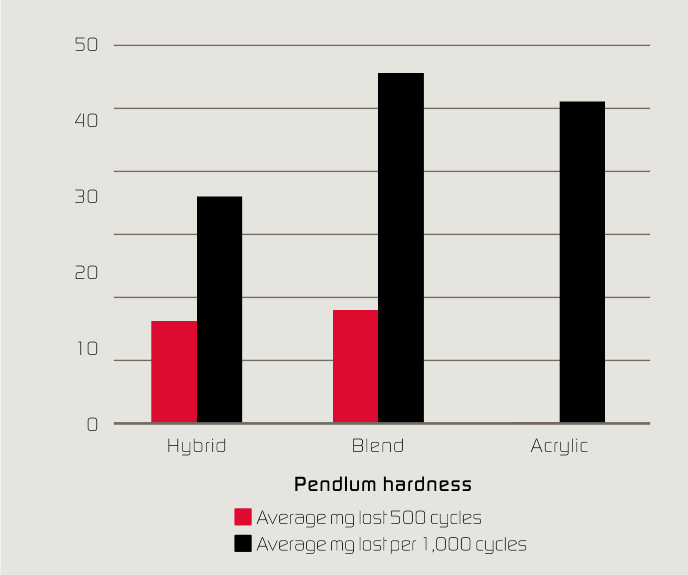


Figure 2: Abrasion resistance (low loss = higher performance).



HYBRID ADHESION IS GOOD OVER MOST SUBSTRATES

Adhesion of a coating to a substrate is critical. Without proper adhesion, the coating is less able to do its job of protecting a substrate from damage and wear. Wet and dry adhesion tests were performed on Hard Maple, Red Oak, and Cherry veneer. The results can be seen in *Table 2*.

After analysing the results of the adhesion test, it should be noted that the hybrid does not exhibit wet adhesion to maple. Hard Maple may exhibit difficulty with bonding; however, Hard Maple can have satisfactory bonding properties as long as the bonding conditions are well controlled [6].

Sanding conditions can also affect the adhesive nature of the wood; different grit sandpapers may be used to improve mechanical adhesion of a coating to wood substrates.

The adhesion to Cherry and Oak, however, make this a very viable product for use in furniture and flooring applications. It is worth noting that the formulation used is not completely optimised and that further optimisation has the potential to increase adhesion to these species.

HIGH RESISTANCE TO STAINS AND SOLVENTS

There are many possibilities of chemicals to choose when evaluating a coating's resiliency towards them. In this study, the selection was narrowed down to eight. Performed as a spot test, the exposure times, ratings, and reasoning for the rating are shown in *Table 3*.

(Rating is 0 - 4, 0 = best, 4 = complete destruction of the coating. The difference between 0 and 1 is negible, coffee staining was extremely minimal, where, unless an observer saw the spot himself before evaluation, he would not see the actual stain afterwards.)

The results of chemical resistance testing show the hybrid generally outperforms the acrylic/PUD blend. Also notable was a complete recovery of the hybrid's initial softening after exposure to 70% isopropyl alcohol and 100% ethyl alcohol when rechecked at 24 hours.

HYBRID SHOWS ENHANCED HARDNESS/FLEXIBILITY BALANCE

Pendulum hardness evaluates the hardness of a coating by measuring the stopping time of a pendulum put to motion on the coating. Therefore, the viscoelastic conduct of the coating governs its hardness. When the motion of the pendulum starts, the steel balls that rest on the coating's surface roll and put pressure onto it.

The harder and less elastic the coating is, the less damping effect it will have on the pendulum; that is, the longer the pendulum will continue to oscillate. In this case, hardness development was measured at one and seven days, the results being shown in *Figure 1*.

It can be seen that the hybrid exhibits early hardness development along with high final hardness, as measured by both pendulum and pencil hardness. This shows that the coating cures quickly, allowing for faster stackability or replacement of furniture if used for flooring applications. It also appears that the hybrid would be less viscoelastic than the acrylic or blend; however, the flexibility tests suggest this is

Table 2: Wet and dry adhesion ratings on various substrates.

Coating type	**Dry on maple**	**Wet on maple**	**Dry on oak**	**Wet on oak**	**Dry on cherry**	**Wet on cherry**
Hybrid	5A	0A	5A	3A	5A	3A
Acrylic	5A	5A	5A	5A	5A	5A
Blend	5A	5A	5A	5A	5A	5A

Table 3: Chemical resistance to solvents, cleaning and staining agents.

Product/ coating	**Mustard (8 hours)**	**Coffee (8 hours)**	**Water (8 hours)**	**70% IPA (1 hour)**	**100% ethanol (1 hour)**	**Formula 409 (1 hour)**	**5% Palmolive (1 hour)**	**Betadine (1 hour)**
Hybrid	3 staining	1 staining	0	2 softening	3 softening	0	0	0
Acrylic	2 staining	0	0	1 softening	2 softening	0	0	2 staining
Blend	3 staining	0	0	4	4	1	0	2 staining

Table 4: Pencil hardness and flexibility measured by both impact resistance and mandrel bend.

	Pencil hardness	**Impact Resistance**	**Mandrel Bend - Fast**		**Mandrel Bend - Slow**	
		Direct Pass (lbs.)	Distance to Break	Elongation	Distance to Break	Elongation
Hybrid	H - 2H	120	0 mm	32%	0 mm	32%
Acrylic	HB	50	0 mm	32%	0 mm	32%
Blend	F *	140	0 mm	32%	0 mm	32%

* F is a hardness grade between HB and H, i.e. slightly harder than HB.

not the case. Flexibility tests are used to evaluate a coating's ability to resist cracking. Impact resistance is a good test for assessing a coating's capacity to avoid cracking and peeling from the substrate when it is exposed to a falling weight which causes a deformation.

This is especially important in applications related to the flooring industry, where a substrate is commonly subjected to falling objects. Bend tests, such as the mandrel bend, give an indication of the elongation of the coating and its adhesive strength when exposed to bending stresses. The results of these tests are presented in *Table 4*.

The hybrid is shown to pair high flexibility with high hardness, making it an excellent choice for use in wood coatings. It is hard enough to be stackable yet flexible enough to expand and contract with the wood.

HYBRID GIVES BEST ABRASION RESISTANCE

For flooring applications it is particularly important that a coating should offer protection against abrasion and scratches. One of the most common tests for evaluation abrasion resistance is the "Taber Abraser". *Figure 2* presents the data obtained from this test and the results are reported as the wear index of the coating: that is, the weight loss for the amount of revolutions made under a specified load of 1000 grams using a specific abrading stone.

It can be seen that the acrylic resin exhibits very poor abrasion resistance. Acrylics are often blended with a PUD in order to increase the abrasion resistance of a coating for flooring applications, and that is seen here in *Figure 2*. However, the hybrid, because of its uniformity, exhibits superior abrasion resistance to the physical blend making it an excellent candidate for flooring applications.

HYBRID GENERALLY OUTPERFORMS BLEND

It must first be noted that the clear formulation for the hybrid is not fully optimised. Further optimisation of the formulation presents the opportunity to increase performance properties.

The hybrid is made without NMP to adhere to new legislature and consumer demands. It outperforms a physical blend of an acrylic and PUD because there are no issues with incompatibility, which can lead to weak spots in the final film.

The hybrid exhibits superior abrasion resistance, hardness paired with flexibility and chemical resistance. These performance properties present opportunities for this new material to be used successfully in furniture and flooring applications.

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> "The final properties of an acrylic-PUD hybrid or blend depend upon the type and amount of acrylic emulsion used."

3 questions to Jennifer Long-Susewitz

What is meant by "self-crosslinking acrylic resin? *A self crosslinking acrylic resin is one that has all the reactive components already present in the polymer, which are long-term storage capable but will react when exposed to the right conditions – high temperature, change of pH or upon evaporation of water. This chemical reaction between the reactive components is referred to as cross linking. Cross linking usually occurs after the inter-diffusion step of polymer chains during film formation. This leads to improved chemical and mechanical properties in the system.*

How limiting is the use of acrylic monomers as solvents according to the ratio of grafting acrylic/PUD and resulting properties? *The final properties of an acrylic-PUD hybrid or blend depend upon the type and amount of acrylic emulsion used. Utilising different acrylic emulsions will enable tuning the properties of the eventual PUD. While making a blend of a PUD-acrylic emulsion, compatibility between the acrylic and PUD has to be considered.*

On maple the wet adhesion seems to be an outlier. How can that be explained? *Adhesion can be difficult to achieve on maple due to its intrinsic properties. This is explained in the adhesion section on page 42, also referenced to source 6.*


Source: Michael Drak - Fotolia.com

FINE-GRAINED ANALYSIS

Predicting changes to appearance and overall discolouration of wood. By Boris Forsthuber, Monika Ecker, and Gerhard Grüll, Holzforschung Austria (published in ECJ 04/2017).

Wood surfaces coated with (semi-) transparent coatings in exterior applications are subject to rapid discolouration. A novel feature-resolved colour measurement procedure has been developed which can be used to predict changes in the overall appearance, not just the average colour, as the wood ages. The effect of maintenance coatings was successfully predicted.

Wood is appreciated as a building material by many building owners, especially due to the pleasing texture and colour of the wood surface. Hence, wood is often used in applications where both technical and aesthetic requirements have to be fulfilled. Typical examples include windows, façades or wooden balconies. In order to retain the initial colour of wood, semi-transparent or even transparent coatings are preferred by customers. However, discolouration of the coated wood surfaces occurs almost inevitably. Here, the overall discolouration is mainly governed by the wood surface itself and can so far only be reduced and/or delayed by (semi-) transparent coating systems. The rate and extend of discolouration depends strongly on the light protective properties and colour tone of the wood coating. It is known that some forms of discolouration are more acceptable than others. Uneven discolouration might be perceived as particularly unpleasant by building owners. The current model of wood discolouration and protection discussed below is initially focused on fully exposed surfaces.

AIMS AND PRINCIPLES OF THE COLOUR PREDICTION MODEL

Wood surface discolouration during weathering is a photo-oxidative process that is induced by both UV and visible light in the presence of oxygen. The rate of discolouration is known to be increased with increasing temperature and humidity. The rate of discolouration of coated wood is very fast at the beginning of the exposure but becomes less as the exposure proceeds.

After a certain time, the discolouration reaches a steady state. Assuming that the coating is still fully functional at this point (no severe surface defects such as cracking/flaking) and has sufficient antifungal performance, the colour of the coated wood surfaces remains almost constant.

The aim of the visual prediction modelling is to give customers and architects a preview of the future appearance of wooden building elements even during the planning stage. This could help customers in the choice of the colour tone of the coating. Light coating colours or even transparent coating systems will probably undergo more severe colour changes than darker colours.

RESULTS AT A GLANCE

→ Wood surfaces coated with (semi-) transparent coatings in exterior applications are subject to rapid discolouration due to photo-oxidation, mainly because of discolouration of the wood surface beneath the coating.

→ A novel feature-resolved colour measurement procedure has been developed which shows the details of grain for these coated wood surfaces. Colour modelling of wood surfaces was then performed.

→ The model can predict changes in the overall appearance of the wood grain, not just the average colour, as the wood ages. Predictions agree closely with xenon exposure testing results. Natural weathering tests are currently being carried out.

→ A discolouration model of the visual effects of the application of maintenance coatings was developed.

→ Visual prediction of discolouration might help building owners and architects in choosing finishes for long lasting customer satisfaction.

Figure 1: Colour measurement of wood surfaces. Structural features such as annual rings are usually much smaller than the aperture size of a conventional spectrophotometer.

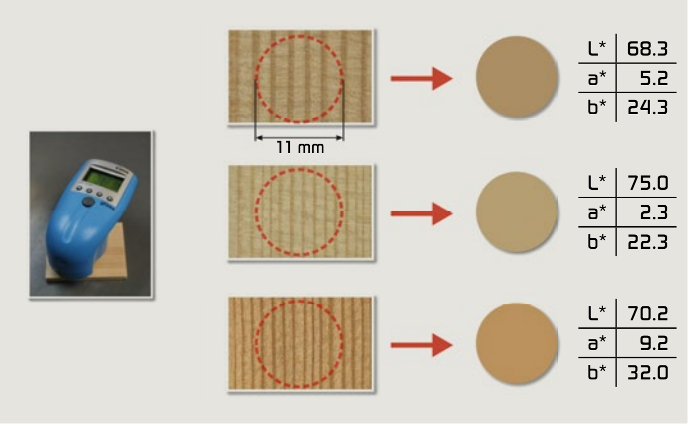


Figure 2: Rendered images of a transparently coated larch wood board at different exposure times: calculation of the colour based on values obtained during a xenon arc exposure trial.

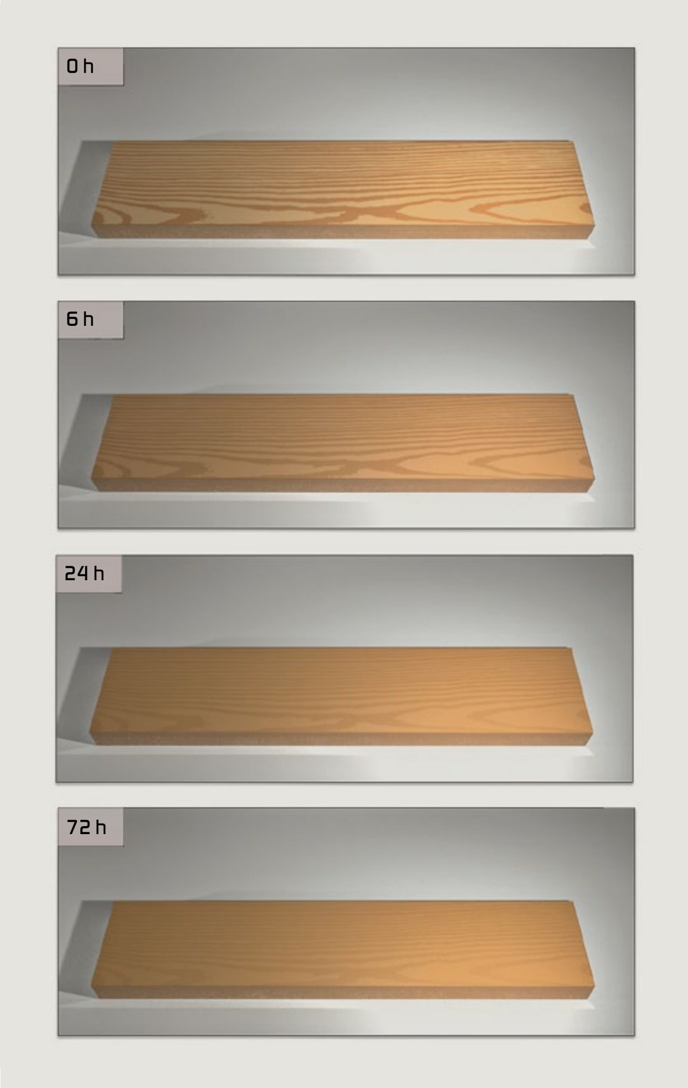
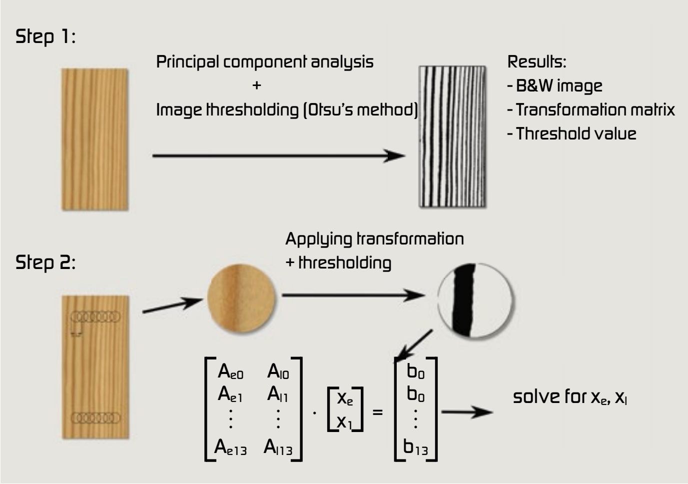


Figure 3: Novel colour measurement procedure to obtain feature-resolved colour values: Step 1: Generating transformation matrices; Step 2: Colour measurement at defined spots and subsequent application of transformation matrices on these spots.



$$\begin{bmatrix} A_{e0} & A_{l0} \\ A_{e1} & A_{l1} \\ \vdots & \vdots \\ A_{e13} & A_{l13} \end{bmatrix} \cdot \begin{bmatrix} x_e \\ x_l \end{bmatrix} = \begin{bmatrix} b_0 \\ b_0 \\ \vdots \\ b_{13} \end{bmatrix}$$

This might be especially disturbing if there are partially protected areas, which might lead to an uneven discolouration of the wooden building element, such as a façade. A further development of the discolouration model, that also takes partially exposed surface areas into account, might also assist architects during the design process to help ensure long-lasting customer satisfaction.

HOW THE DISCOLORATION MODEL IS CREATED

Colour measurements are usually performed using spectrophotometers with aperture sizes typically between 3 and 11 mm. This is sufficient for homogeneous surfaces such as metal or plastics. Wood, however, has a unique, inhomogeneous surface texture, which is one of the reasons for its appealing appearance.

The surface texture is mostly determined by annual rings, consisting of a lighter coloured early wood and a darker coloured late wood. These structural features are usually smaller than 3 mm and hence colour measurements usually result in mean values over both early- and late wood (*Figure 1*). Although these values are sufficient e.g. for determining the light stabilising performance of wood coatings, the values obtained are hardly suitable for visual representation of the wood surface colour. This task is rendered even more difficult by the fact that the rate of discolouration is different for early- and late wood.

In *Figure 2*, rendered synthetic images from the discolouration models developed are shown. The renderings show a board of European larch wood, coated with a transparent coating system at different exposure times. It is important to emphasise that the colours of the rendered image are calculated solely from colour measurement data and are not based on photographs. This is a major improvement compared to photographs or scans of the wood surface. Furthermore, these renderings can be made directly from a CAD dataset. Further development could also take into account areas partially protected from weathering such as those beneath canopies or other projecting building components.

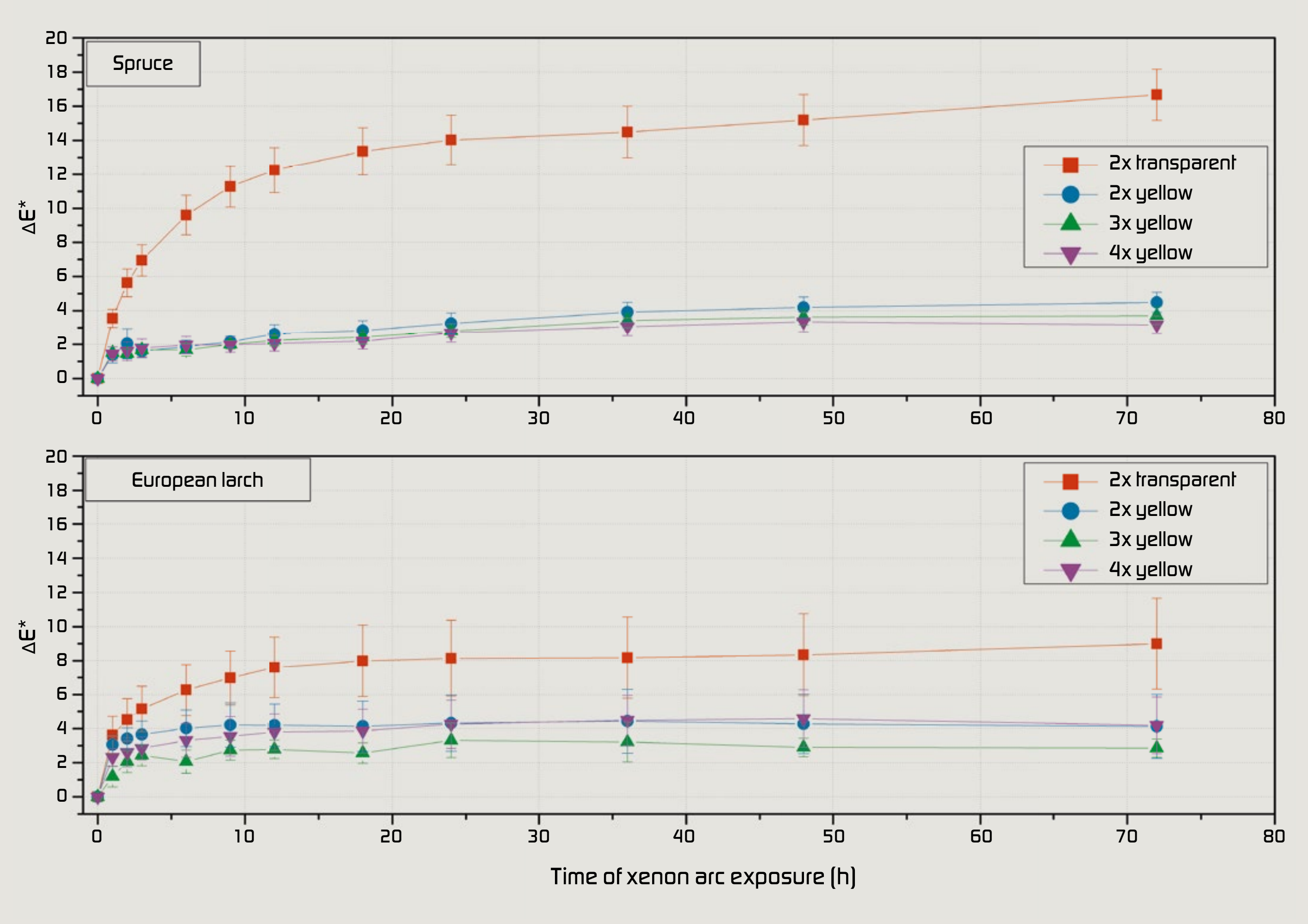
HOW FEATURE-RESOLVED COLOUR MEASUREMENT IS PERFORMED

As part of the EC FP7 funded “Servowood” project, which is aimed at improving service life prediction of wood coatings in exterior applications across various climatic zones, a new colour measurement procedure was developed. This procedure is based on colour measurements and image processing algorithms, from which wood textures with accurate colour values can be generated.

The main focus was on the different colours of early- and late wood as the most prominent features defining the wood surface. The colour measurement procedure developed is summarised in *Figure 3*. The first step is the colour measurement of the wood, using a conventional spectrophotometer with e.g. 3 mm aperture size (typically with D65 light source and 10° normal observer) on specified spots, using a measurement template.

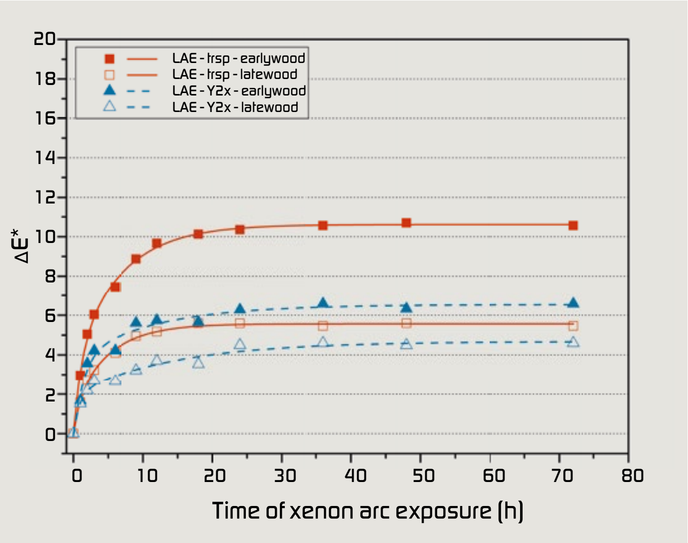
Next, the wood surface as well as the measurement template are scanned, using a conventional flatbed scanner. Subsequently, an im-

Figure 4: Discolouration of transparently and yellow coated larch and spruce wood samples during a xenon arc exposure trial. The yellow coating was applied with 2-, 3- and 4-layers (i.e., increasing dry film thickness).



age processing procedure is applied on the image of the wood surface in order to separate the early- and late wood areas. Finally, the early wood/late wood ratio for each measurement spot is calculated, again using an image processing procedure.
The result of this approach is a set of linear equations, where the colour of each measurement spot is expressed as a linear combination of the colour of the early- and late wood. By solving this set of linear equations, the colour of the early-and late wood can finally be obtained.

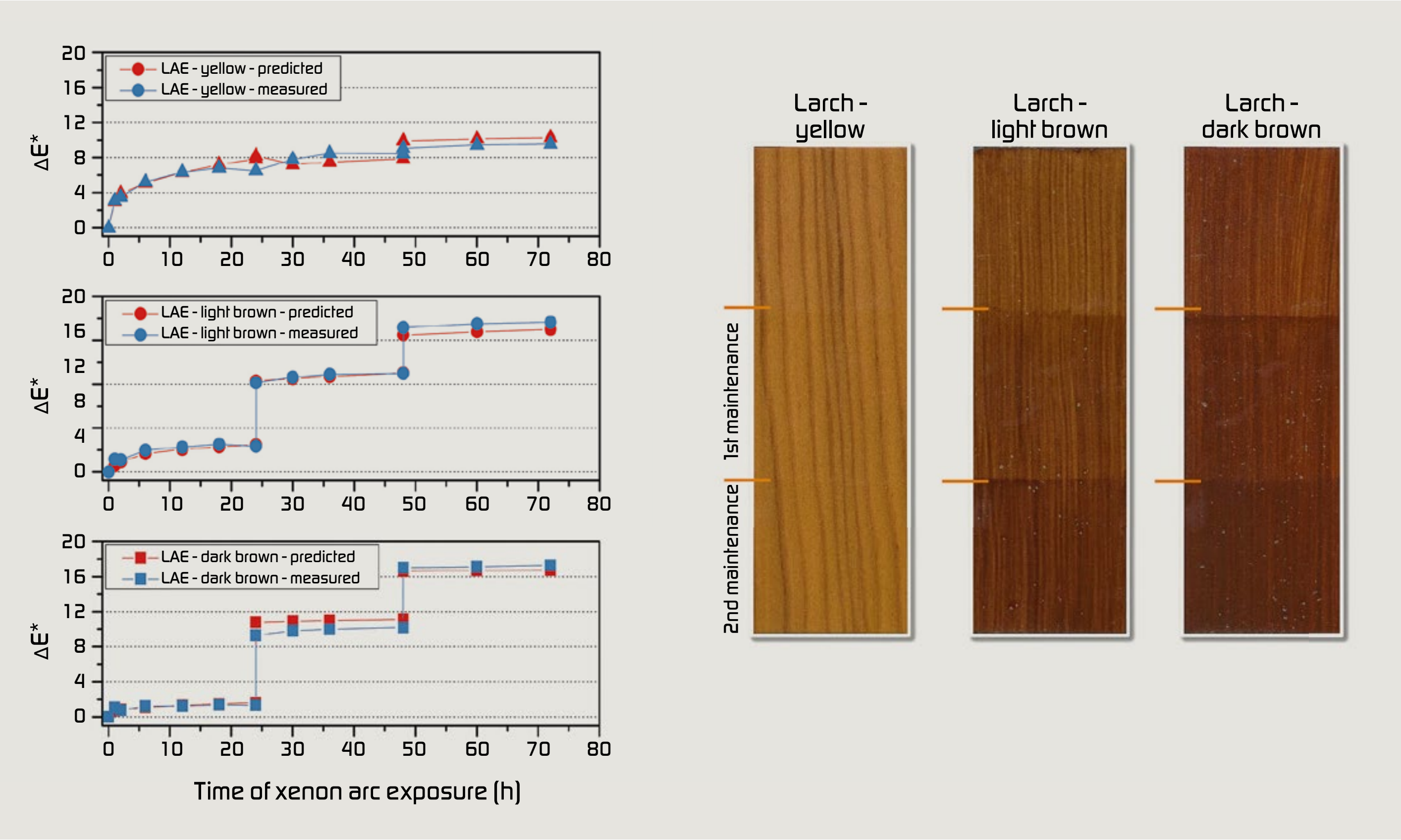
Figure 5: Differences in discolouration of the early- and late wood for transparently and yellow coated larch wood samples.



MODELLING OF THE WOOD SURFACE DISCOLOURATION

In order to estimate the surface colour of coated wood at specific irradiation dosages, laboratory xenon arc exposure trials with four different coating systems on two wood species (European larch and spruce) were performed. The coating systems were all based on the same guidance recipe and varied only in the colour tone (transparent, yellow, light brown and dark brown).
Three replicate samples were used for each colour tone and wood species. Colour calculations were performed in the CIE-L*a*b* colour space. Colour changes were calculated as the Euclidean distance of the colorimetric L*, a* and b* values at a certain time point and the initial colour values and are expressed as ΔE* values.
The overall discolouration for spruce and larch wood, coated either with a transparent or two or more layers of the yellow pigmented semi-transparent coating, are shown in *Figure 4*. It can be seen that for both wood species and all coating systems, the initial discolouration is fast, followed by a much slower discolouration afterwards.
This discolouration behaviour has also been described by various researchers. Further, it can be noted that with both wood species, the discolouration ΔE* is much higher for the transparent than for yellow pigmented coatings.
This was expected, since the transparent coating did not contain UV absorbers or comparable light stabilisers. It can be further noted that in comparison to spruce, the discolouration of European larch with the transparent coating was significantly lower.
The variation in dry film thickness, expressed as two or more coating layer applications, also showed lower discolouration with higher dry film thickness, although the differences were comparatively low. While

Figure 6: Discolouration of yellow, light brown and dark brown coated larch wood samples due to the application of maintenance coatings at regular intervals.



with spruce wood, discolouration was very similar for all three replicates, strong deviations were observed for larch wood.

It is known that the initial colour of larch wood varies strongly compared to other wood species such as spruce or pine. Hence it is difficult to predict the discolouration for a specific larch wood sample, since no correlation between the initial colour and discolouration has yet been established.

IMPROVING THE CALCULATION

The major aim of the discolouration modelling approach is to express the colour of the coated wood surface as function of exposure dose. This can be achieved by approximating the discolouration dataset with suitable fitting functions. Although it is not a necessary precondition, it is convenient if the data are monotonously increasing/decreasing. This is not the case for the discolouration data in the CIE-L*a*b* colour space, especially with the a* values. Re-transformation of the CIE-L*a*b* values into the CIE-xyz colour space gives the desired property. The best fitting results were achieved by using a bi-exponential fitting function of the form:

$$\Delta x(t), \Delta y(t), \Delta z(t) = A1 \cdot \exp(-k1 \cdot t) + A2 \cdot \exp(-k2 \cdot t) + y0 \quad (1)$$

Where A_1, A_2 are pre-exponential factors and k_1 and k_2 are rate constants that have to be determined experimentally. Based on this model, the colour values at specific time points or after certain irradiation dosage can then be calculated.

Using the feature-resolved colour measurements, modelling of the wood surface discolouration can also be carried out for early wood and late wood. In *Figure 5*, the discolouration of the early- and late wood of European larch is plotted against the time of xenon arc exposure, here for the transparent and two-layer yellow coating.

It is apparent that the colour change ΔE* of the late wood is much lower than of the early wood. Hence, it can be concluded that the annual ring contrast decreases with increasing exposure time. This can also be seen in the rendered images in *Figure 2*.

HOW MAINTENANCE COATINGS AFFECT PERCEIVED COLOUR

In order to enhance the lifetime of coating systems, the application of maintenance coatings at regular intervals is strongly recommended. Often, the same coating system as for the initial coating application is used. The additional coating layer, however, leads to an increase of the dry film thickness and changes the colour of the coated wood surface.

In order to include this in the discolouration model, xenon arc exposure trials were conducted, where maintenance coatings were applied at regular intervals (*Figure 6*). It can be seen in the discolouration curves that the yellow-coated larch wood surfaces showed significant colour change during the xenon arc exposure trial. However, the ap-

Figure 7: Novel multifaceted exposure rig (MFER). The same coating systems are exposed at four compass directions and with three inclination angles. Source: PRA

"Predict the overall colour of a maintained façade"

Dr. Boris Forsthuber
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3 questions to Boris Forsthuber

How could the meaning of the pre-exponential factors and rate constants be explained? *The pre-exponential factors and rate constants are related to the extend and speed of the coated wood surface discolouration. Higher rate constants indicate a higher discolouration speed, while higher pre-exponential factors correspond to a higher overall discolouration of the coated surfaces during exposure.*

How does the discolouration model include the initial amorphous color structure of wooden substrates? *The current discolouration model takes the mean colour of early- and latewood that constitutes the main textural features of wooden surfaces into account. These initial colour values are a required input for the discolouration model and thus reflect the fact that the initial colour of different wood surfaces may vary strongly within the same wood species.*

Is the discolouration modelling suitable to predict the application of maintenance coating in time? *The current discolouration model is able to predict the overall colour of a maintained façade after the application of one or more coating layers in time. Although no explicit recommendation of the time of maintenance is intended, the model can help the landlord by visually predicting the appearance of his façade after the application of a maintenance coating of his choice.*

plication of a maintenance coating after 24 hours and 48 hours did not significantly influence the overall colour.

This can also be seen in the corresponding sample image on the right. Light and dark-brown coatings showed a lower photo-oxidative discolouration but a strong colour change due to the application of a maintenance coat. Modelling of the maintenance-induced discolouration was conducted, using UV-Vis spectral data, obtained from transmission measurements on free coating films. As can be seen from the discolouration curves in *Figure 6*, the colour change could be predicted quite accurately.

EXTENDING THE COLOUR MODEL WITH NEW DATA

The current discolouration models are based on laboratory xenon arc exposure trials. Hence, the discolouration values give only an estimate of those occurring during outdoor exposure. In order to extend the modelling approach to outdoor weathering data, natural exposure trials are currently being carried out.

The rate of wood surface discolouration is a function of the weathering dosage. It is also known that the irradiation dosage varies between different compass orientations and inclination angles. As a part of the "Servowood" project, a novel weathering device was developed (*Figure 7*). This multi-faceted exposure rig (MFER) includes four compass orientations (N, W, S, E) and three inclinations (vertical, 45° and horizontal).

On each orientation/inclination combination, the same coating systems are exposed to natural weathering. Aside from the discolouration data, valuable information concerning the rate of photo-degradation under the different micro-climatic conditions is obtained. As soon as the data from this weathering trial is available, the new data will be used to enhance the discolouration models.

CURRENT LIMITATIONS AND OUTLOOK

The discolouration modelling approach developed serves as an initial basis for the simulation of discolouration of (semi-) transparent coated wooden building elements. Currently, the model is limited to fully functional coating systems. Hence, colour changes induced by coating failure such as cracking, flaking etc. are not covered by the present model. Combining the discolouration model with a service life prediction model, which could for example include the probability of the occurrence of cracking and flaking of the coating, could give a greatly improved model. Further improvement of the present discolouration model could be achieved by taking the partial protection due to projecting building elements into account.

Since it is known that the weathering dosage is lower under e.g. canopies or balconies, a proper implementation of these less severe conditions would again increase the quality and versatility of the discolouration model.

With the present discolouration modelling approach, it was shown that it is possible to achieve accurate prediction and visualisations of the ageing of (semi-) transparently coated wooden building elements. Improvement of the current model can hence lead to a versatile and useful tool for architects and building owners.

ACKNOWLEDGMENTS:

The project SERVOWOOD (www.servowood.eu) receives funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement FP7-SME-2013-606576. Contributions to the project from all consortium members are gratefully acknowledged.

Source: Fotolia/ ajlatan

COATING PERMEABILITY ON WOOD

Developing effective methods to measure the permeability of coatings on wood. By Peter Svane, Coating Consultancy Copenhagen and Dr Gerhard Grüll, Holzforschung Austria, Vienna (published in ECJ 06/2017).

Water vapour permeability of wood coatings is an essential property to steer moisture dynamics and to enable entrapped water to escape. Ideally, permeability measurements are made on a wood substrate, but the variability of the material poses a problem. Two methods are presented that overcome the difficulty of wood substrate variability and offer simple and flexible ways of sample preparation and measurement.

Coatings interact with their substrate. The interaction with wood is particular as the coating material partly penetrates the substrate and the coating has a key influence on wood moisture. Wood moisture in turn also influences the coating. Wood shrinks and swells with changing moisture content, causing stresses and eventually cracks both in the wood and in the coating film. Coating systems must be able to "breathe" to some extent; ideally, they also need to protect against rain and allow water to evaporate from the substrate. Another issue is the risk of wood decay at high moisture levels. The interaction between moisture and wood is referred to as "moisture dynamics", a subject that has been the focus of numerous investigations, however without achieving complete clarity. Finally, a coating's adhesion depends on the humidity level at the interface between coating and wood.

EN 927-2 [1] gives some guidance as to liquid water absorption when measured by EN 927-5 [2]. For "stable" wood constructions, i.e. windows and doors, an interval between 30 and 175 g/m^2 x 72 h is specified. The method is a "dip-and-weigh" test, and it mimics how water, for example, from rain, may penetrate the wood through the coating. EN 927-2 however has no specifications for the transmission of "non-liquid" water, i.e. for water vapour diffusion resistance. This property relates to how entrapped moisture can escape from the substrate through the coating. The EN 927-series does not even contain a test method to determine the diffusion resistance of wood coating systems. One might argue that there is no need for such a method if the basic question of moisture dynamics is not completely understood. However, a measurement method is a prerequisite to understanding the complex mechanism behind the inward and outward movement of water through a coating film ("If you cannot measure it, you cannot improve it" – Lord Kelvin (1824-1907)).

NATURAL WOOD VARIATION POSES MEASUREMENT PROBLEM

ISO 7783 describes how to measure water vapour permeability of coatings using the so-called cup method [3]. The coating film is placed

RESULTS AT A GLANCE

→ Measurements of water vapour permeability are made according to ISO 7783 but on real wood substrates.

→ The presented methods ensure equal substrate properties for coated and uncoated wood samples in cup tests.

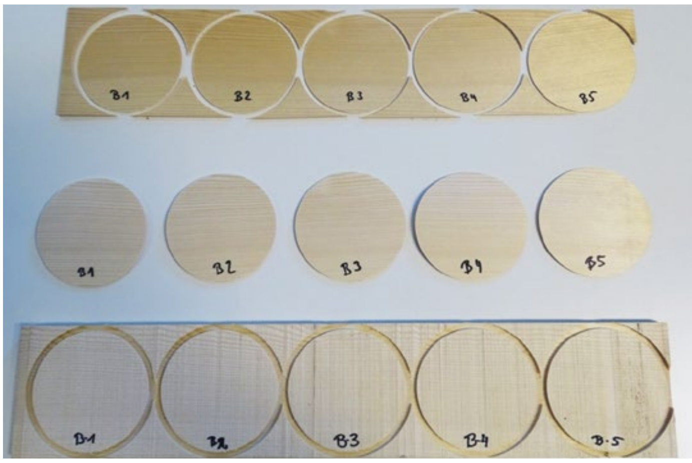
→ The Austrian measurement method has proven to be highly flexible as different wood species can be used as well as varying surface machining.

→ The CCC method to measure diffusion is simple, inexpensive and reasonably precise. It also eliminates any uncertainty caused by different wood samples.

→ It is hoped that these approaches may contribute to future standardisation of methods to measure coatings for this substrate.

Figure 1: Panel of spruce wood with coating on top, ring grooves drilled to prepare coated disc samples.

Figure 2: Samples produced from the coated wood panel, coated discs and coated residual material (top), uncoated discs (centre), rest of the panel (bottom).



as a “lid” on a “cup” containing either a desiccant (dry cup) or a saturated salt solution (wet cup), and placed in a climate chamber. The diffusion rate is tracked by weighing the cup at intervals. Knowing the weight change over time, the moisture gradient across the film, and the area of diffusion, the permeability of the film can be calculated.

ISO 7783 also provides for the application of coatings on a substrate. However, the substrates mentioned in the standard (glass frits or ceramic tiles) are so different to wood that it is unlikely that a wood coating system would achieve the same performance on the specified materials as would be expected on wood. Coating systems for wood should of course, in principle, be tested on wood.

To measure the permeability of a coating system on a substrate, firstly the diffusion resistance of the substrate is determined, then the resistance of the coated substrate. Finally, the one resistance value is subtracted from the other to provide an approximation of the coating’s own resistance. ISO 7783 recommends that the diffusion resistance of the substrate should be low in comparison with that of the coating; more specifically the water vapour diffusion rate of the substrate should exceed 240 $g/(m^2 \times 24 h)$. This value corresponds to a 1-2 mm thick layer of spruce.

A major difficulty using wood substrate in permeability measurements is the inhomogeneity of the material; no two pieces of wood are alike and neither is their permeability. This is quite different from the suggested substrates in the standard: glass frits and ceramic tiles, which are uniform and homogeneous industrial compounds. Wood is a naturally grown material with great variation.

Therefore, when using wood as the substrate in permeability measurements, some aspects must be considered:

- 1. The wood substrate should be as thin as possible to suit the recommendations of ISO 7783 (high water vapour diffusion rate)
- 2. The same piece of wood should preferably be measured with and without the coating (to exclude variations from the substrate)
- 3. If different pieces of wood are measured with and without the coating, care should be taken to select substrates that are as uniform as possible
- 4. The method should allow for coating application on different wood species and by different application methods commonly used in the industry

It goes without saying that the test method ought to be reasonably simple to perform, and sufficiently precise.

TWO APPROACHES

Paint companies and institutes in Europe conduct permeability measurements on coatings for wood – some with wood as the substrate, some on free films, some on paper.

Holzforschung Austria (HFA) in Vienna has several years’ experience with a cup method using circular wooden discs of 90 mm diameter and 1.7 mm thick.

Coating Consultancy, Copenhagen (CCC) has recently developed a simplified method using commercial grade 0.7 mm thick spruce veneer on rectangular cups approx. 120 mm x 180 mm.

The two institutions have agreed to briefly present their two different approaches to the paint industry as a contribution to discussion, and may-be as an inspiration to future standardisation. The methods described in extenso may be found on the homepage of the contributors [4, 5].

A FLEXIBLE METHOD

The Austrian method makes it possible to test a full multi-layer coating system applied with the same methods that are used in practice, such as dipping, brushing, flow coating, spraying, roller coating or others. This is done on a normal wood panel of selected quality and the coating is dried and cured under normal conditions for testing or in practice. After the coating is cured, thin plates of coated wood are machined out of the surface of the panel which are used for permeability testing. A second set of thin plates is taken from the same areas of the panels, beneath the coated ones, to serve as the uncoated reference substrate. This is then made of the same growth rings as the substrate of the coated samples.

Boards of spruce wood are selected to produce panels with growth rings perpendicular to the test surface, free from knots, straight grained and without any defects. The panels are machined to a size of 500 mm x 100 mm x 20 mm and conditioned in a climate chamber at 20 °C/65% relative humidity. The wood coating system under test is applied to one side of a panel according to the manufacturer´s specifications. Multi-layer systems can be applied easily using various methods, spreading rates and intermediate sanding.

When the coating is finished and cured, five ring grooves are machined into the coated surface of the panel with a diameter of 90 mm (inner circle) and a depth of approx. 12 mm (*Figure 1*). The surface of the panel is then cut off with a band saw to a thickness of approximately 2 mm, giving five coated wood discs of 90 mm in diameter and approx. 2 mm thick. It also yields some residual material of the coated surface which is used for dry film thickness measurements. On the rest of the spruce

Figure 3: Vacuum holder and sanding machine for parallel sanding of the samples from the reverse side to a defined thickness.

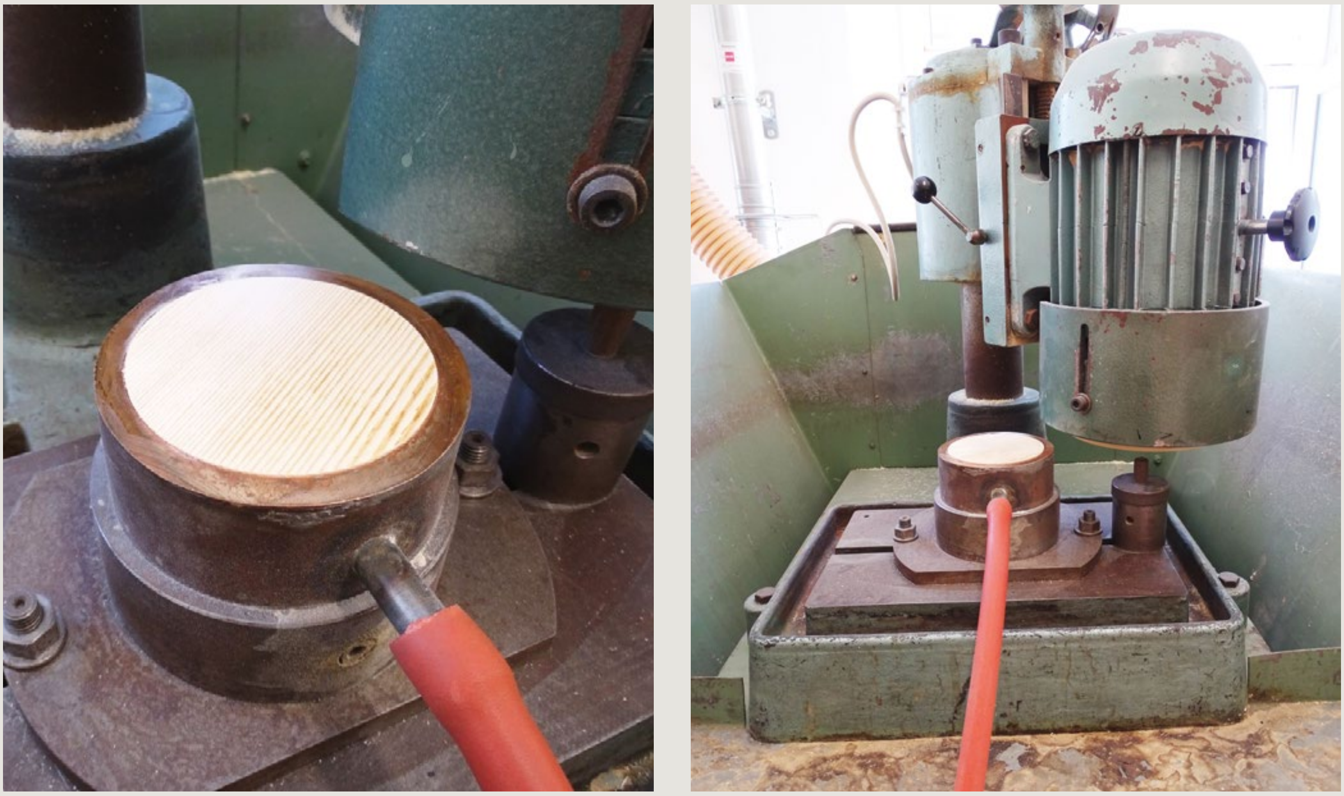


Figure 4: Cutting veneer to appropriate size.

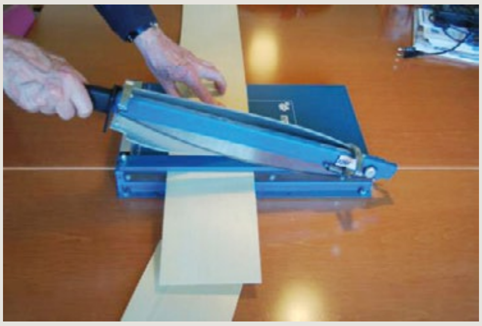


Figure 5: Sealing cup to veneer substrate. Cup upside down.

panels there is a rough sawn surface and the drilled ring grooves are still present. This wood surface is planed smooth and once again, a layer of approx. 2 mm is cut off with a band saw, yielding five uncoated wood discs, 90 mm in diameter and approx. 2 mm thick, made of the same growth rings of wood as the coated ones (*Figure 2*).

The next step is to sand all the disc samples from the rough sawn reverse side using a vacuum holder and a sanding machine with parallel guide to a thickness of 1.7 mm (*Figure 3*). The samples can then be conditioned before they are tested in suitable cups according to ISO 7783. This method is highly flexible because the panels can be made of different wood species and may include variations of (industrial) surface machining such as different grades of sanding, intermediate sanding and some surface structuring such as brushing. However, with structured surfaces care must be taken to seal the samples properly when installed in the cups for testing. This might require additional liquid sealants. This flexibility of the method was demonstrated in a study on industrially applied non-film forming coatings on wood flooring of different wood species and surface machining as well as thermally modified wood [6].

SIMPLIFIED AND PRECISE MEASUREMENT

CCC's method is a simple, cheap and reasonably precise laboratory method utilising 0.7 mm normal spruce veneer as the standard substrate, and commercially available transparent polystyrene archive boxes as diffusion cups. Apart from a climate chamber providing 23 °C/50% relative humidity, no special equipment is required, and a laboratory scale that weighs to 0.01 g is sufficient for the determination. As in the Austrian method, the diffusion measurement is carried out as a "wet cup" experiment according to ISO 7783.

Figure 6: Suitable "cup". Supplier: Hofstätter & Ebbesen (www.ultraplast.dk).

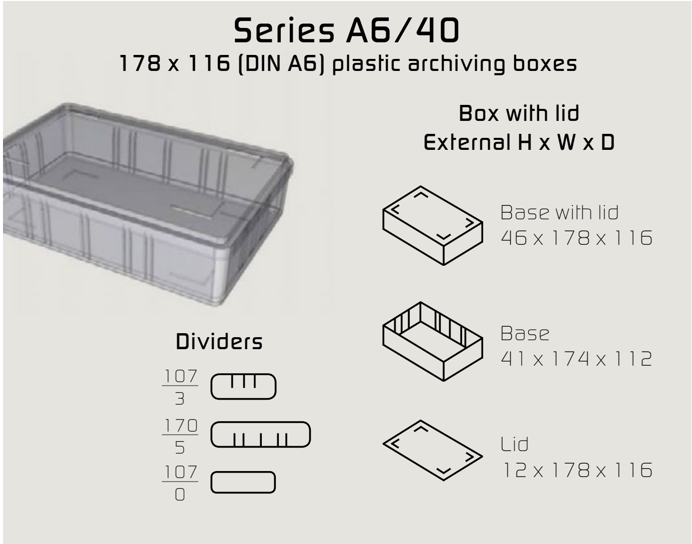
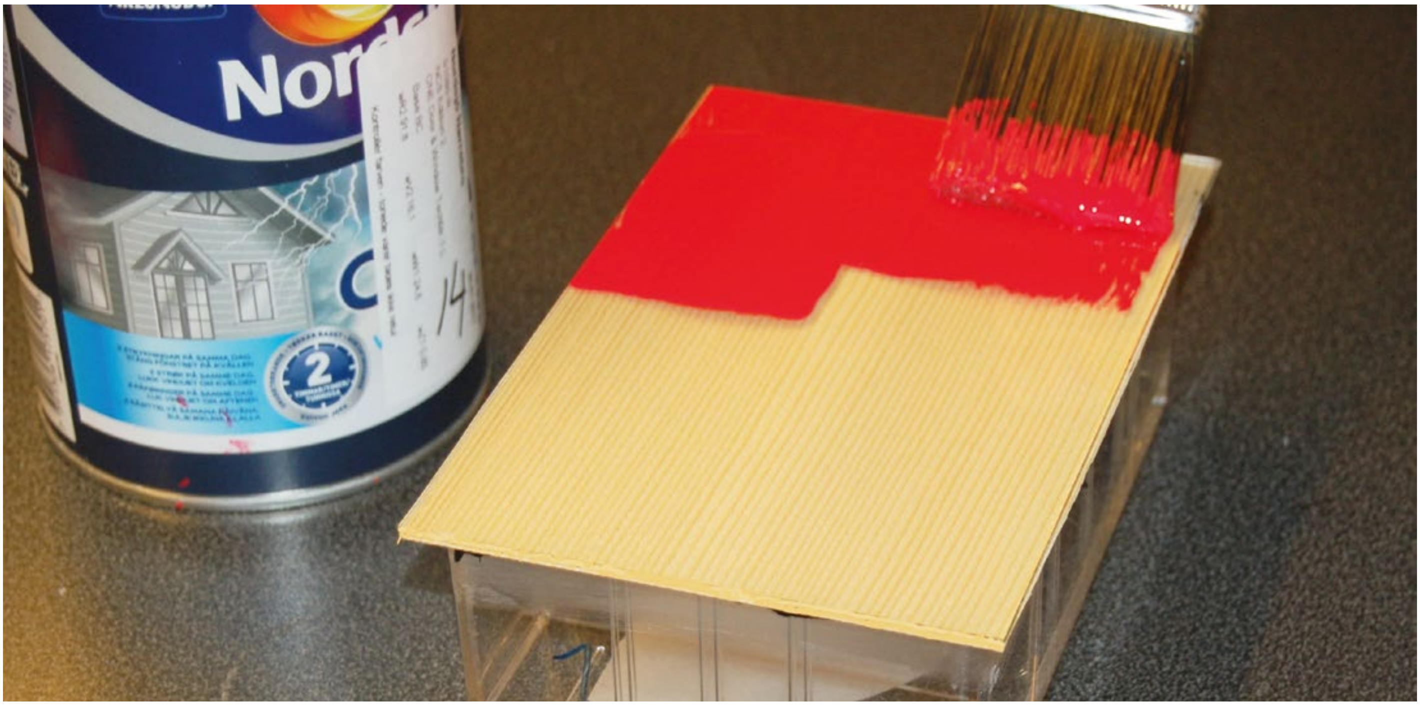


Figure 7: Filling with saturated salt solution though a 3 mm hole drilled in the side of cup.

Figure 8: Application of coating system directly on the cup.



The procedure includes the following steps:

- > 1. 0.7 mm thick spruce veneer is cut on an ordinary office paper guillotine (*Figure 4*). The dimensions 122 mm x 185 mm are suitable.
- > 2. The veneer substrates are conditioned some days at 93% relative humidity and ambient temperature. Conditioning can be performed, for example, in a desiccator with saturated $NH_4H_2PO_4$ at the bottom.
- > 3. The veneer is sealed to the "cups" with a joint sealant (*Figure 5*). A suitable cup is shown in *Figure 6*. Any cup of hard polystyrene may do. Hard polystyrene is chosen because it is almost impermeable to water vapour diffusion. "Sikaflex 11FC" has proven to be a reasonable sealant (Sika AG). The sealant must cure for 24 hours.
- > 4. The cup is filled with the proper amount of saturated $NH_4H_2PO_4$ through a small hole in the side of the cup (*Figure 7*). Afterwards the hole is sealed with a piece of aluminium tape.
- > 5. At this stage, the diffusion resistance of the substrate (without coating) can be determined according to ISO 7783. Weighing results must be corrected because there is a little "leak" along the edge of the cup, which is the unsealed rim of the veneer. The correction has been experimentally determined once, and it is applied to all measurements.
- > 6. The coating system is then applied by brush, roller or by spraying according to specifications (*Figure 8*) directly on the cup. Intermediate sanding may be carried out.
- > 7. When the coating is dried and cured, the diffusion resistance of the coated substrate can be determined according to ISO 7783.
- > 8. The diffusion resistance of the coating system is calculated as the difference between the value for substrate with coating and for the substrate alone.

The advantage of the method is its simplicity, and the large area of veneer increases precision. Furthermore, the diffusion resistance of the substrate and of the coated substrate is measured on the same piece of veneer, which eliminates uncertainties caused by different wood samples.

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Peter Svane
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> "There must be no leaks anywhere"

3 questions to Peter Svane

In how far does the sample preparation influence the diffusion behaviour of the sample? *The main thing is to determine the diffusion resistance of the uncoated sample and of the coated sample as precise as possible. That calls for a uniform substrate and a uniform application of the coating system; and of course, there must be no leaks anywhere. Another important issue at sample preparation is the determination of the dry coating's film thickness (DFT). This can be achieved by weighing the applied amount of coating(s), provided the dry matter content and the density are known, but as coatings may penetrate wood to some extent one might prefer to determine the DFT by microscopy according to ISO 2808 Meth. 6A.*

What impact does the structure of the wood surface, which results from the sanding process, have? *The structure will influence the surface area. A very rough surface will have a larger area than corresponding to the apparent size (as measured with a ruler). And as the area of diffusion enters into the calculation of diffusion resistance, the figure should be as correct as possible. Whether a surface is sanded or planed however, is of minor importance, as most coating systems will fill the microscopic irregularities in the surface anyway, i.e. in this case the apparent area is the same as the directly measured area.*

How can a comparability of coating properties be achieved, considering the diffusion protection and the reversible swelling behaviour of wooden substrates? *Wood swells and shrinks depending on its humidity content. A coating on wood is able to follow these movements. These variations however are limited to a few per cent, and probably without any significant influence on the diffusion properties of a coating system. Another theoretical complication is that the permeability of the wood substrate changes with its moisture content, however the diffusion resistance of the substrate itself normally is so much smaller than that of the coating, that these variations will have a negligible influence on the final calculation.*

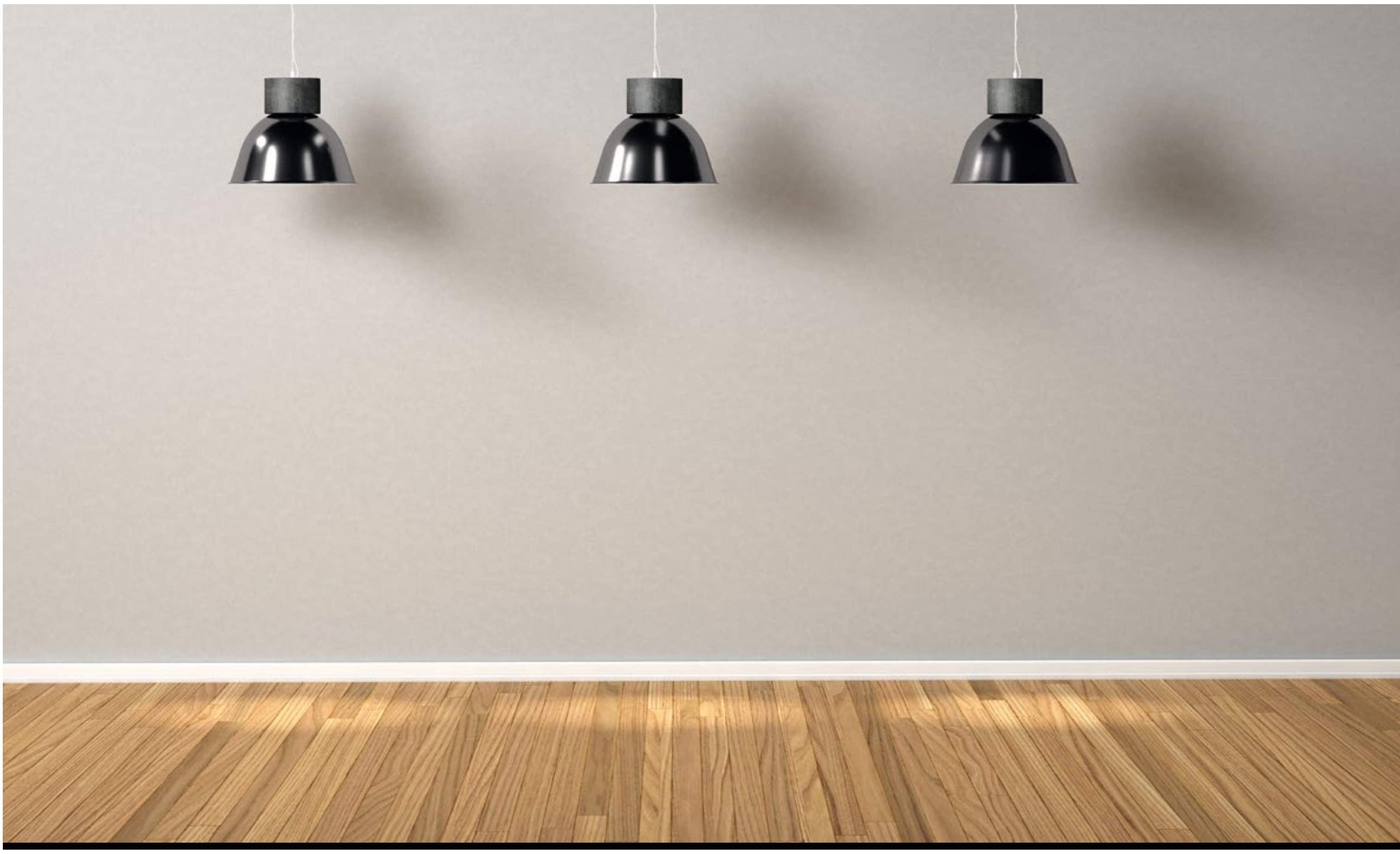
A GRUESOME TREND

During the 16th and 17th century a pigment entitled „mummy brown“ was popular, especially among pre-raphaelite painters. One of the main ingredients were remains of Egyptian mummies, mixed with pitch and myrrh.

Source: Dieter Hawlan - Fotolia.com

SUBSTITUTES

During the early 20th century, production decreased due to exhaustion of the supply of available mummies. Today, the pigment is a mix of kaolin, quartz, goethite and hematite. It varies from yellow to red and dark violet.


Source: Bounlow - Fotolia

POLYAMIDES SHOW PERFORMANCE GAINS

Novel self-crosslinking polyurethane dispersions for wood coatings. By Nina Musche, Gabor Erdodi, Jonathan Bird, Israel Skoff, Naser Pourahmady and Rebecca Gibson, Lubrizol Advanced Materials (published in ECJ 07-08/2017).

A series of water-borne polyurethane/urea copolymer dispersions was made by incorporating polyamide segments in the backbone of the resins. Excellent hydrolytic stability, heat and UV resistance and mechanical properties were obtained. In a formulation optimised for wood coatings, good performance was achieved across a wide range of resistance tests.

The end-use performance of water-borne polyurethane dispersion (PUD) coatings is mainly derived from the large polyol segments used in their production. A majority of PUD offerings in the marketplace are made with common polyester, polyether or polycarbonate polyols. Each of these classes offers some performance advantage, but falls short on other properties. Polyester polyols give good mechanical properties and UV resistance, but suffer from poor hydrolysis resistance. Polyether polyols have better hydrolytic stability, but fall short in UV resistance. Polycarbonate polyols offer improved hydrolysis resistance with some degree of increased hardness, but they are much more expensive than other polyols.

A series of polyamide oligomers was synthesised from conventional difunctional acids and amines. These oligomers contain amine or hydroxyl terminations, and in reaction with diisocyanates form a polyamide-urethane or polyurea backbone. The polyamide building blocks in these new dispersion polymers provide excellent hydrolytic stability, superior heat and UV resistance and better overall mechanical properties in comparison to polyester and polyether segments. In addition, the amine chain termination in these oligomers forms urea linkages (instead of the urethane link from the polyol) in reaction with isocyanates. Polyurea linkages are known to have stronger intermolecular attractions that act more like a true crosslinked polymer, resulting in performance advantages over urethanes, including better solvent resistance and elasticity.

PAST WORK ON POLYAMIDES IN POLYURETHANES

The incorporation of polyamide into urethane coating system has been tried in the past with very limited success. Various methods including polymer backbone modifications, dispersion of solid polymers in water by grinding and emulsification

RESULTS AT A GLANCE

→ Water-borne polyurethanes may be based on polyester, polyether or polycarbonate polyols, each of which has advantages and disadvantages.

→ A series of water-borne polyurethane/urea copolymer dispersion was made by incorporation of polyamide segments in the backbone of the resins.

→ The polyamide provides excellent hydrolytic stability, heat and UV resistance and mechanical properties in comparison to polyesters and polyethers. The amine chain termination also forms urea linkages in the reaction with isocyanates.

→ The general chemical and physical properties of these new copolymers and comparisons with conventional water-borne resins are discussed. Some interesting differences in behaviour and formulation requirements are highlighted.

→ Detailed testing of a formulation optimised for wood coatings showed that good performance could be achieved across a wide range of resistance tests.

and simple blending have been tried. In the early 1990s some polyamide-modified urethane coatings were reported [1] Small quantities of polyamide were incorporated into urethanes by this method.

In 2008 Locko and his co-workers disclosed the synthesis of several polyamide polyols and also polyurethanes made from those polyols [2]. The focus of their work was the polyols and their use in solvent-based and bulk urethane resins.

In 2002, Inoue and his group from Toyohashi University of Technology in Japan reported some novel polyurethane-polyamides made from urethane prepolymers and reactive polyamides [3].They found that incorporation of polyamide improved the thermal properties of the resulting polyurethanes.

RESOLVING THE CHALLENGES OF POLYAMIDE INCORPORATION

One major challenge in incorporation of polyamides into urethane polymers is the process issues associated with this technology. Due to strong intermolecular hydrogen bonding, polyamide oligomers are usually very viscous and hard to handle for further modification. Common polyamide segments made of diacids and diamines are not suitable as soft segments for the synthesis of multi-segment polyurethanes.

Therefore, a series of telechelic or reactive N-alkylated polyamide oligomers which do form nice soft segments in polyurethanes [4] had to be developed. It was then found possible to make water-borne elastomeric polyurethane and polyurea using these telechelic oligomers [5, 6]. In this paper discusses their mechanical properties and application performance will be considered. The scope of this technology is very broad. Various combinations of monomers and reaction conditions were examined and the properties of resulting polymers were studied. Representative examples from different series of polymers will be discussed and their properties will be presented in comparison to conventional polyurethane dispersions (PUD). The following designations are used:

› PETU or PETUD	Polyether-Urethane (Dispersion)
› PESU or PESUD	Polyester-Urethane (Dispersion)
› PCAU or PCAUD	Polycarbonate-Urethane (Dispersion)
› PAMU or PAMUD	Polyamide-Urethane (Dispersion).

BASIS OF COMPARATIVE TESTING

Several polyurethane dispersions also had to be synthesised using a variety of common polyols to allow some comparative evaluation with polymers made from polyamide polyols. Obviously, a side-by-side evaluation of representative polymers from various classes for general chemical and mechanical properties could be misleading. Each type of polymer chemistry offers its own scope and fine-tuning possibilities to obtain the best properties for a desired application.

Several representative compositions from each class of polyols were obtained from commercial sources, then the properties best achievable with each class of chemistry were determined. A series of water-borne dispersion polymers was made with various compositions of polyamide segments in the backbone. Samples with differences in crystallinity, glass transition temperature, molecular weight, segment polarity and alkylated amide type were prepared.

The films prepared from these polymers with minimum formulation (coalescent added if necessary) were evaluated for application properties along with similar polymer films made with polyether, polyester or polycarbonate polyols.

The effects of formulation additives and crosslinking components were eliminated as much as possible to gain a fair comparison between polymers. However, a side-by-side comparison of representative samples from all classes of chemistries was not completely possible due to lack of comparable raw materials or the inability of some polymers to form films without any further formulation.

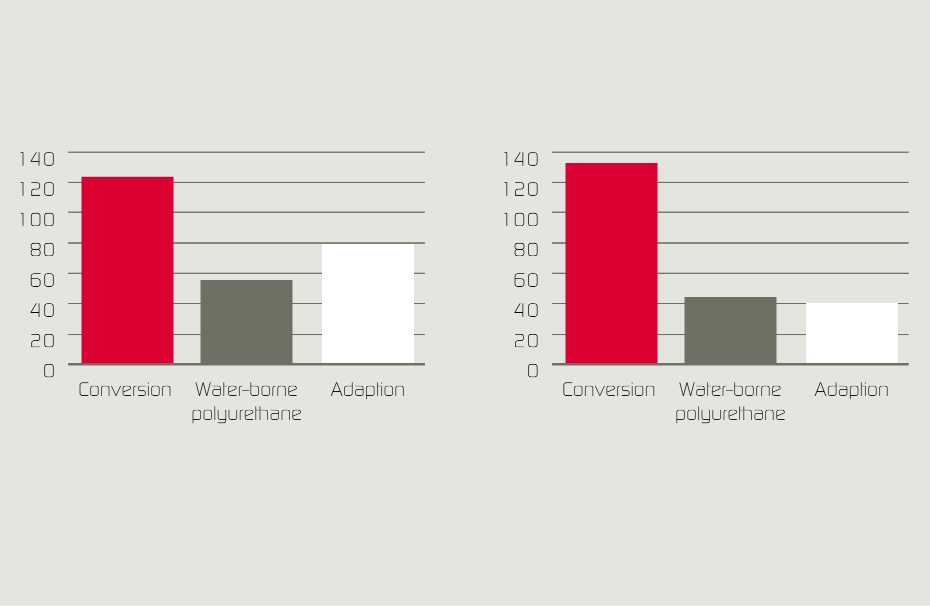
General mechanical and chemical proper-

Table 1: Application properties of wood coatings made from PAMUD compared with commercial alternatives.

	Commercial solvent 2K PU	Commercial solvent 1K	Commercial water 2K	PAMUD polyamide urethane 1K
Gloss 60°	103	86	90	92
König Hardness (oscillations)	125	79	36	79
Black heel mark	7	9	9	8
Taber abrasion (mg lost)	132	50	58	45
Chemical resistance	106/107	110/110	87/103	104/108

Figure 1: Hydrolytic stability (top) and UV resistance (bottom) evaluated in terms of strength retention.

Figure 2: Left, pendulum hardness (higher is better); right, Taber abrasion values (lower is better).



ties were studied. Adhesion to low-surface-energy (LSE) and high-surface-energy (HSE) substrates was evaluated. Chemical resistance against common solvents (methyl ethyl ketone, isopropyl alcohol, ammonia, vinegar, gasoline/petrol) were tested. Hydrolytic stability and UV stability were tested as discussed above. Heat stability was analysed by thermo-gravimetric (TGA) and thermo-mechanical analysis (TMA).

The results obtained from all analyses were compared and a general rating of performance for each class of chemistry was determined. Comparison is also made with typical results obtained from evaluation of acrylic polymers.

HIGH STABILITY ACHIEVED ACROSS A BROAD RANGE OF TESTS

Figure 1 shows the results from an evaluation of hydrolytic stability in a humidity chamber for the films prepared from PAMU with two different compositions, and similar films from a polyurethane dispersion made from a polyester polyol and polyether polyol.

After 2-3 weeks of exposure to humidity and heat, the samples from polyester-urethane lose their mechanical integrity while both samples with polyamide segments maintain considerable strength even after 1000 hours. It is interesting to note the sharp increase in tensile strength of PAMU1 at the earlier stage of testing. This is due to the annealing effect observed in all polyamide-urethanes upon heat-ageing, even under high humidity.

Also shown in *Figure 1* is the UV stability of the same polymers as measured by exposure to QUV tests. Samples made from polyamide polyols show UV resistance comparable to polycarbonate-urethanes. The sample made from polyester polyol also shows good UV stability. However, the sample of polyurethane with polyether segments (PETU) starts losing its strength after 500 hours of exposure to UV.

Overall, polyamide segmented polymers show excellent tensile, heat stability, hardness development and chemical resistance. The abrasion resistance, hydrolytic stability and UV resistance of these polymers are comparable to high quality coating resins (solvent-borne and water-borne). All other properties are comparable to urethane or acrylic resins used in conventional coating products. No major weakness was observed in any of the polymer samples evaluated.

The adhesion property of these polymers is of particular interest. They exhibit strong adhesion to selected polar substrates such as polyesters, nylon and cellulosic substrates. They also show good adhesion to cold-rolled steel (CRS). Interestingly, most properties of polyamide segmented polymers are improved by heat-ageing (annealing). Some high-crystallinity samples develop mechanical properties twice as high as the original value upon annealing at elevated temperatures (120-130 °C). This property may be significant for some high-temperature applications and is under further investigation.

EVALUATION IN WOOD COATINGS

Polyamide-segmented polymers were evaluated in a coating formulation for wood substrates. The results are shown in *Table 1*. The gloss and König hardness evaluations were done using a 75 µm wet drawdown. The chemical and black heel mark evaluation was made by applying three coats of the formulated coating using a foam brush onto a maple veneer panel, allowing at least two hours between each coat.

The results are compared against commercial finishes; a solvent based finish using an external crosslinker, a solvent based finish with no crosslinker and a water-based finish with an external crosslinker. All tests were run seven days after the coating was applied. Based on the results of this study it appears possible to create a water-based finish with the performance of the solvent-based finishes on the market.

It is worth mentioning that although most common formulation ingredients for various coating applications are compatible with polyamide-segmented polymers, the efficiency of these additives are not always the same as their effect on common coating resins. The exchange of cosolvents from DPnB to DPM, TPM, TPnB, EB or combinations of these in a formulation with the same PAMUD (PAMUD1, designed for wood coatings) showed a major impact on chemical resistance – ranging from almost perfect down to medium performance. This is an example of how performance can be affected by the ingredients chosen. There-

Figure 3: Scratch width of PAMUD 1 (lower trace) is better than that of self-crosslinking PETUD.

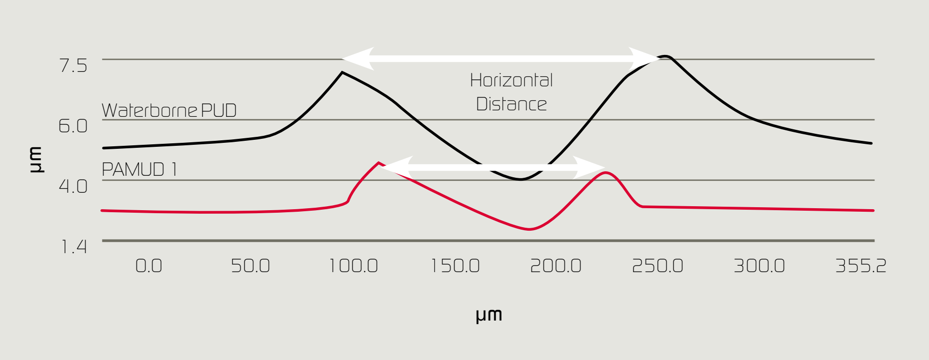


Figure 4: Key properties for wood floor coatings: wood coating PAMUD 1 in comparison with other technologies.

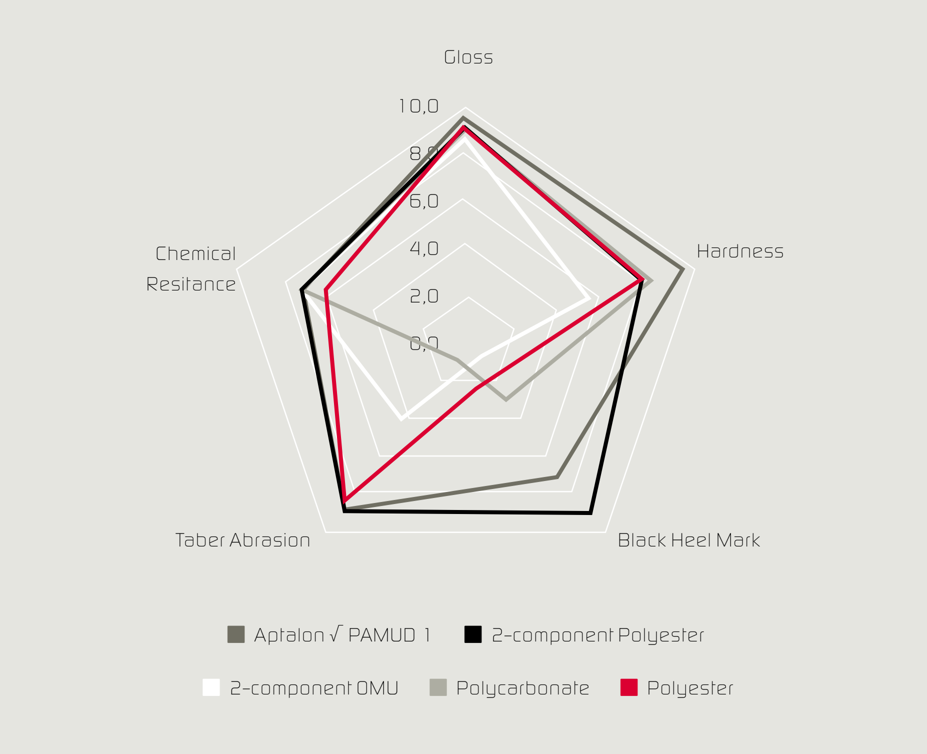


Table 2: Application results comparing PAMUD 1 with other PUD technologies and an acrylic.

Test	**Method**	**PAMUD 1**	**PESUD**	**Self-X-linking PESUD**	**Self-X-linking PETUD**	**Self-X-linking acrylic**
Gloss	60°	92	89	93	89	86
Haze	20°+/- 3°	31.8	19.9	24.4	39.8	26.9
Opacity	DE* /%	0.73	0.72	0.73	0.73	0.76
Taber	CS 17/mg	19	30	37	21	147
Pendulum hardness	König oscillations @ 14d RT	119	88	109	76	80
Black heel mark *	After 7d RT	6	6	7	8	3
Black heel mark *	After 14 d RT	9	8	9	8	3

* Tested on flat panel, Rating 10 = no effect, 1 = total destruction of film

fore, any coating formulation optimised for other polymers may not work best with these new polymers. This creates new challenges for formulators but also an opportunity to develop new improved formulated solutions for existing applications and some solutions for new applications where common coating resins do not meet all performance requirements.

HIGH CHEMICAL RESISTANCE AND HARDNESS

The tailor-made product for wood coating application PAMUD 1 (also referred to in figures as "Aptalon W8060") went through thorough testing for all the necessary final properties expected from a polymer on that substrate. These evaluations took place in several internal and external laboratories. The results compared to other water-borne technologies can be found in *Table 2*.

Appearance and mechanical properties show very good overall quality. PAMUD 1 is a hard and durable resin, fulfilling for example the needs for floor coating applications. It is no longer necessary to sacrifice hardness for abrasion resistance. As can be seen in *Figure 2*, it combines both properties on a high level for highly durable films.

Hardness usually comes with a certain amount of brittleness. In order to make sure that there is no brittleness that can lead to low scratch resistance the materials were tested with a diamond stylus. The device measures the force to make a scratch into the film as a rating for both hardness and scratch resistance, by looking at the width (*Figure 3*) of the resulting scratch (method ASTM G171). The results showed that PAMUD 1 gains high numbers in hardness, while keeping a small scratch width. See *Table 3* for detailed results.

The chemical nature and the bonding strength of this polyamide-based product also lead to enhanced chemical resistance. Straight PESUD materials can have performance gaps, for example in ethanol resistance, others in water or coffee resistance. *Table 4* summarises test results according to EN 68861 1B on oak. In other tests with iodine, gelled hand sanitiser or hair colourants, similar trends were observed. PAMUD 1 materials thus feature very balanced properties on a high level.

Table 3: Feel vs durability for selected DOE "Extremes".

ASTM G171	Normal force	Ave. scratch width (µm)	Scratch hardness (GPa)
PAMUD 1	1N	90.4	0.312
Water-borne OMU 2K	1N	108.4	0.217
Water-borne PUD (1)	1N	136.0	0.138
Water-borne PUD (2)	1N	144.2	0.123
Water-borne PC PUD	1N	123.5	0.167
Water-borne PUD (3)	1N	151.8	0.111
PAMUD 1	2N	155.0	0.212
Solvent-borne 2K	2N	134.6	0.281
Solvent-borne PUD	2N	194.7	0.134
Moisture cure urethane	2N	159.4	0.200

Table 4: Chemical resistance on oak comparing PAMUD 1 with other technologies (EN 68861 1B: 5 = excellent, 0 = severe damage).

Agent	Duration	PAMUD 1	PESUD	Self-X-linking PESUD	Self-X-linking PETUD	Self-X-linking acrylic
Water	16 h	4	5	1	5	5
Coffee	16 h	3	4	1	0	5
Red wine	6 h	5	5	3	4	5
Ethanol	1 h	5	2	4	5	5
Ammonia	2 min	5	5	5	4	3

BROAD RANGE OF PERFORMANCE ADVANTAGES SUMMARISED

A series of novel water-borne polyurethane/urea copolymer dispersion has been made by incorporation of polyamide segments into the backbone of the resins. These new segmented copolymers exhibit outstanding properties for coating applications.

The performance advantage is most pronounced in heat-resistance, hydrolytic stability, chemical resistance, hardness development and adhesion to a variety of substrates. The general chemical and physical properties of these new segmented copolymers and comparison to conventional water-borne resins are discussed. Potential use in wood coatings where conventional polymers fail to meet some of the performance requirements is suggested (see *Figure 4*).

This new technology platform is as versatile as other technologies for PUDs. One product for wood coatings is currently available, but more will follow.

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“Equal to common aliphatic polyester or polyether bases“

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3 questions to Nina Musche

What are the differences between the two PAMUDs? *PAMU1 and PAMU2 are made of two experimental polyamide polyols, to explore the difference for example in tensile strength or hardness.*

How is the scratch width (shown in Table 3) influenced by the layer thickness? *With these crosslinked polymers we don’t expect any influence of the film thickness on the resulting scratch width. The scratch depth with the applied forces only gets into the top 5% of the film volume, if the dry film thickness is >75µm.*

How sensible is the PAMU in terms of yellowing? *Yellowing has been tested via Xenon testing and Delta b is less than 1 after 1000h of testing. It does of course depend on the building blocks used, but in case of the tested prototypes the results are equal to common aliphatic polyester or polyether bases.*

Source: Fotolia/ litchi cyril

BRINGING OUTSIDE COATINGS INSIDE LIMITS

ADH-free water-based binder for durable, EU Ecolabel-compliant lasure coatings. By Massimo Longoni, EPS B.V., Netherlands (published in ECJ 07-08/2017).

Formulators have relied on cross-linkers such as adipic acid dihydrazide (ADH) as a way of enhancing the performance of exterior wood coatings despite this being a hazardous substance. A new polymer has now been developed that retains the durability of the final coating and offers an environmentally friendly solution to comply with the EU Ecolabel.

In the past two decades the environmental impact of products has become a key discussion point in the European Union and a development focus for paints and varnishes producers. One of the main outcomes of the EU effort in this area was a voluntary programme to recognise environmentally friendly products. The EU Ecolabel award [1] aimed to promote products that present a reduced environmental impact throughout their life cycle and, no less important, to provide customers with environmental impact information based on scientific data. As of September 2015, 10% of all labels awarded had been given to products in the paint and varnish sectors [2, 3]. The ecological criteria of the EU Ecolabel award are product or service specific and are not everlasting. In fact, the requirements are updated regularly to take account of innovations and regulatory changes that affect the specific field of interest. In 2016 the paints and varnishes evaluation criteria were reviewed in terms of the hazardous content in the final material and a new category covering indoor and outdoor products was introduced [4]. Depending on the type of paint or varnish, some or all of the performance criteria are taken into consideration. Requirements for solvent and hazardous material content are fixed and mandatory for all types of paint and varnish but derogations to the use/presence of certain substances in final products are allowed when 'hazardous' substances are necessary to maximise durability in real-life conditions. Consequently, substances that are hazardous to the aquatic environment and normally banned in the EC may be permitted.

The Ecolabel classification method was introduced to help consumers identify products with lower environmental impact, which is why it is of particular interest in consumer-focused coatings sectors: interior paints, exterior paints, wood lasures, etc.

The term lasures identifies DIY low-solid varnishes for exterior wood. The main task of these kinds of products is to protect and decorate exterior wood, extending the life of wood and wooden products without gloss loss and minimal/no structural damage.

LOW LEVELS OF ADH PERMITTED

Acrylic dispersions (AC) represent the best class of water-based polymers for exterior applications. When compared with other polymer technologies, AC offer a better balance between cost-performance and environmental benefits. But not all offer good outdoor durability; the combination of monomer composition and cross-link density are key determinants in achieving high performance. Various monomers and compositions can be used for good performance initially, but using a low-temperature cross-linker, primarily adipic acid dihydrazide (ADH), is mandatory to enhance the final performance of those so-called self-cross-linking acrylics.

RESULTS AT A GLANCE

→ Conventional ADH-based polymers used in the architectural exterior wood segment are hazardous to the aquatic environment.

→ The aim of this study was to develop a new acrylic polymer without ADH and offering equal or better performance than those currently available.

→ Optimising the polymer backbone and cross-linker achieved these goals.

→ Two new products provide an EU Ecolabel-compliant solution for exterior wood coatings that retain high durability of the finished coating.

In the literature, introducing ADH as a room temperature cross-linker is reported to have major benefits for block resistance, water resistance and outdoor durability; all aspects necessary for good exterior lifespan. The mechanism of the ADH cross-linking reaction is a Michael's Addition [5,6], which occurs at low curing temperature between hydrazide groups and available CO double bonds, resulting in new cross-links between the acrylic polymer chains in the dried film. At the beginning of 2016, ADH producers requested that the ECHA reclassify the product as hazardous to the aquatic environment (Chronic Category 2) with the associated hazard statement H411. In theory this new classification means that ADH does not meet Ecolabel criteria. This would have meant the EU Ecolabel award being withdrawn from all the products containing ADH. The Commission Decision (EU) 2016/397 [3] granted a derogation for the presence of 1.0% ADH max in finished paints and varnishes, stating that there are no alternative technologies that enable the same durability to outdoor products. The derogation was required to achieve the longer lifespan of finished goods combined with the overall lower environmental impact.

A key research area of the EPS technical center, the Netherlands, in the last couple of years has been a specific focus on developing ADH-free acrylics to find an alternative solution.

NOVEL POLYMER DEVELOPMENT

The EPS research and development center has worked intensively to optimise a new acrylic polymer without using ADH or acetoacetoxyethyl methacrylate (AAEM) – sometimes associated with yellowing – suitable for architectural exterior wood applications. The main aim was to determine a new acrylic polymer to produce an EU Ecolabel-compliant coating with no environmentally hazardous components. Primarily, different two phase-polymers with various monomer compositions and alternative cross-linkers were investigated to identify the optimal ratio that could guarantee a minimum film forming temperature (MFFT) of zero, or close to zero, and good performance.

A new polymer was considered a valid option if it achieved block resistance, water and early water resistance, and could produce a solvent-free formulation. Having zero VOC would be a plus if the new polymer was comparable to the standard technology and was in line with the core message of the EU Ecolabel. *Table 1* shows a selected number of the synthesised polymers, limited in order to show the most interesting ones compared to internal standards.

Table 1: Acrylic polymer specifications.

	Solids (%)	pH	MFFT (°C)	Particle size (nm/mean)	Cross-linker
Comm ADH	44	7.0-8.0	<5	55	√ (ADH)
Std ADH	44	7.0-8.0	<5	55	√ (ADH)
Std ADH-free	44	7.0-8.0	<5	60	×
ML-745	44.5	7.0-8.0	<3	50	√
ML-745-A	44	7.0-8.0	0	55	√
ML-747	44.5	7.0-8.0	<3	50	√

The 'Comm ADH' sample is an acrylic polymer widely used in the architectural exterior wood segment. Samples 'Std ADH' and 'Std ADH-free' are EPS internal references: the first is a proven, commercially available product that contains ADH, the second is the same product but without ADH. These two are listed to show how ADH impacts performance in terms of the fixed polymer backbone and morphology.

ML-745 and ML-745-A are characterised by the same cross-linking mechanism but the monomer composition presents minimal differences so that the second phase of ML-745 is harder than ML-745-A. ML-747 is an improved version of ML-745-A presenting the same monomer composition and two-phase combination but with the introduction of a different cross-linker.

The results of the broad study show that it is possible to achieve the target milestones with just the correct combination of cross-linker and polymer backbone.

The block and water resistance of the listed polymers relates to the non-formulated polymer – directly applied, 100 micron WFT (wet film thickness), on black Leneta foil and dried under standard conditions (50% relative humidity and 23 °C) prior to testing.

Block resistance is measured by applying a 0.5 kg x cm^2 weight pressure in one set of samples at room temperature for 24 hours (*Figure 1*), and 0.5 kg x cm^2 weight pressure to a second set of samples for 1 hour at 50 °C (*Figure 2*). Test results are rated on a scale of 1-5 where 5 is the best and 1 a complete failure.

Table 2: Acrylic polymer specifications.

	ML-19-E	ML-39-D
ML-745	50	
ML-747		50
Defoamer	0.40	0.40
Deareator	0.50	0.50
Substrate wetting agent	0.20	0.20
Neutralising agent	0.10	0.10
"Texanol"	1.00	1.00
UV absorber	1.00	1.00
Water	45.40	45.40
Slip agent	0.20	0.20
In-can preservative	0.10	0.10
Pseudoplastic HEUR thickener	0.40	0.40
Newtonian HEUR thickener	0.70	0.70
	100	100

Water resistance (*Figure 3*) is tested again on polymer films applied on black Leneta after 24 hours drying time in standard conditions and putting the water in direct contact for an additional 24 hours. This is rated on a scale of 1-5, with 5 being the best – no changes - and ratings below 2 considered a fail. Comm ADH and Std ADH samples are taken as benchmarks, setting the minimum performance level for a polymer to be successful in exterior wood applications. As expected, removing ADH from a standard grade without changing the polymer backbone (Std ADH-free in *Figures 1*, *2* and *3*), results in a worse performance overall. ML-745 and ML-747 are as good as Std ADH in presence of No-VOC coalescent to improve film formation. But comparing the polymer films with the solvent-free films shows a clear advantage in the performance of these two newly cross-linked polymers. ML-745-A is lower performing than 745, 747 or the standards. This confirms that the correct combination of the two-phase composition and cross-linker is necessary to get the best results.

LASURE FORMULATION STUDY

As the best performing products in the first part of the study, ML-745 and ML-747 were used in the following part of the work and compared in a lasure formulation with commercially available EU Ecolabel products. Two benchmark products from a DIY store were initially characterised to adjust the reference formulation and compare lasures with the same general characteristics. Benchmark products, Ref.A and Ref.B, are glossy lasures, low solids – ranging from 22-23% in weight, and suitable for brush application (specific rheology profile). The formulations ML-19-E and ML-39-D (*Table 2*), based respectively on ML-745 and ML-747, were used in comparative tests with commercial lasures: block resistance, dry and wet adhesion on bare wood, accelerated weathering, natural exposure.

BLOCK RESISTANCE

The lasure samples were applied directly by brush on bare pine wood substrates in three layers:

- › 100 g/m^2 of each layer;
- › 4 hours drying, laboratory conditions, between layers;
- › 16 hours (overnight) drying before block resistance test.

In this test, the coated face is placed in direct contact under a weight pressure for a fixed period of time. In these specific experiments, 1.0

Figure 1: No-VOC coalescent influence on polymer block resistance.

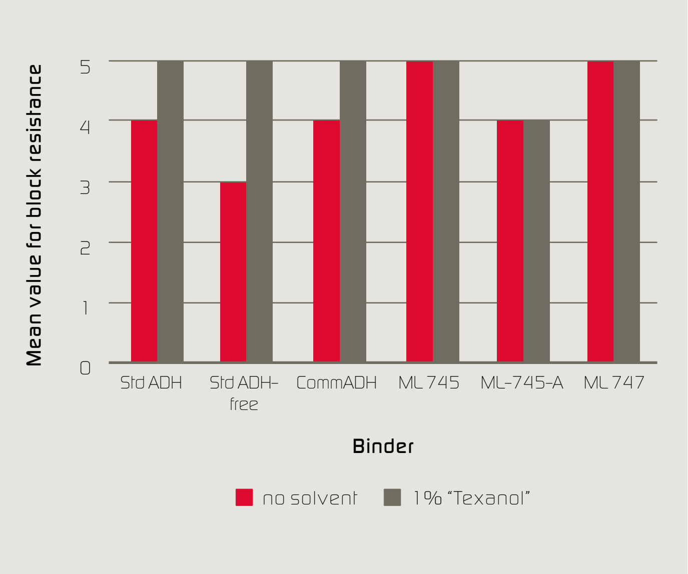


Figure 2: No-VOC coalescent influence on hot block resistance of polymers.

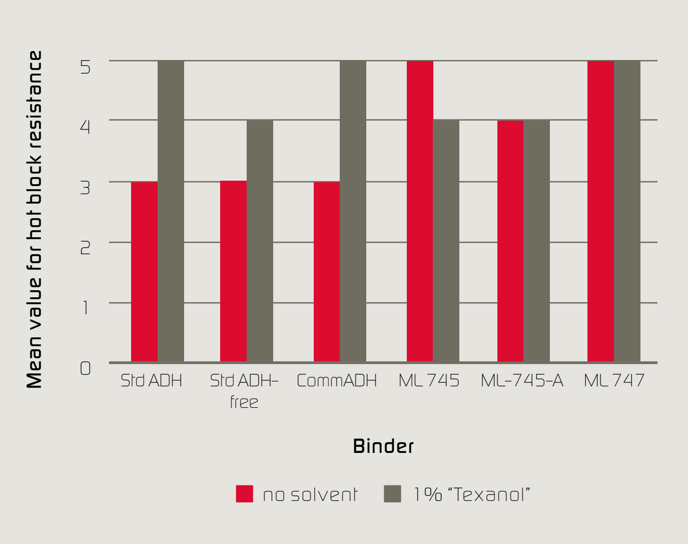


Figure 3: No-VOC coalescent influence on polymer water resistance.

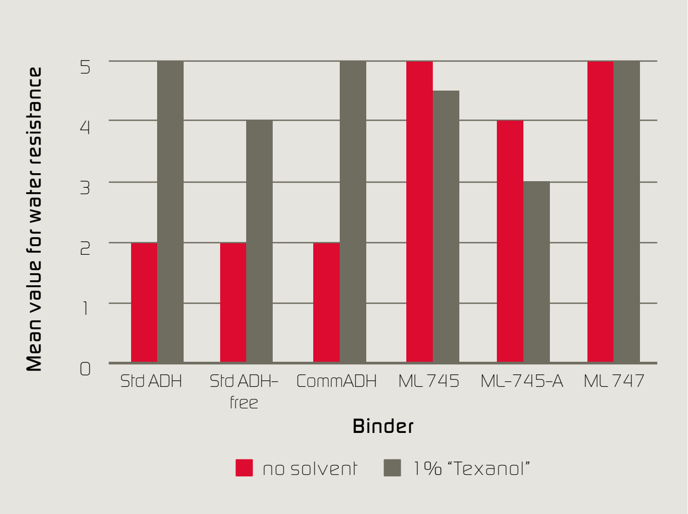


Table 3: Block and hot-block resistance results.

	Ref. A	Ref. B	ML-19-E	ML-39-D
1 hour at 50 °C, weight pressure of 1 kg * 1 cm²	5B	5B	5A	5A
24 hours at RT, weight pressure of 1 kg * 1 cm²	5A	5A	5A	5A

Table 4: Discolouration after one year of natural exposure.

	ΔL	Δb	ΔE
Ref. A	4.68	6.85	8.37
Ref. B	1.05	4.29	4.61
ML-19-E	0.30	3.78	3.97
ML-39-D	1.04	4.32	5.23

kg/cm^2 weight pressure is applied to one set of samples for 24 hours at room temperature and to a second set for 1 hour at 50 °C. Test results are rated on a 1-5 scale, with 5 being the best and rating 1 a complete failure. See *Table 3*.

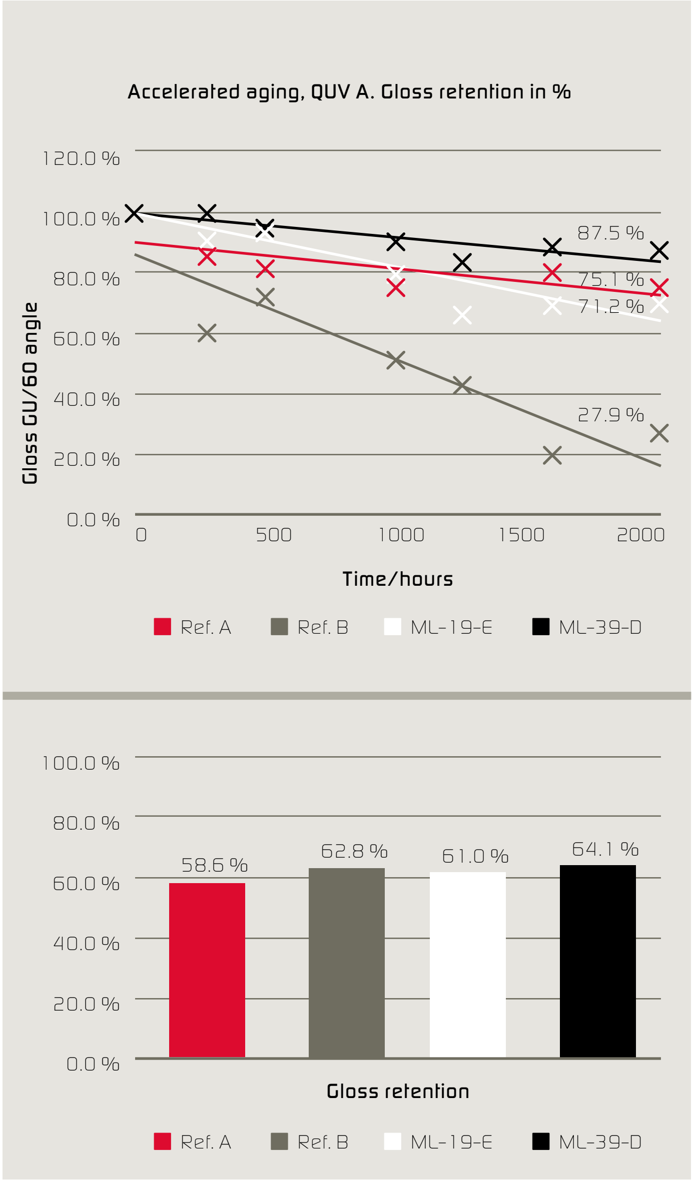
All the samples show good block resistance, and there is no indication of damage or gloss change in any of the two sample sets. There is only one minimal, non-critical difference between the samples tested for hot block resistance: sample ML-39-D based on Sample 747 fell apart directly when the test piece was checked for damage; sample ML-19-E based on Sample 745 needed to be separated but made no noise; the reference samples made a little 'tac' noise when separated although this caused no damage to the coating film. The minimal difference recorded in hot block resistance can be attributed to different possible causes: solvent type and amount, thermoplastic film, cross-linker used.

DRY AND WET ADHESION

Adhesion was directly tested on pine wood because lasures are usually directly applied in multiple layers on bare wood. Test formulations were applied in the same numbers of layers and drying conditions of the samples used for block resistance. Adhesion was tested using the cross-cut adhesion test: cross-cut in the coating film and performance check using a tape; adhesion failure is assessed according to coating removal. Dry and wet adhesion testing differs only in additional step. The cross-cut is covered with water for 1 hour, which is then wiped off and the surface dried with a piece of cloth before applying the tape to evaluate the adhesion. Test results are rated from 0 = failure, removal of >50% of the coating, to 5 = no coating adhesion loss.

Adhesion of the formulations ML-19-E and ML-39-D is generally good and doesn't present any failure in either the wet or dry (rate 5) adhesion, the two commercial references have excellent dry adhesion but one - Ref.B, has lower wet adhesion (rate 3).

Figure 4: Gloss retention in accelerated aging test (a) and after one year of natural exposure (b).



WEATHERING RESISTANCE

The four formulations were glossy lasures. Two key aspects of these types of products are the weathering resistance and the gloss retention, which are evaluated via an accelerated aging test and natural exposure. Accelerated weathering is performed using Q-LAB test equipment, QUV/se, and the samples were exposed for 2000 hours to the following cycle:

24 hours condensation at 45 °C,

5 hours UV-A irradiation (0.89 W/m^{2}nm) at 60 °C followed by 1 hour in the dark at 35 °C – repeated 24 times prior to restart with condensation.

All the test samples were prepared applying 3 layers on pine wood, as specified previously, and dried for one week under standard conditions before starting the test.

The test gloss is regularly measured and monitored (*Figure 4*) using a glossmeter – TQC GL0030 – and discolouration is measured using a spectrophotometer BYK spectro-guide sphere gloss. The spectrophotometer works in the CieLab colour space and discolouration is measured in delta E, which represents the combination of the variation on the three axes of the CiaLab system: L – white/black, a – green/red, b – blue/yellow.

Figure 4a shows the gloss retention throughout the accelerated aging test. The ML-39-D formulation is obviously better than the other three. Ref.B shows the worst gloss retention, Ref.A and ML-19-E present acceptable gloss retention, although Ref.A is slightly better than ML-19-E. Discolouration during the accelerated weathering test is minimal and fully aligned for samples ML-39-D and Ref. A, delta E measured after 2000h test is close to 4. Discolouration of the samples ML-19-E and Ref. B is slightly worse and delta E values are higher. Differences in discolouration may be due to substrate failure/change or pigment fading. The four samples were pigmented with the same amount and combination of pigment preparations. We can assume therefore that discolouration is principally due to substrate change and, indirectly, to the protective effect of the lasures.

Boards prepared as described previously, were also subjected to natural exposure on the EPS test fence in the Netherlands. These samples were checked after one calendar year to evaluate gloss retention, discolouration and general appearance.

Table 4 and *Figure 4b* show the changes after one year of natural exposure. These generally confirm that the performance of the formulations ML-19-E and ML-19-D are at least equal to lasures based on a standard ADH-containing binder. The consistency and confirmation of the results in real-life conditions provides another strong indicator to assess the success of the development. Discolouration following natural exposure of ML-19-E is aligned with ML-39-D and Ref. B while in this case, Ref. A underperforms.

The difference in discolouration after natural exposure or accelerated weathering shows that there is not a 100% linear correlation between the two testing methods and that it is good practice to run both in parallel.

After one year of natural exposure, none of the samples show any visual defects such as cracking, flaking or delamination.

Figure 5 visually summarises the performance of the four tested lasure

➔

formulations, showing that ML-19-E and ML-39-D are high performing. Moreover, it confirms that the two new acrylic polymers ML-745 and ML-747 are the optimal choice for formulating architectural exterior wood products. The differences between Ref. A and Ref. B remind us of the formulation's impact on the final lasure performance. Binders specifically designed for exterior application are needed to support formulators in getting a successful varnish or lasure with real-life durability.

NEW POLYMER OFFERS ECOFRIENDLY SOLUTION

The purpose of this study was to invent a new acrylic polymer with low MFFT and ADH-free offering comparable or better performance than standard ADH-based polymers used in the architectural exterior wood segment to formulate lasures and varnishes. Both goals are achieved by using an optimised polymer backbone and cross-linker. The selected products ML-745 and ML-747 offer an EU Ecolabel-compliant solution for exterior wood coatings that are free from environmentally hazardous components whilst retaining high durability of the finished coating.

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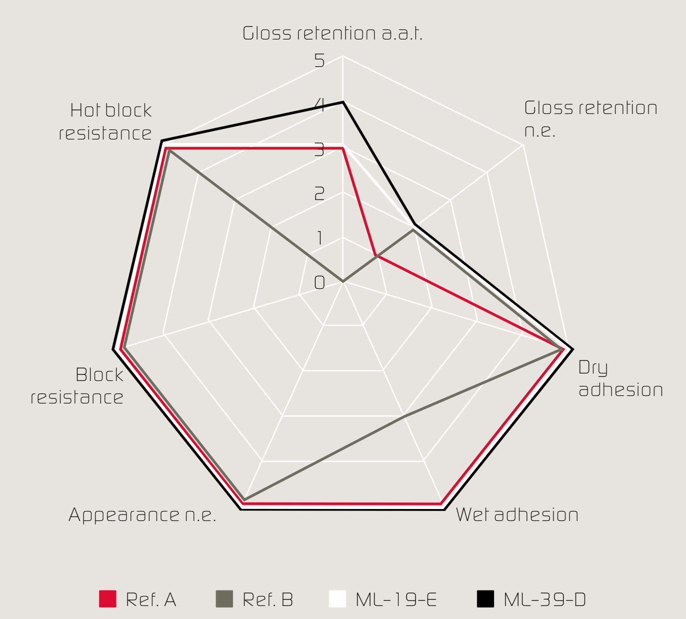
ACKNOWLEDGMENTS

Thanks to the R&D team in EPS B.V. for the high value polymer synthesis work that is the foundation of this study: Dr. Andrew Hearley*, EPS B.V.; Emile Stevens, EPS B.V.; Ibrahim Kemikkiran, EPS B.V. (*Dr. Hearley moved to The Valspar corporation beginning of 2016).

Figure 5: Overall comparison of the four tested lasure formulations.



Gloss retention a.a.t. (accelerated aging test): ratings from 0 (> 50 %) to 5 (90/100 %).
Gloss retention n.e. (natural exposure): ratings from 0 (< 50 %) to 5 (90/100 %).
Appearance n.e. (natural exposure): ratings from 0 (defects on mor than 50 % of the test panel) to 5 (no defects). Dry adhesion, wet adhesion, block resistance an hot block resistance: ratings as described in this article.

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> "Colour deviation is a very difficult topic."

3 questions to Massimo Longoni

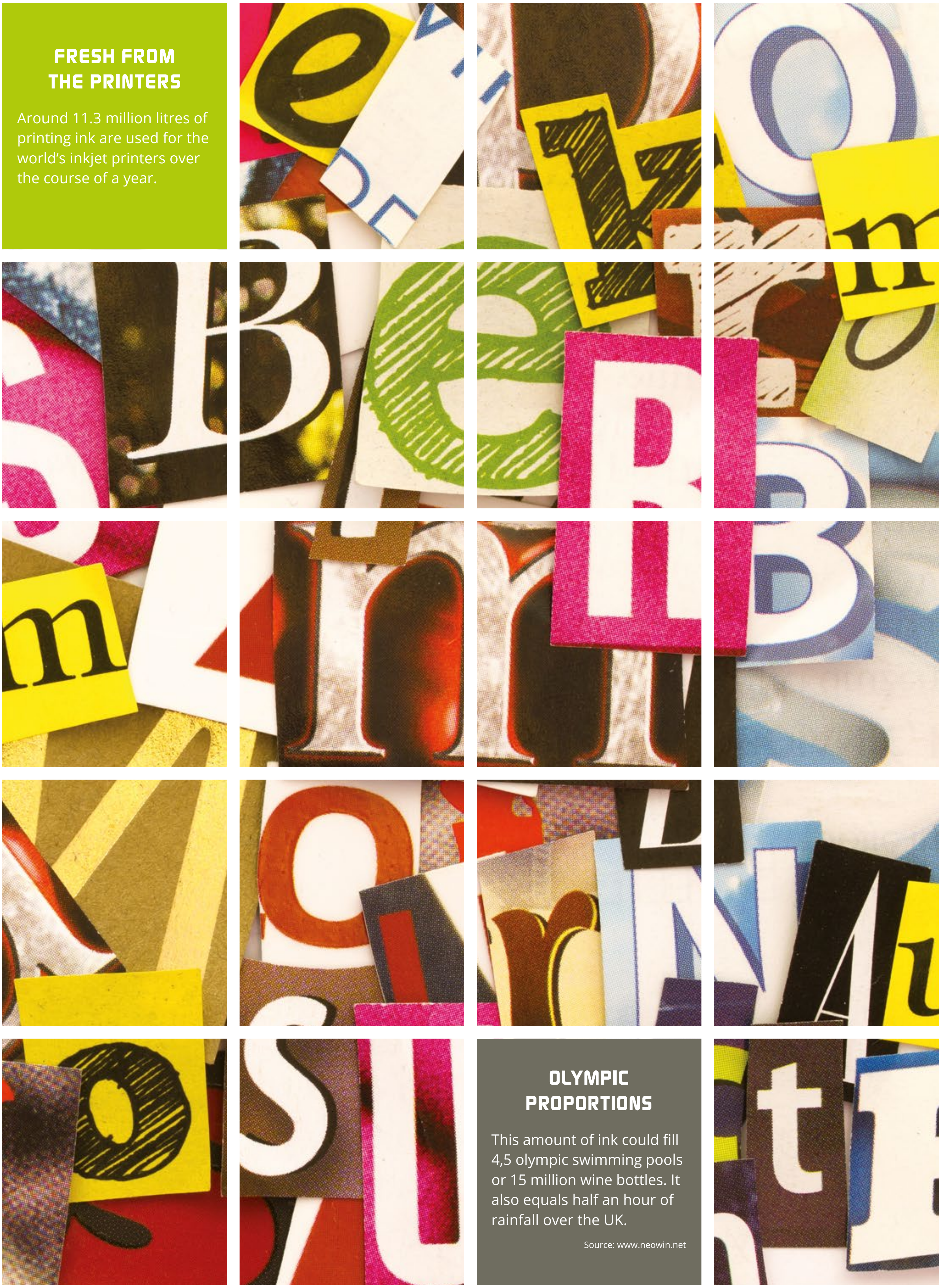
In how far does the monomer composition of ML 745 (harder phase) influence the low block resistance at 50 °C with 1% "Texanol"? *In two-phase acrylics the block resistance is definitely influenced by the hard-phase and ML 745 behaviour reflects this concept. The two phase composition is fine-tuned, so that the film formation is optimal without any addition of coalescing agent and the hot block resistance is perfect. The introduction of "Texanol", that is a no-VOC coalescing agent with an high boiling point and slow release, can plasticise the polymer film in such extent that the block resistance at 50 °C with 1% "Texanol" is inferior to the block resistance without it.*

Is the significant colour deviation of ML-39-D related to the modified cross-linking of ML-747 or to the modified monomer composition? *Colour deviation is a very difficult topic and referring to the study in the article we have not identified any direct correlation with monomer composition or cross-linking. If we look at the results of the accelerated weathering and natural exposure tests ML-39-D performs well in both and better than references A and B that are worse in one test or the other. If I take a step back and look critically at all the formulations' results there is no evidence of which is the key factor in colour deviation between monomer composition, cross-linking and formulation.*

Does the improved gloss retention of ML-39-D result from the modified cross-linking of ML-747 or from the modified monomer composition? *ML-39-D formulation is based on ML 747 that contains a cross-linker, no ADH or other carbodihydrazide, that is not in use in ML 745. If we compare ML-39-D and ML-19-E (formulation based on ML 745) the cross-linker probably plays the mayor role in the different gloss retention performance. ML 747 is the outcome of an incremental improvement process which results in an two phase acrylic that combines optimised composition and cross-linking which are both contributing to match or overcome gloss retention of reference formulations based on ADH containing acrylics.*

FRESH FROM THE PRINTERS

Around 11.3 million litres of printing ink are used for the world's inkjet printers over the course of a year.



Source: Vesna Cvorovic - Fotolia.com

OLYMPIC PROPORTIONS

This amount of ink could fill 4,5 olympic swimming pools or 15 million wine bottles. It also equals half an hour of rainfall over the UK.

Source: www.neowin.net

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DOUBLE CROSSLINKING FOR GREATER EFFICIENCY

A new PU dispersion for fast-curing UV furniture coatings. By Eva Tejada Rosales, Berta Vega Sánchez, Matthias Wintermantel, Covestro (published in ECJ 11/2017).

Water-borne UV-curing wood coatings are already used as standard for high productivity, quality and environmentally friendly demands. A new polyurethane solution introduces two crosslinking mechanisms to increase robustness of the system. This further crosslinking mechanism also improves drying times, which reduces energy consumption, improves productivity, and gives furniture manufacturers greater flexibility to react to market requirements.

UV-curing polyurethane (PU) wood coatings have been on the market since the 1990s. The combination of positive market relevant properties led to the current outstanding market position. First, they exhibit extremely fast curing and high productivity. Market analysts describe the reduction in production times associated with UV-curing products as one of the key cost-influencing factors [1]. Second, those products emit fewer volatile organic compounds (VOCs) than conventional solvent-borne coatings. Third, they are highly resistant to chemicals and mechanical influences.

To ensure the coatings can cure perfectly, the UV light must be able to reach every part of the coated object. This is usually not a problem on flat surfaces such as tabletops and furniture doors, however, three-dimensional furniture items with a relatively complex shape, can lead to incomplete curing in shadow areas. Moreover, UV light can be absorbed by pigments or cannot always reach the whole coating if the film is too thick. This problem of “lack of curing” limits a broader application of UV-curing technology on wood coatings.

GREATER FLEXIBILITY WITH WATER-BORNE SYSTEMS

UV coatings are the best choice when high productivity is needed. Three main options are available: 100% systems, solvent-borne reduced UV or water-borne (WB) UV-curable dispersions [2].

Water-borne UV coatings have some benefits over other systems. They can use water to reduce coating viscosity instead of the solvents or monomers (reactive diluents) used by other systems. This is why water-borne UV-curable coatings are particularly environmentally friendly and are advantageous when it comes to hazard categorisation and labelling. Furthermore, WB systems can be applied by spray application, are easier to down-gloss, do not show shrinkage during radiation curing and allow products with higher flexibility.

RESULTS AT A GLANCE

→ UV curing technology could be more extensively used in wood coatings, if sufficient curing in shadow areas or pigmented coatings could be achieved.

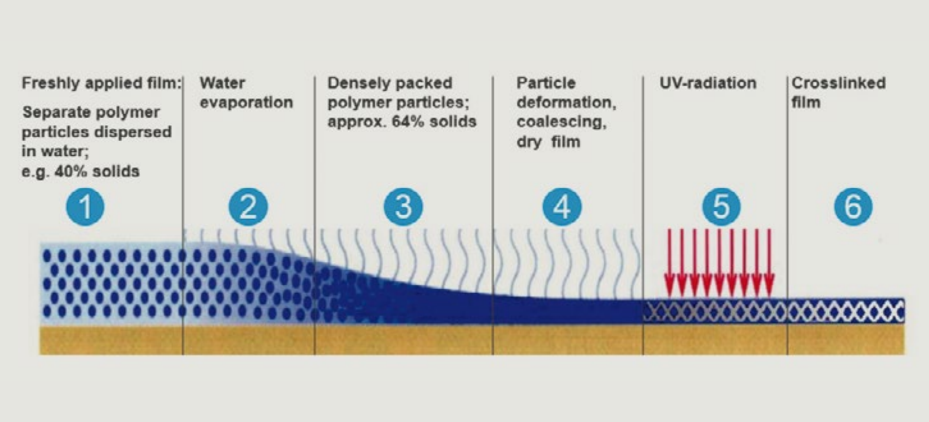
→ A new polyurethane dispersion (PUD) for UV-curing wood coatings has been developed that can accelerate the coating process by as much as 50% thanks to faster drying.

→ Coatings based on this new PUD for UV curing use two different curing mechanisms – in addition to the conventional UV curing, it is also capable of oxidative self-crosslinking.

→ The dispersion enables wood coatings to achieve outstanding chemical resistance and hardness even in areas that receive little or no UV light.

→ Combining UV and oxidative curing in polyurethane dispersions provides high performance, versatility, robustness and higher efficiency and presents an environmentally friendly solution for wood coatings

Figure 1: The drying process for water-borne UV-curing wood coatings.



The biggest disadvantage of water-borne UV-curable dispersions is that they involve a first step to evaporate water before the UV curing.

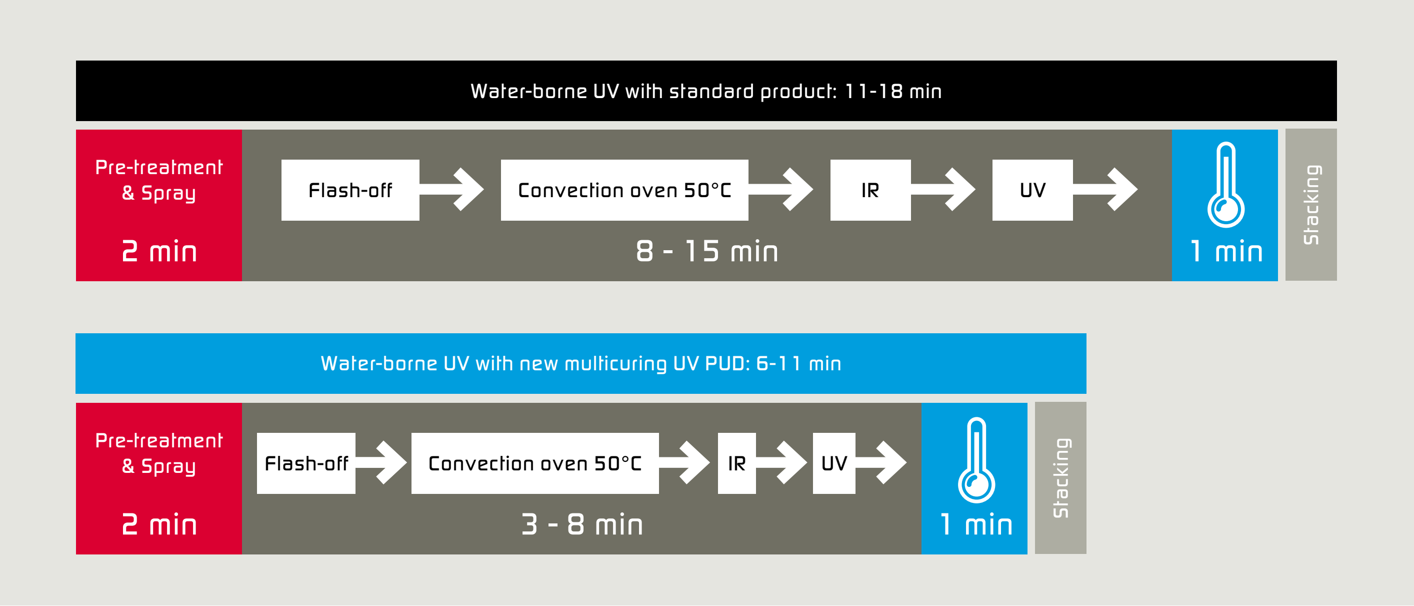
REDUCING DRYING TIME

This initial water evaporation step strongly affects the total drying time of water-borne UV curing systems.

A typical WB UV-curable system has a solid content of around 40%. After application water starts to evaporate reaching a 64% solid content (close packing), and the material loses most of its flowability. After that point, the polymer particles begin to coalesce and the coating film is formed. Normally, it is only at this point that UV radiation takes place, and this crosslinks the polymer molecules to form the final coating (*Figure 1*). For a water-borne UV-curing standard clear coat, this takes between 10 and 20 minutes (for a coating with 80-100 g/m^2 film thickness) as can be seen in *Figure 2a*.

By introducing a further crosslinking mechanism, this drying time for conventional water-borne UV-curing coatings can be shortened by up to 50%. Formulations based on a novel multi-curing PU dispersion (multi-curing PUD) ensure that coatings are sufficiently dried so that they can be exposed to UV radiation 3 to 8 minutes after application (*Figure 2b*), depending on the line speed, oven temperature, air flux, substrate and amount applied. The product has a strong physical drying and fast water evaporation. *Figure 3* illustrates how quickly two formulations dry in the oven at 50 °C. The bottom formulation uses this double crosslinking mechanism,

Figure 2: Duration of the coating process, a) when using water-borne UV-curing standard coatings, b) when using water-borne UV-curing coatings based on the new multi-curing PUD.



while the top one is based on a PU dispersion that previously set the standard for quick drying. It is clear that the new multi-curing PUD is almost dry after 3 minutes under these conditions, while the standard product needs around 6 minutes to avoid white spots caused by water remaining in the dried film.

DUAL CROSSLINKING REDUCES COSTS

The drying behaviour of formulations based on the new quick-drying dispersion results from the fact that they use two different curing mechanisms: One mechanism is the conventional radical polymerisation that forms the basis of all radiation-curing coating systems. In addition, the new UV-curable PUD has an alkyd modification showing oxidative crosslinking in contact with air [3, 4, 5]. This second crosslinking takes place without radiation. Due to the presence of air, the crosslinking begins as soon as the first water evaporates and continues for several days. After 3–7 days at room temperature the coating has reached its final properties. Apart from enhancing the coating properties via this second crosslinking mechanism, the alkyd modification also brings additional hydrophobicity to the coating. This hydrophobicity helps to improve the water release of the film during the drying process, which reduces energy costs and increases productivity.

CURING EVEN UNDER LOW LEVEL UV RADIATION IMPROVES ROBUSTNESS

Wood coatings based on conventional UV-curing PU dispersions cannot always display their outstanding quality standard in practice because of incomplete UV curing. Three-dimensional components are one example, where areas that do not receive enough light from the UV sources in the coating system can occur (shadow curing). In such cases the resulting coating is not fully crosslinked in these areas and thus, also does not exhibit the level of mechanical and chemical resistance that it would otherwise achieve. The same applies to parquet coatings applied on-site. Sometimes it is not possible to perfectly cover every inch of the parquet area using the mobile UV curing equipment. The quality of craftsmanship may also make some sections of the surface inaccessible to the UV light.

There is a third scenario where conventional water-borne UV-curing systems are unable to perform to their full potential – the combination of thick layers and fast process speeds can lead to a situation where the energy of the UV source used is not always sufficient to completely crosslink the resulting coating. Using the new multi-curing dispersion is beneficial in all these scenarios, bringing robustness to the coating systems.

Figure 3: Drying time using water-borne UV-curing standard coatings (top) and based on the novel multi-curing PUD (bottom).

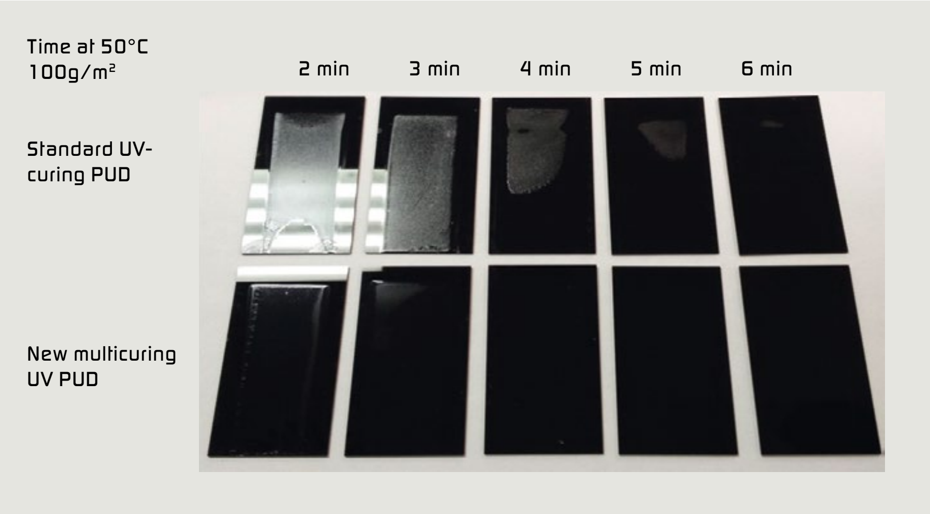


Figure 4: Comparison of ethanol resistance of coatings at various photoinitiator concentrations and line speeds.

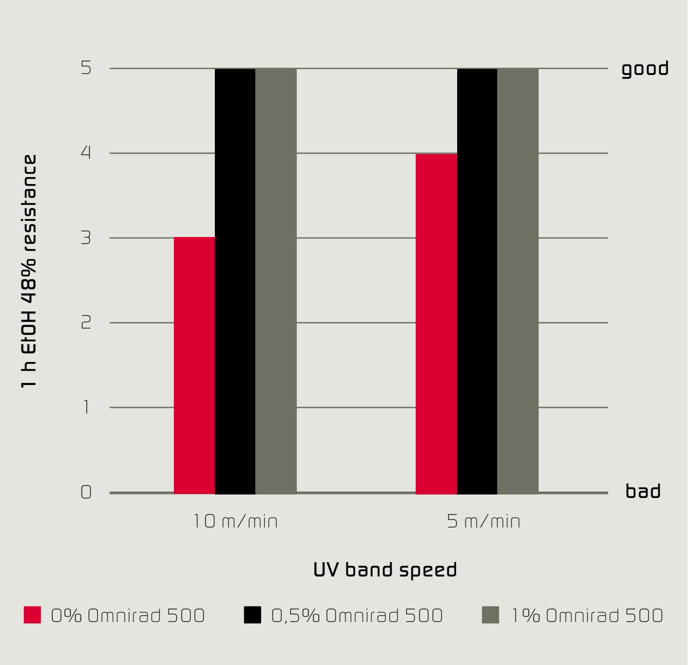


Figure 5: Diverse range of potential applications for the new PU dispersion.

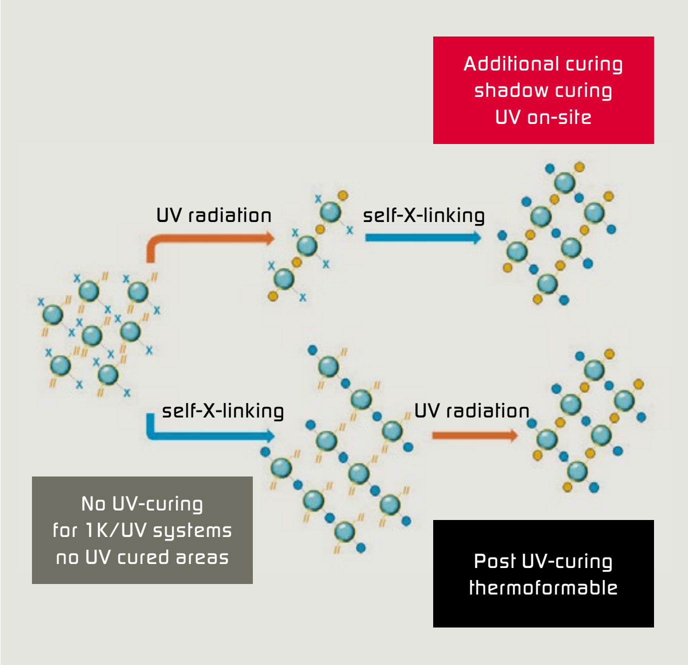


Figure 6: Characteristics profile of the new PU dispersion (red line) compared with two conventional water-borne UV-curing binding agents (black and blue).

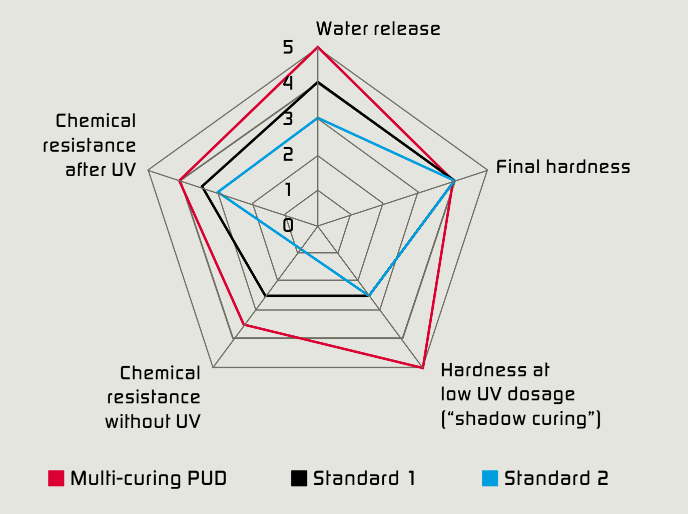


Table 1: Properties of a water-borne clear-coat formulation based on the novel PUD, with and without UV curing.

	Without UV curing	**After UV curing**
König hardness (100 g/m^2 on glass)		
after 1d, RT	40 s	70 s
after 7d, RT	100 s	150 s
Chemical resistance on beech panel according DIN 12720		
Ethanol 48% - 1 h	3	5
Water - 24 h	5	5
Red wine - 6 h	5	5
Coffee -16 h	5	5
Hand cream - 6 h	5	5

INCREASING PROCESS EFFICIENCY

Formulations based on the fast-drying PU dispersion (new multi-curing PUD) cure using both UV-curing and oxidative self-crosslinking, which also means in principle that it is possible to use lower-output and thus energy-saving UV sources. In some cases, it is also possible to reduce the quantity of photoinitiator used without negatively impacting the characteristics of the resulting coatings. *Figure 4* illustrates this using the example of resistance to 48% ethanol solution during a one-hour exposure period. The coatings were applied in a thickness of 100 g/m^2 on melamine, dried for 10 min at 50 °C, and cured using an 80 W/cm UV Hg lamp (256 mJ/cm^2). A clear coat formulation based on the new polyurethane dispersion, containing only 0.5% photoinitiator, performed equally as well as an identical formulation using a more typical 1% photoinitiator. Using a lower oven temperature for water evaporation, lower energy on UV sources, extending the life-time of lamps and reducing the quantity of photoinitiator overall, substantially reduces the costs of the coating process. Together, the use of the new fast-curing PUD creates a cost-effective and efficient process that also offers the possibility of increasing line speed.

MULTIPLE USES

Figure 5 shows at a glance the diverse range of application possibilities for the new PU dispersion thanks to its two curing mechanisms. The UV-cured coatings formulated with this dispersion continue to cure as a result of oxidative self-crosslinking and performance improves over time, which is particularly important in the UV shadow areas of furniture coating or for the UV on-site parquet coating. No additional curing agent is required to achieve an excellent standard of coating quality, as in standard dual-cure UV systems. One-component UV coatings are particularly easy to handle and there is no pot life to consider.

In addition, the coating characteristics that can be achieved using the new PU dispersion simply because of oxidative self-crosslinking are so good that furniture manufacturers can use appropriate formulations as both conventional water-borne one-component coatings and UV-curing one-component coatings, depending on the application requirements. This simplifies stockholding and enables furniture manufacturers to quickly adapt their production when their order situation requires it.

This product could also be used in applications which need a certain level of performance initially and further crosslinking is achieved afterwards by UV curing.

In summary, the new multipurpose fast-curing PU dispersion offers plenty of flexibility in UV-curing furniture coatings – it is suitable for use in both topcoats and primers, and can be used in clear coats or pigmented coatings.

IMPROVED CHEMICAL RESISTANCE

Clear coats based on the new fast-drying PU dispersion exhibit a high resistance to water, red wine, coffee and hand cream even without UV treatment, see *Table 1*. The table shows the results when two layers of the clear coating 100 g/m^2 were applied to a beech wood panel, dried for 10 minutes at 50 °C and UV cured under a 120 W/cm Hg lamp at 10 m/min (dose 440 mJ/cm^2). However, the UV radiation further boosts chemical resistance to ethanol, for example, and also increases hardness. Overall, the novel dispersion can be used to achieve similar – or even better – characteristics to those achieved with other water-borne UV-curing binders and provides other advantages such as faster drying and robustness.

White-pigmented coatings based on the new PU dispersion were tested under the same conditions as the clear coats, with the addition of 2 x 120 W/cm Ga lamp (dose 1,173 mJ/cm^2) and show good resistance to water for 24 hours and for 6 hours in contact with hand cream (*Table 2*). However, good chemical resistance to stains requires the addition of a hydrophilic polyisocyanate. The medium resistance to red wine and coffee can be improved by adding 10% of the right hydrophilic polyisocyanate to the formulation.

The product also shows advantages even in critical coloured pigmented coatings. Compared with established products for coloured systems, the new dispersion offers benefits in colours such as yellow or red (see *Table 3*).

Figure 6 gives an overview of the properties of the new PU dispersion. The water is expelled particularly quickly from freshly applied coatings based on the new PU dispersion. The comparison with other UV-curing standard high-performance binders shows that the final hardness achieved in the resulting coatings is almost the same in all of them, but only when the UV radiation is applied with sufficient intensity. With a low UV dose, as received by shadow areas in practice, the hardness achieved in coatings based on the new polyurethane dispersion is far higher

Table 2: Properties of two water-borne white-pigmented furniture coating formulations based on the multi-curing PUD.

	Glossy coating	**Matt coating**
König hardness (100 g/m² on glass)		
after 1d, RT	60 s	60 s
after 7d, RT	105 s	90 s
chemical resistance on beech panel according DIN 12720		
Ethanol 48% - 1 h	5	4
Water - 24 h	5	5
Red wine - 6 h	5	4
Coffee - 1 h / 16 h	5 / 4	5 / 3
Hand cream - 6 h	5	5

than with conventional formulations. This effect is similar when it comes to chemical resistance, which is higher in coatings based on the novel PUD cured without UV radiation than in conventional formulations.

FLEXIBLE RESPONSE TO MARKET NEEDS

The new multi-curing PUD offers a number of key benefits for coatings manufacturers. It supports a diverse range of applications for both clear coats and pigmented coatings, for one-component systems and for UV- or dual-curing systems. Clear coatings can be formulated without additional curing agents and still meet the highest quality requirements. Less photoinitiator is required, saving formulation costs. Finally, coatings manufacturers can use the new PU dispersion to formulate coatings that emit very few VOCs, require no reactive thinner and which are consequently better in terms of labelling.
Manufacturers of furniture or furniture parts

Table 3: Pigmented coatings performance of different UV-curing PUDs tested after 7 days at RT according to DIN EN 12720. UV curing: Hg and Ga 80 W/cm lamp, 5 m/min (dose 950 mJ/cm²).

		Standard UV-curing resin for colours	**New multi-curing UV dispersion**
Red pigmented coating	König hardness (measured on coated glass)	100 s	120 s
	Chemical resistance		
	Ethanol 48% - 1 h	4	5
	Water - 24 h	5	5
	Red wine - 6 h	5	5
	Coffee - 16 h	5	5
	Hand cream - 6 h	5	5
Yellow pigmented coating	König hardness (measured on coated glass)	80 s	130 s
	Chemical resistance		
	Ethanol 48% - 1 h	1	5
	Water - 24 h	5	5
	Red wine - 6 h	4	5
	Coffee - 16 h	5	5
	Hand cream - 6 h	5	5

“You can start UV curing earlier.“

3 questions to Matthias Wintermantel.

Can you give an estimate on how fast your new film reaches acceptable properties for further use in areas that suffer from shadow curing? For example, when can I step on a not perfectly UV-cured parquet? *In terms of chemical resistance, after 3 days you are getting already good resistance against chemicals like water, coffee or wine. In terms of hardness, after 3 days you get around 75% of final hardness. Final properties are obtained after 7 days, but as shown in Table 1, you do not reach the same performance without UV curing as with UV curing, even after longer time.*

Figure 5 implies that the fully cured films are exactly the same, no matter in which order both mechanisms take place. Is that actually the case or can you see/measure differences? *We have not observed difference on chemical resistance of the fully cured films, both first dried and then UV cured or the other way around. However the final hardness obtained if film is directly cured with UV is higher than if the film is cured at room temperature for a week and afterwards the UV light is applied. Possibly the higher molecular weight of the polymer after self-X-linking does not allow the same yield in the UV curing.*

Is the water evaporation for your new PUD so much higher that you start UV curing at the same solids share like in conventional films or can you start earlier because of the secondary crosslinking? *You can start UV curing earlier because water is released faster. The cross-linking mechanism is based on fatty acid modification, giving the product around 30% bio-based content. This modification increases hydrophobicity of the system which is helping for the faster water release and allows an overall faster process (or lower temperature during drying) and therefore improves productivity and energy consumption.*

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can look forward to further benefits: since drying occurs faster than with conventional water-borne UV-curing coatings, furniture manufacturers can shorten the coating process and reduce energy costs. In addition, lower-output UV sources can be used because the resulting coatings achieve an extremely high quality even with a low dose of UV radiation. Both of these possibilities increase the efficiency and cost-effectiveness of the coating process. Moreover, coatings based on the new PU dispersion can be used both with and without UV curing. This enables furniture manufacturers to respond extremely flexibly to changing customer requirements. Finally, furniture manufacturers gain greater design freedom, since three-dimensional parts with shaded areas can be coated to a high level of performance.

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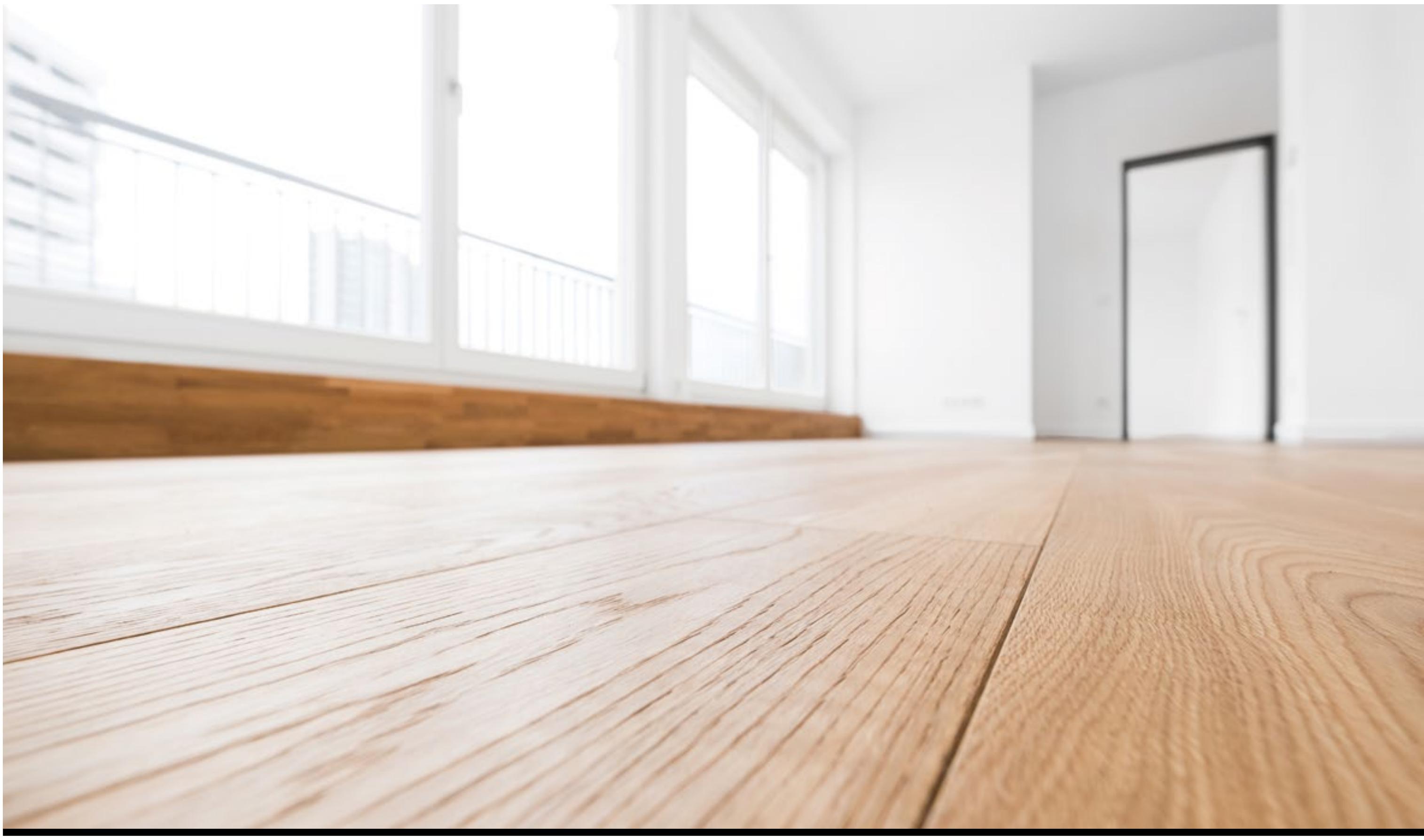

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SEEKING SYNERGY

Acrylic dispersions with oil-modified shell show versatile performance. By Andreas J. Steiner, F. Lunzer, L. Khatai, T. Kittler, L. Sterckx and K. Gariepy, Allnex Austria (published in ECJ 01/2018).

Water-borne alkyd and acrylic binders each have significant advantages and limitations for wood coatings. Core-shell emulsions were prepared using acrylic copolymers with oil-modified alkali soluble resins as the emulsifier/shell. Good substrate penetration, weathering resistance and adhesion to many different substrates were achieved.

Water-borne binder resins for state of the art wood coating technologies are mainly based on two different polymer systems: water-borne alkyd binders and water-borne acrylic dispersions. Each of these binder technologies of course features some advantages as well as drawbacks.

In order to combine the 'best of both worlds', different hybrid technology approaches have been exploited, mainly based on blending and mini-emulsion polymerisation technologies.

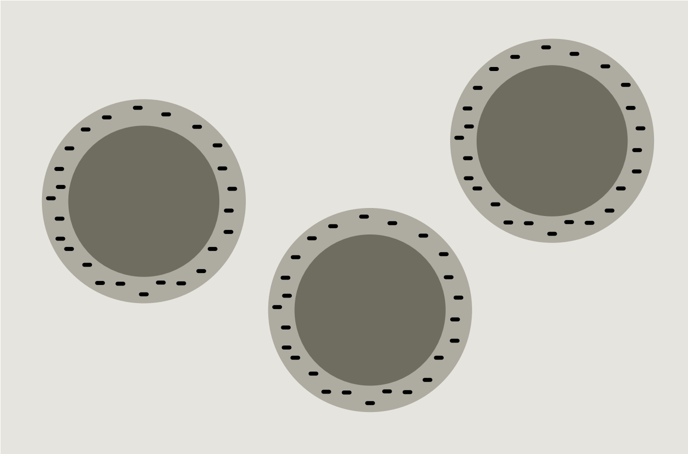
The work outlined below discusses a new approach towards oil-modified acrylic multi-domain dispersions that aims to combine the positive application properties and enhanced wood penetration of alkyd resins with the good chemical resistance, high hardness and fast drying characteristics of acrylic dispersions.

ADVANTAGES AND LIMITATIONS OF WATER-BORNE ALKYDS

Alkyd binders generally exhibit a high level of wood penetration as well as favourable application characteristics, especially very good flow and levelling behaviour in brush and roller application. High gloss levels can also be achieved in wood coating formulations.

Due to the high percentage of unsaturation in the fatty acid side chains, alkyd resins can cure via oxidative cross-linking ('drying') when

Figure 1: Schematic drawing of electrostatically stabilised ASR-based core/shell particles with negatively charged ASR shell (light grey) and hydrophobic core polymer (dark grey).



RESULTS AT A GLANCE

→ The two main binder resin technologies used in wood coatings each have significant advantages and limitations.

→ Alkyds offer good penetration, flow and gloss but are slow drying and require cobalt or other heavy metal driers. Acrylics offer fast drying and excellent weathering resistance but inferior penetration and gloss and may crack during weathering.

→ Alkali soluble resins (ASRs) can be used as polymeric emulsifiers in preparing acrylic copolymer emulsions, where they create the shell in core-shell particles, but these then have poor water resistance.

→ ASRs were modified with drying oil components. Core-shell emulsions prepared using these as emulsifiers forming the shell layer showed much improved water resistance and substrate penetration.

→ Additional tests confirmed that the novel binders had good weathering resistance and also good adhesion to a wide range of different substrates.

combined with suitable catalysts. This increases the overall molecular weight of the polymer and enhances the coating's chemical resistance properties. However, as the oxidative cross-linking reaction takes some time to complete, alkyds are generally limited in their drying speed and early hardness development.
Very often heavy metal based dryers need to be added to the formulation to speed up the oxidative curing process, which limits the environmental friendliness of this coating technology and often raises regulatory compliance issues.
As the alkyd's polymer backbone is built up from polyester-based structures that are prone to being attacked by water, the general hydrolysis resistance and weatherability of the coating is of course limited in outdoor applications. However, this fact may also play in favour of this technology as alkyd binders typically wear off over time and may then be recoated without sanding.

ACRYLIC DISPERSIONS SHOW VERY DIFFERENT PROPERTIES

Acrylic dispersions, on the other hand, show extended weatherability due to the hydrolysis-stable polymeric backbone based on carbon-carbon bonds. Using various well established core/shell approaches, these binder technologies can be designed to combine fast drying with low minimum film forming temperature and fast hardness development.
Dryers are not needed as oxidative cross-linking typically does not occur with this resin technology. However, very often acrylic dispersions are limited in their wood penetration performance and application characteristics (limited flow and levelling). Acrylic-based wood coatings are also typically lower in gloss than their alkyd counterparts.
The high hydrolysis resistance of acrylic binders combined with the lack of wood penetration very often leads to film cracking and flaking during outdoor use, which then typically requires sanding before recoating.

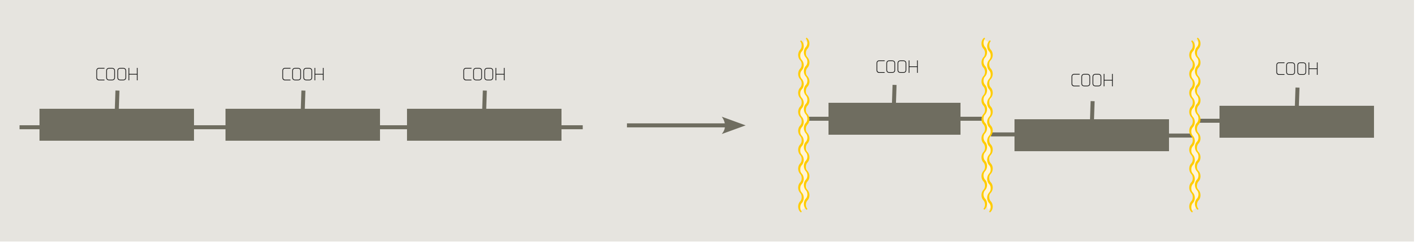
INTRODUCING ASRS – THE BASIS FOR A NEW APPROACH

Alkali soluble resins (ASRs) are widely used in acrylic emulsion polymerisation technologies. ASRs are typically low molecular weight (Mw ~ 3000 – 10,000 Da) random copolymers with a high acid value, usually > 200 mg KOH/g.
Due to their high acid content, these polymers are completely soluble in alkaline water at pH values greater than the pKa of the acid moieties built into the ASR backbone. In alkaline solution, ASRs act as ionic polymeric surfactants that can stabilise hydrophobic polymers without the need for additional classical low molecular weight surfactants.
Typically the observed particle morphologies of ASR-based dispersions have a defined core/shell-structure with the hydrophilic, negatively charged ASR forming the shell which stabilises the hydrophobic core polymer via electrostatic stabilisation (see *Figure 1*).
The absence of low molecular weight surfactants can be seen as a clear advantage over conventional emulsion polymerisation technologies, as surfactant migration after film formation is minimised. However, due to the hydrophilic character of the alkali soluble resin, ASR-based coatings typically exhibit only limited early water resistance and very little alkali resistance, which can be seen as the major drawback of this technology.

ACHIEVING THE BEST PROPERTIES OF BOTH BINDER SYSTEMS

Based on a novel synthetic approach, ASRs were modified with various drying oil components derived from (for example) tall oil, soybean oil or linseed oil by grafting and/or incorporation of the oil component into the polymer's backbone during free radical polymerisation.
The oil components are attached to the ASR emulsifier resin via hydrolysis-stable carbon-carbon bonds of the unsaturated fatty acid moieties of the oil component linking to the polymeric backbone of the alkali soluble resin (*Figure 2*).
These novel oil-modified alkali soluble resins were successfully used as polymeric emulsifiers in the emulsion polymerisation of hydrophobic acrylic and styrene-acrylic copolymers, yielding oil-modified acrylic dispersions. As is the case for standard ASRs, the oil-modified alkali

Figure 2: Schematic drawing of standard ASR (left) versus oil-modified ASR (right). Oil components are represented by yellow fatty acid chains bound via stable carbon-carbon bonds to the polymeric backbone.



soluble resin forms the shell domain, while the hydrophobic acrylic copolymer is found in the core of the dispersed particles.
The polymerisation of the acrylic core domain can even be done sequentially, using different monomer mixtures, to create particles with multiple distinct core domains. These multiple core domains can be different in their hydrophilic character, functionality or glass transition temperatures, just to name a few possible examples.
Multi-domain core structures may offer several advantages over mono-core structures, as already seen in the classical acrylic core/shell approaches (*Figure 3*). For example, the right combination of a high Tg domain with a low Tg domain in the hydrophobic core region may result in a low film forming temperature combined with high film hardness of the resulting multi-domain dispersion.

IMPROVED WATER RESISTANCE AND SUBSTRATE PENETRATION

The biggest advantage of the oil-modified dispersions described above can be seen in the very hydrophobic nature of the film surface, which drastically enhances the early water resistance of the binders. Standard ASR-based reference dispersions showed severe whitening

Figure 3: Schematic drawing of mono-core (left) versus multi-domain-core (right) particle morphology. Red and dark grey areas represent separate core domains with different monomer compositions.

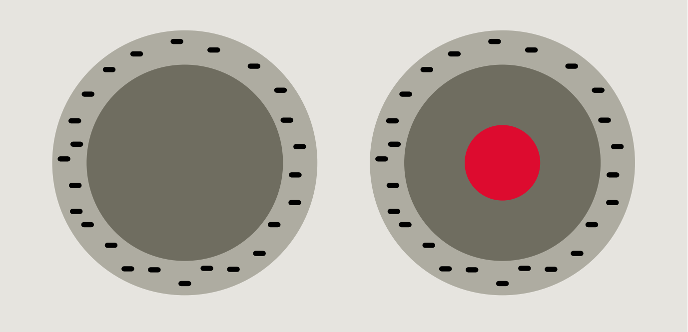


Figure 4: Water drop resistance testing of oil-modified dispersion (left) and standard ASR-based binder (right). The picture was taken after one hour of water drop exposure following 24 hours of drying at ambient temperature on glass.

Figure 5: Test results according to DIN EN 927-6:2006-10 (3000 hrs). From left to right: acrylic binder; core-shell acrylic binder; oil-modified multi-domain dispersion; alkyd-acrylic hybrid binder; alkyd binder.

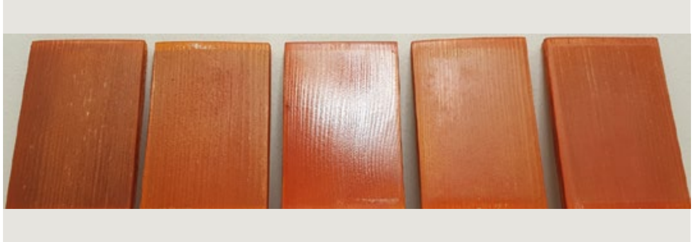


Figure 6: Outdoor testing results (Graz/Austria; 24 months; 45° south). From left to right: acrylic binder; oil-modified multi-domain dispersion; alkyd binder. Top of each board double-coated; bottom of each board single-coated.

Table 1: Trim testing formulation.

Substance	**Amount [%]**	**Comments**
Additol XW 6535 (dispersing agent)	3.106	Mix and disperse approx. 30 min. on dissolver (9-11 m/s)
Additol VXW 6205 (dispersing agent)	0.172	
Kronos 2310 (pigment)	25.288	
Methoxypropoxy propanol	1.380	
Deionised water	4.244	
Aqueous ammonia 25%	0.069	Mix in given order
AMP 90 (neutralising agent)	0.069	
Tego Foamex 805 (defoamer)	0.172	
Oil-modified multi-domain dispersion (binder resin)	60.500	50% solids content
Tego Foamex 805 (defoamer)	0.800	Mix in given order
Rheolate FX 1070 (rheology modifier)	1.000	
Methoxypropoxy propanol	1.500	
Additol XW 6569 (1:10 MPP; defoamer)	0.700	
Additol VXW 6503N (substrate wetting additive)	1.000	
Total	**100.000**	

and blistering of the film within the first five to ten minutes of water drop exposure after 24 hours of drying prior to testing. However, the corresponding oil-modified dispersions all exhibited a water drop resistance of longer than two hours before a slight whitening of the film could be noticed with the human eye, and this was found to be fully reversible upon drying (see *Figure 4*).

Additionally, the oil modification of the ASR shell domain was found to drastically improve substrate penetration characteristics, especially for organic substrates such as wood, paper and cellulose.

Laboratory testing on binder penetration into standardised cellulose-based filter plates revealed that the novel dispersions exhibited similar penetration characteristics to commercial water-borne alkyds – giving approximately three times higher penetration than the commercial water-borne acrylic dispersions and standard ASR-based systems tested.

HIGH PERFORMANCE IN DECKING STAINS

Durability and weatherability performance of the novel oil-modified acrylic multi-domain dispersions was tested in a very basic decking stain formulation. This was compared with commercial water-borne acrylic, core/shell acrylic, water-borne alkyd and alkyd/acrylic hybrid binders.

All resin systems were formulated in the same way without UV-absorbing or UV-blocking additives. First, all binder resins tested were adjusted with deionised water to a solids content of 22%. Then, based on the total formulation, 1.5% of pre-dispersed transparent iron oxide pigments (yellow : red = 1:1) were added and mixed in upon stirring. Commercial Co-based driers were added to the alkyd-based binders in the recommended amounts.

Accelerated aging testing according to DIN EN 927-6:2006-10 (artificial weathering using fluorescent UV lamps and water spray) was carried out on untreated standard European pine wood boards, double-coated with the deck stain formulations.

After 3000 hrs of testing was completed (1.5 times the standard testing duration), the erosion characteristics and gloss retention of the deck stain coatings were compared to unaged reference samples.

The commercial water-borne acrylic and core/shell acrylic binders all exhibited significant film cracking, discolouration and loss of adhesion over the testing period. The alkyd and alkyd/acrylic hybrid reference binders were found to show a severe loss of film integrity due to erosion based wear-off as well as a very strong decrease in gloss level.

The novel oil-modified acrylic multi-domain dispersions, however, showed no cracking, very high gloss retention rates combined with perfect film integrity and insignificant erosion wear-off (see *Figure 5*).

NATURAL WEATHERING TEST CONFIRMS LABORATORY RESULTS

The testing results from accelerated weathering testing according to DIN EN 927-6:2006-10 were also verified in real outdoor aging testing. Untreated European standard pine wood boards were single- and double-coated with the deck stain formulations under consideration and exposed to outdoor weathering in Graz/Austria for 24 months at 45° south orientation. *Figure 6* shows the test specimens after completion of 24 months of outdoor exposure.

The results from real outdoor exposure testing are found to be perfectly in line with the findings from accelerated weathering testing. The commercial acrylic binder resin showed severe cracking and flaking after 24 months of outdoor exposure. The commercial water-borne alkyd resin tested suffered significant erosion-based wear-off, especially in the single-coated area, combined with an obvious decrease in gloss level in the double-coated area.

All tested novel oil-modified acrylic multi-domain binders showed a high level of gloss retention and no significant cracking, flaking or wear-off, confirming the excellent outdoor and weathering resistance properties of this resin technology.

TRIM PAINT SHOWS GOOD GLOSS AND CHEMICAL RESISTANCE

Further testing was carried out on a representative oil-modified acrylic multi-domain dispersion in a trim formulation as given in *Table 1*.

The trim paint was coated onto a ceramic tile and subjected to 1000 hours of xenon testing according to ISO 4892-2 (method A; cycle 1). This accelerated aging testing revealed a very high gloss retention rate after this testing period, even in the very critical 20° testing angle. Furthermore, yellowing of the trim paint was not observed. Detailed results are summarised in *Table 2*.

Chemical resistance of the trim formulation based on the oil-modified acrylic multi-domain dispersion was evaluated on a wooden substrate. An untreated standard European pine wood board was double-coated with the trim formulation shown in *Table 1*. Then the coating was allowed to dry for seven days at ambient temperature and humidity prior to testing.

Table 2: Xenon testing results according to ISO 4892-2 of white trim coating on ceramic tile.

	Initial	**500 hrs**	**1000 hrs**
L*	97.48	97.13	97.03
a*	0.43	0.44	0.42
b*	1.52	1.58	1.64
gloss (20°)	72 GU	68 GU	66 GU
gloss (60°)	86 GU	87 GU	87 GU

Table 3: Chemical resistance testing after 3 hours of exposure. Rating from 0 (no effect on film surface) to 5 (film deterioration).

Substance	**Chemical resistance rating**
Aqueous ammonia 25%	1
Coffee	0
Tea	1
Red wine	1
Mayonnaise	0
Ketchup	0
Detergent / water (1/10)	1
Kitchen oil	0
Vinegar	0

Chemical resistance was tested by putting a drop of the testing chemical onto the surface of the coating for three hours at ambient temperature, followed by cleaning with a wet towel and subsequent visual inspection. The trim formulation tested showed excellent chemical resistance against all chemicals under consideration as well as perfect ‘easy-to-clean’ properties due to the very hydrophobic surface nature of the oil-modified dispersion-based coating. Detailed results are outlined in *Table 3*.

HIGH ADHESION TO MANY DIFFERENT SUBSTRATES

In order to evaluate the adhesion properties of the novel oil-modified multi-domain binders to a wide range of substrates, a representative prototype resin was compared to a commercial acrylic market benchmark specially promoted for this type of application.

Both binders were adjusted to the same overall solids content of 40% prior to testing. The use of coalescing agents was completely avoided here in order to evaluate the performance of the pure binders without any film-forming additives.

Table 4: Adhesion testing according to DIN EN ISO 2409 after one week of drying.

Substrate	Commercial acrylic reference	Oil-modified multi-domain dispersion
Wooden substrates		
Merbau	Gt 2	Gt 0
Teak	Gt 5	Gt 0
Cedar	Gt 5	Gt 0
Pine	Gt 4	Gt 0
Maple	Gt 3	Gt 0
Plastic substrates		
PET	Gt 1	Gt 1
PS	Gt 5	Gt 0
PC	Gt 5	Gt 0
PP (flame treated)	Gt 3	Gt 0
PVC	Gt 1	Gt 0
PA6	Gt 5	Gt 1
Metal substrates		
Copper	Gt 1	Gt 5
Aluminium	Gt 1	Gt 0
Sheet steel	Gt 1	Gt 1
Sandblasted steel	Gt 0	Gt 0
Sheet zinc	Gt 1	Gt 1
Special substrates		
HPL (fine structured)	Gt 3	Gt 0
HPL (smooth)	Gt 1	Gt 0
HPL (kitchen board)	Gt 1	Gt 0
Glass	Gt 0	Gt 1
Concrete	Gt 2	Gt 0

The binders were applied on various substrates at a wet film thickness of 150 µm using a standardised coating bar. After one week of drying at ambient temperature and humidity, the substrate adhesion properties were tested according to DIN EN ISO 2409 and rated from Gt 0 (best) to Gt 5 (worst). The results are summarised in *Table 4*.

As shown in *Table 4* the oil-modified acrylic multi-domain binder clearly outperforms the commercial acrylic market benchmark in terms of universal multi-substrate adhesion.

This outstanding binder performance can be attributed to the design of the multi-domain setup (high film hardness combined with low minimum film forming temperature) as well as to the unique, hydrophobic surface properties resulting from the intrinsic oil modification of these newly developed binder systems.

CLOSING THE PERFORMANCE GAP WITH A VERSATILE CONCEPT

Following a new synthetic concept, oil-modified acrylic multi-domain dispersions were developed based on oil-modified alkali soluble resins that act as polymeric emulsifiers (shell polymers) in combination with hydrophobic acrylic core copolymers.

This new technological approach yields novel hybrid binder systems with outstanding chemical and weathering resistance, high gloss and hydrophobic surface characteristics, combined with high film hardness and low minimum film forming temperature.

In addition, water resistance and substrate penetration of coatings can be drastically improved. The binder system is especially suitable for the preparation of high performance wood coatings with extended outdoor durability as well as for coating systems with ‘universal’ adhesion.

This unique combination of properties closes the gap between alkyd and acrylic resin technologies and therefore fulfils the requirements of applications as different as deck stain, trim, stain blocking primer and multi-substrate adhesion primers on difficult substrates such as high pressure laminates (HPL).

> “The very hydrophobic character of our novel oil-modification is for sure one of the major driving forces for enhanced wood penetration.“

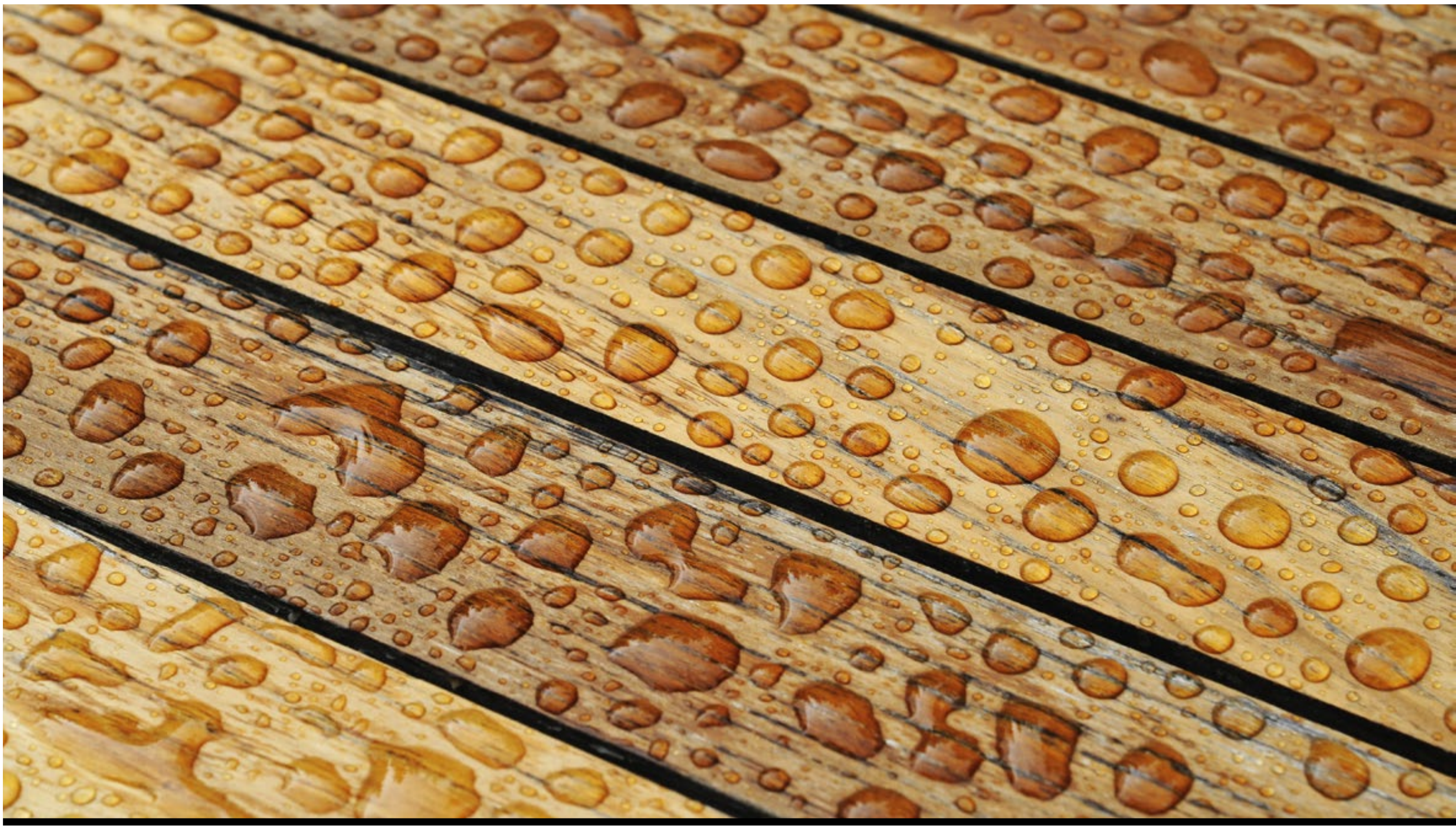
Andreas Steiner
Allnex
andreas.steiner@allnex.com

3 questions to Andreas Steiner

How do you explain the excellent penetration properties, do they solely result from the hydrophobic character of the oil modification? *The very hydrophobic character of our novel oil-modification is for sure one of the major driving forces for enhanced wood penetration. Furthermore, we have also seen that the overall amount and type of oil-modification significantly influences the penetration characteristics of various binder prototypes. We think that this may correlate with findings regarding the very good wood penetration of alkyd resins in general, which is also largely influenced by the fatty acid moieties present in the alkyd's backbone. Last but not least, the very small particle size of our novel oil-modified acrylic multi-domain dispersions (typically 60 – 80 nm) further enables efficient pore-penetration for wooden substrates*

Does the oil modification preclude oxidative drying, or can an oxidative drying partly be maintained? *Most reactive double bonds of the oil-components are already consumed during our grafting/incorporation process into the polymeric backbone, but of course some reactive double bonds remain in the system. We have seen that this residual double bond content is too low for significant oxidative drying in case our new products are used as sole binders. In combination with oxidative drying alkyds, however, our new binders have the potential to “co-dry” with the alkyd resins, which leads to very efficiently cross-linked polymeric networks. This is a clear advantage of our technology over “standard acrylic binders”, which are often used in blends with water-borne alkyds.*

The overall remarkable adhesion properties show one outlier. What is the reason for the unsatisfactory adhesion on copper? *This is indeed a very good question! Up to now we do not have a full explanation for this phenomenon, but we have already multiply reproduced this result. One possible explanation might be that copper – like other metal-based catalysts – may enhance oxidative drying of a binder. In case this enhanced oxidative drying happens mainly at the binder/substrate interface, the resulting higher cross-linking density might negatively influence the adhesion properties of the binder to the underlying substrate. We are currently working on the verification of this hypothesis.*



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INVISIBLE PROTECTION

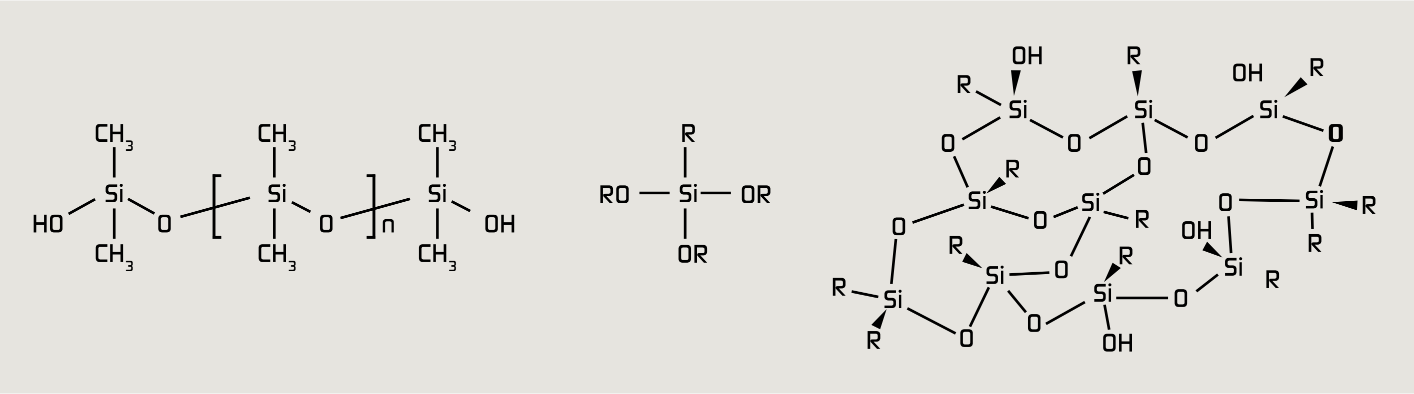
Organosilicon-based hydrophobic impregnation treatments for wood. By J.-P. Lecomte, S. Sabrina Salvati, S. Derocker, Dow Construction Chemicals; J. Van Acker, J. Van den Bulcke, Ghent University, Laboratory of Wood Technology; M. Kutnik, M. Montibus, FCBA Technological Institute (published in ECJ 02/2018).

An EU-funded project seeks to demonstrate that treatments with silicon-based hydrophobisers can protect exterior wood against water penetration, extend its service life and so potentially minimise the use of biocides. Both brush and vacuum impregnation processes showed significant levels of protection and a reduction in water pick-up.

Wood is an important renewable construction material. As well as its use indoors, it is also used for outdoor applications, whether for furniture, decking, cladding or increasingly for façades. Wood is subject to water infiltration by both liquid and vapour. As the moisture content increases, the wood will swell.

Rapid dimensional changes resulting from changes in the level of bound water cause the wood to crack and split. These cracks will then

Figure 1: Structure of polydimethylsiloxane, alkyl trialkoxysilane and schematic representation of a silicone resin (R can be ethoxy, methoxy, R1 can be methyl, phenyl or octyl groups).



RESULTS AT A GLANCE

- → Research was carried out within the framework of an EU-funded project aimed at demonstrating that treatments with silicon-based hydrophobisers can protect wood against water penetration, extend its service life and thus potentially minimise the use of biocides.
- → Five different silicon-based water repellents were applied to wood either by vacuum impregnation or by brushing.
- → The greatest differences in the level of pick-up of the liquids were associated with differences in wood species, though pick-up was also significantly higher with the vacuum process than by brushing.
- → Significant protection against wood decay fungi and partial protection against termite attack were achieved.
- → A moisture pick-up test based on rain exposure showed significant reductions in pick-up for softwood but not for oak

allow moisture to absorb easily and quickly into the wood. At some moisture content levels, and depending on the duration of wetness, moisture will be present as free water, which in turn promotes wood decay.

Both physical and biological degradation are greatly reduced when water penetration is dramatically reduced (by coating or impregnation) and/or when wood is modified (by chemical or thermal treatment). Silicon-based hydrophobic agents have demonstrated their benefit in reducing water penetration in many inorganic construction materials [1] and several studies have also explored their use as hydrophobisers for wood [2-6]. This paper focuses on minimising liquid water penetration of treated wood by using non-film-forming hydrophobisers.

This study is part of an EU-funded project named SILEX ("Improving sustainability of construction materials using innovative silicon based treatment"), a Life+ project initiated in 2013 which sets out to demonstrate that organosilicon compounds can be used as wood treatments to give extended durability.

FIVE IMPREGNATING MATERIALS TESTED

Alkyltrialkoxysilane, polymethylsiloxane and silicone resin (shown schematically in *Figure 1*) are the three main chemical components used for formulating silicon-based water repellents. Their low surface tension and high spreading ability, their ability to react with silanol-rich substrates, their good resistance to UV radiation and high gas permeability are of great benefit in the field of hydrophobic treatment of construction materials.

It is often the case that the chemicals used as water repellents need to be further formulated by simple dilution in a proper solvent or as an emulsion to make their use effective.

A water-soluble silane (SIL A = "DOWSIL 1-6184"), an emulsion of a mix of siloxane/silane/resin (EM A = "DOWSIL IE-6683") and a microencapsulated siloxane polymer (MIC A = "DOWSIL DS 9000") were used for vacuum impregnation.

In addition, a cationic emulsion of an organofunctional siloxane (EM B = "DOWSIL 6696") and an unmodified and undiluted silane/resin formulation (RES A = "DOWSIL Z-6690") were used for brush application.

WOOD SPECIMENS AND APPLICATION TEST PROTOCOLS

Scots pine, oak and beech samples ((50 ± 0.5) mm x (25 ± 0.5) mm x (15 ± 0.5) mm) without visible defects were selected. Laboratory vacuum impregnations were carried out on Scots pine sapwood, beech and oak specimens. Wood specimens were dried in an oven at 60 °C to constant weight. They were then introduced into a glass flask and put under vacuum.

The specimens were submitted to a vacuum of 50 mbar for 20 minutes. 1500 g silicon-based water repellents were added while still under vacuum, diluted so as to contain 1% of active material. Air was then released to atmospheric pressure. Samples were kept in the glass flask full of solutions for 20 minutes.

Samples were finally left in the laboratory to allow drying and further dried in an oven at 60 °C to constant weight. Samples were weighed before and after treatment to calculate the Weight Percent Gain (WPG) as follows:

$$WPG = (Wf - Wi) / Wi \tag{1}$$

Where
Wi = initial weight
Wf = weight of impregnated sample after drying at 60 °C to constant weight.

Water uptake was calculated to study the absorption and desorption rate of the treated wood. Specimens were weighed and then put in contact with water to measure 'longitudinal' or end-grain water absorption by placing them on metallic supports so that a small surface is in contact with water (*Figure 2*).

Figure 2: Experimental set-up to measure 'longitudinal water absorption'.

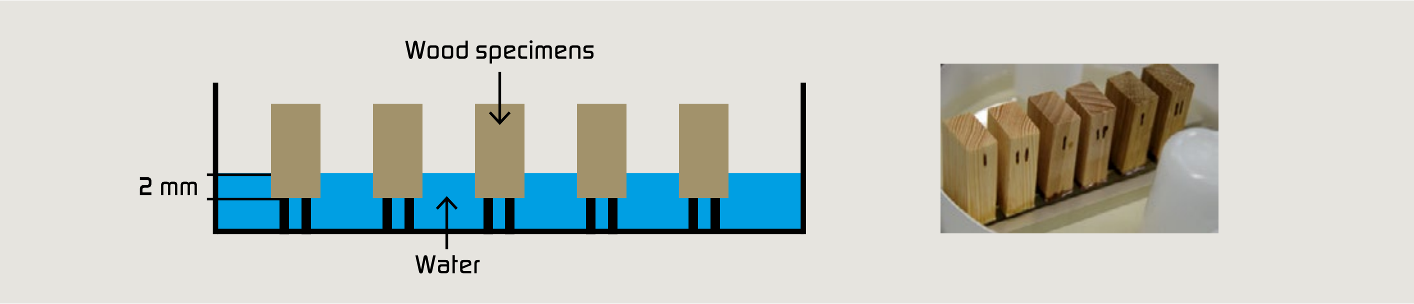


Figure 3: Water uptake (as % of initial wood specimen's dry weight) as a function of contact time with water and after 72 hours, as a function of drying time.

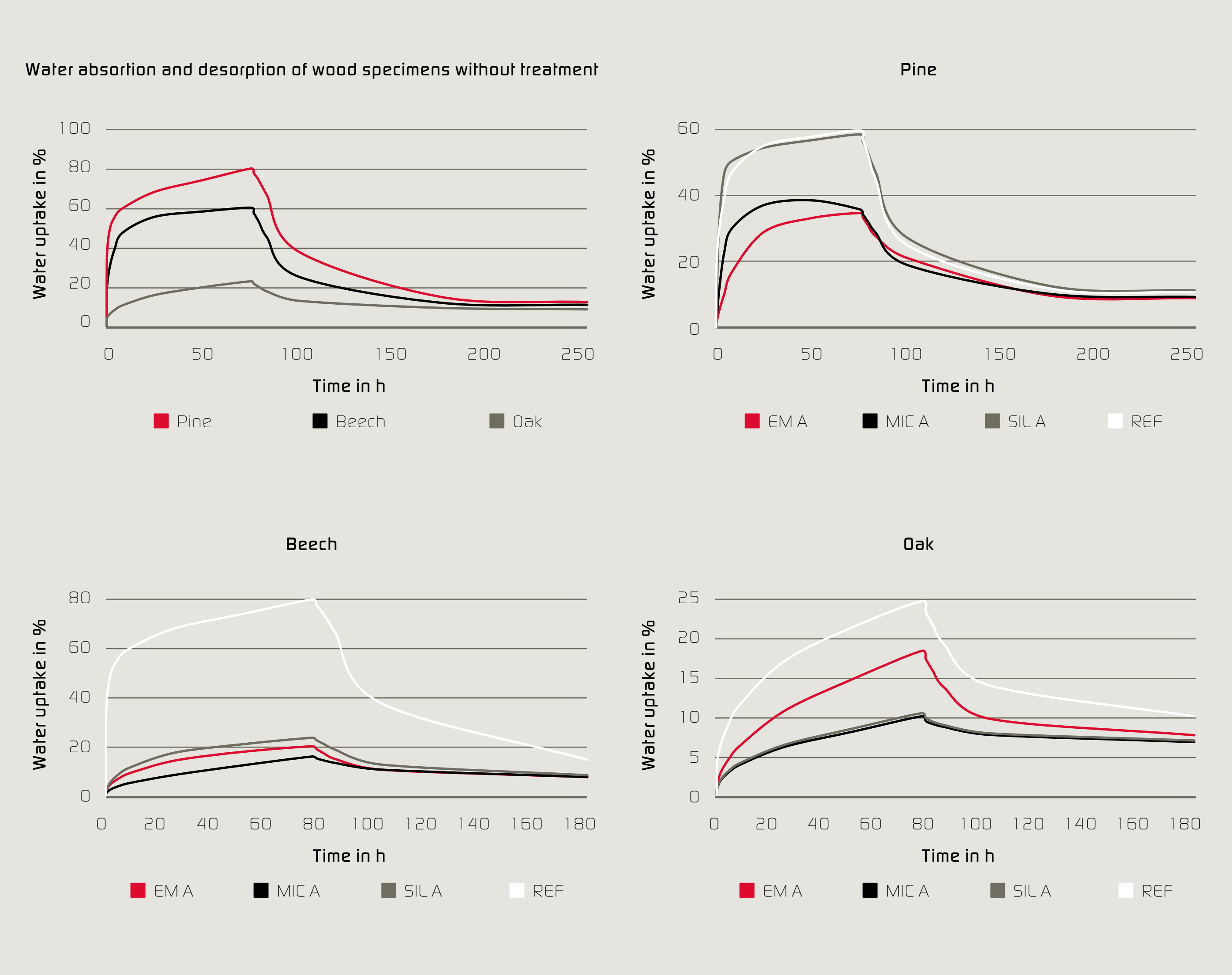
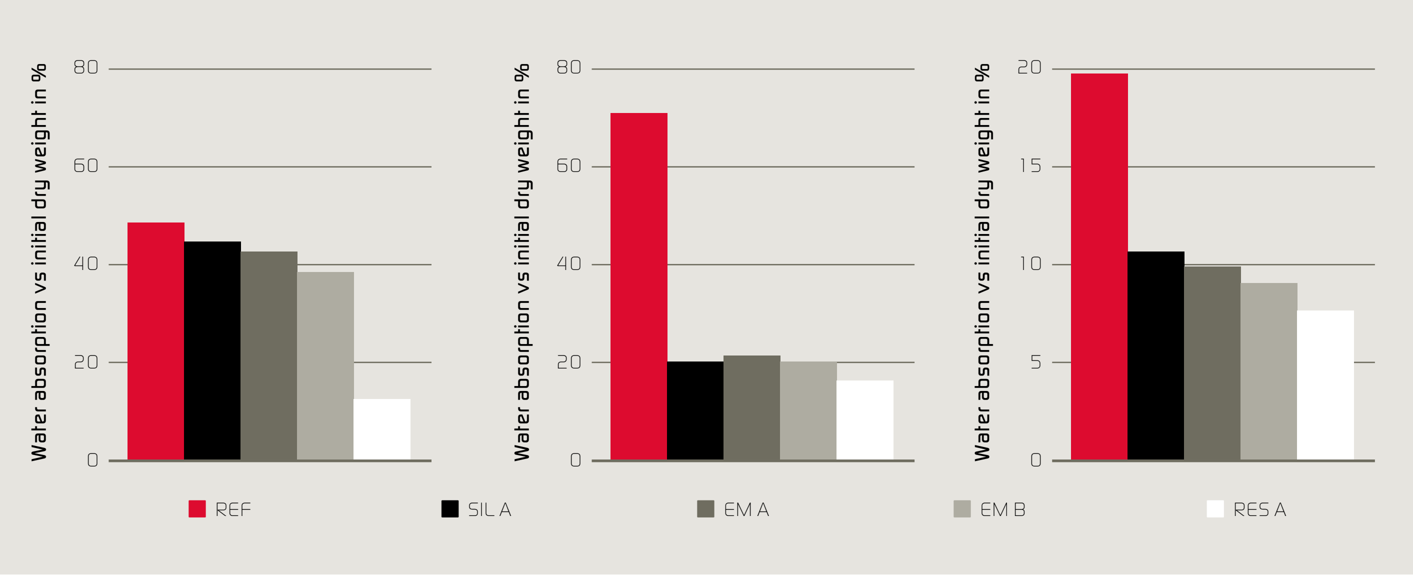


Figure 4: 'Longitudinal' water absorption (as % of water uptake vs initial dry weight) after 48 hours contact time with water for the wood specimens treated by brushing with the selected water repellents.



Wood specimens were removed, blotted and weighed at regular time intervals. The drying rate was assessed by removing wood specimens from water after 72 hours, placing them on grids in the laboratory and further weighing over a period of time until they reached a constant weight.

VACUUM PROCESS PICK-UP DEPENDS MAINLY ON WOOD TYPE

Three water repellents (SIL A, EM A and MIC A) differing not only in their active material but also the delivery system were used side by side to treat wood specimens by vacuum impregnation. *Table 1* shows the weight percent gain measured after impregnation. Despite the very different type of delivery system, no major differences of weight percent gain for a given wood species were observed.

The graphs in *Figure 3* show the weight gain (averaged value of three individual measurements) due to the water uptake (as % of the initial dry weight) plotted as a function of contact time with water or drying time. Wood specimens were placed in contact with water for 72 hours and then left to dry for the remaining duration of the experiment.

It is clear that the use of different silicon-based water repellents reduces water penetration to different extents with different wood species. It can be observed that this treatment of wood specimens with silicon-based water repellent does not slow down the rate of drying; this was expected as they are not film-forming.

Treatment with the water soluble silane (SIL A) led to some change of the wood specimen colour (some colour enhancement). It was also visually observed and measured (data not reported here) that leaching of extractables (probably tannins) from the wood specimens (especially oak specimens) is much reduced when wood is treated with SIL A.

DETAILS OF WATER REPELLENT APPLICATION BY BRUSHING

In addition to SIL A and EM A, EM B and RES A were applied on wood specimens by brushing. Wood specimens were conditioned in the laboratory (25 °C, ca. 50% relative humidity). After brushing with water repellents (diluted with water so as to reach 10% active content, though RES A was diluted in silane), wood specimens were dried for seven days in the lab under the same conditions before measurement of the 'longitudinal' water uptake.

Table 1 gives the weight percent gain after application and after drying/reaction (average of two individual measurements).

Figure 5: The continuous moisture measurement (CMM) setup.

'Longitudinal' water absorption was calculated by measuring the weight of wood specimens as a function of contact time with water, following the test protocol already mentioned.

Figure 4 shows water absorption (as % of water uptake vs initial dry weight) after 48 hours contact time with water for the wood specimens treated by brushing with the selected water repellents.

APPLICATION METHODS AND PRODUCTS COMPARED

Application by brushing does not allow the loading of large quantities of water repellent on the wood specimens. This reduces the efficiency of the water repellent treatment when applied on pine. Beech and oak specimens seem to be rather less sensitive to the quantity of water repellent required to effectively minimise water penetration. It is probable that brushing leads to a higher concentration of active material close to the surface and can still provide an effective treatment at a lower loading. Brushing of the silicone resin/silane mix strongly minimises water penetration, which is most probably related to the higher weight gain obtained when a neat resin/silane blend is used.

The contact angles of 2 µl water droplets placed on the largest surface of the wood specimens were measured directly and 20 s after application with the help of a "VCA optima XE" video contact angle device. *Table 2* gives the contact angles of water droplets placed on the different wood specimens treated by brush application.

An increase of contact angle of the water droplets is observed when wood is treated. However, there is no clear correlation between the

Table 1: Weight percent gain after vacuum impregnation or brushing of wood with different water repellents.

WPG (%)	**Scots pine sapwood**	**Beech**	**Oak**
Vacuum impregnation			
EM A	1.10	1.09	0.43
MIC A	1.13	1.50	0.46
SIL A	1.17	0.97	0.40
Brush application			
EM A	0.70	0.72	0.32
EM B	0.70	0.73	0.35
SIL A	0.63	0.69	0.36
RES A	3.8	4.0	1.3

Table 2: Contact angles of water droplets placed on the different treated wood specimens.

Contact angle (°)	**Pine**		**Beech**		**Oak**	
	t = 0 s	t = 20 s	t = 0 s	t = 20 s	t = 0 s	t = 20 s
REF	88	45	109	66	106	100
SIL A	107	92	108	101	106	100
EM A	128	126	140	140	126	122
EM B	125	120	136	117	126	117
RES A	113	109	126	126	101	79

contact angle of water droplets and the reduction of water penetration. This lack of correlation is already known and further confirmed here.

This contribution shows that different product concepts (different water repellent active materials, different delivery systems) can be used as water repellents for wood. Water soluble active materials or oil in water emulsions can be used for vacuum impregnation or surface brushing. The silane based formulation applied by brushing is quite effective, most probably due to the higher loading of active material on the wood specimens.

SIGNIFICANT PROTECTION AGAINST WOOD DAMAGING FUNGI

The impact of the treatment by the water-soluble silane (SIL A) and the two emulsions (EM A and EM B) on biological degradation and resistance to termites was assessed.

All these three water repellents tested failed to provide long-term protection of wood against blue stain in a real-use situation (outdoor exposure). However, the results obtained for in vitro experiments demonstrated that the products had an effect on the development of moulds and blue stain fungi, slightly reducing their growth [7].

The tests aimed at determining protective efficacy against basidiomycete decay fungi were the most conclusive. Among the three products tested, the cationic emulsion and water-soluble silane significantly reduced mass loss caused by fungal degradation compared to the untreated controls.

Water-soluble silane and the cationic emulsion were both found to improve the resistance against fungal decay of Scots pine and beech to a level comparable to the natural durability of European oak, which has a natural durability class ranging from 1 to 3 according to [8]. Further artificial weathering tests are required in order to evaluate the suitability of the two water-repellent formulations as wood protection products for outdoor above-ground use.

PARTIAL PROTECTION AGAINST SUBTERRANEAN TERMITES

In artificial situations of forced feeding, termites appeared to attack wood impregnated with the water repellents out of necessity, but could not sustain themselves and died after a few weeks. In situations where there is a choice between different sources of food, which are more representative of real-life situations encountered by subterranean termites, they tended to avoid the wood treated with the water repellents.

Little damage and low mortality were recorded in the ‘choice’ tests, demonstrating that termites were poorly attracted by wood treated with SIL A, which in turn resulted in indirect protection of the treated samples. On the other hand, the cationic emulsion resulted in low damage to the wood and a high mortality of termites for both test protocols.

FIELD TESTING CONFIRMS DIFFERENCES IN WATER PICK-UP

A continuous moisture measurement (CMM) set-up as detailed in *Figure 5* was first installed to assess the moisture dynamics of plywood [9]. This methodology was already in use to assess modified wood [10] and has now been used to follow a set of organosilicon treated specimens. The edges of the specimens were sealed and they were placed at an angle of approximately 45°.

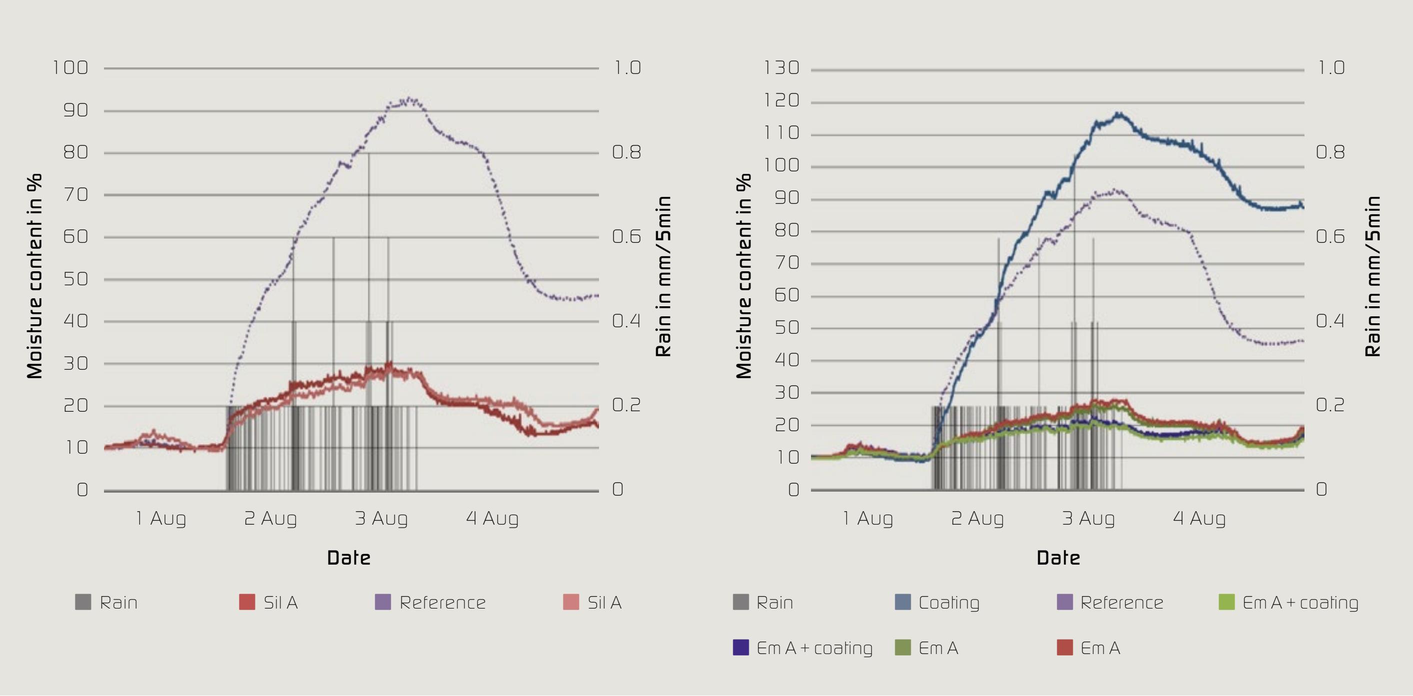
After installation in May 2015 a specific rain event at the end of August 2015 was inconclusive [11]. The rain event from August 2016 was selected and showed larger differences between reference and treated wood specimens (*Figure 6*).

Continuous moisture measurements of specimens of Scots pine sapwood treated with water repellents SIL A and EM A (used as examples here) showed a significant decrease of water absorption relative to the reference specimens. Much smaller differences between treated and untreated specimens were found with oak specimens. In the case shown in *Figure 6*, a coating alone actually increased final water pickup due to retarded drying, whereas EM A (with or without subsequent coating) reduced maximum moisture pickup to about a third of the untreated wood level.

SIGNIFICANT THOUGH VARIABLE BENEFITS ACHIEVED

Silicon-based water repellents can be used to minimise water penetra-

Figure 6: The diluted impregnation agent was applied to the sanded-down concrete floor of a production hall at the Agricolae Kft. fruit preserves plant in Jánkmaitis, Hungary.



> “A set of new silicon-based water repellent products are now promoted for the treatment of wood.“

3 questions to Jean-Paul Lecomte

What are the interim results of the project? *The main objectives of the SILEX project, financed by Life (from EU), were to identify impregnation hydrophobers for wood, to demonstrate their efficiency to reduce water ingress and therefore, to reduce wood degradation induced by microorganisms. This set of data is described in the paper. Continuous moisture measurement clearly demonstrates the reduction of water uptake, in “real life condition”, leading to reduced fungal degradation of treated wood specimens.*

What will be the next steps of the SILEX project? *Based on the learning of SILEX project, a set of new silicon-based water repellent products are now promoted for the treatment of wood.The next steps will be related to the wider market use of these impregnation hydrophobers into formulations providing protection for wood. Thanks to the reduction of water ingress, it is hoped that biocide levels could be reduced, while providing the same level of protection against biological decay. This is well aligned with the EU-driven reduction of biocide utilisation.*

Where did you conduct the field testing? *Within the SILEX consortium, exposure field tests were conducted in Bordeaux and Ile dOléron (France) and Ghent (Belgium). The SILEX project was also looking at new low VOC hydrophobers for concrete. For this part, some treated concrete blocks were exposed in Germany (close to a highway and in a forest) and the Netherlands (facing the North Sea).*

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tion into various wood species. The extent of reduction of water penetration depends on the treatment and on the specific wood species. Continuous moisture measurement clearly demonstrates a reduction of water uptake, under ‘real-life conditions’.
Treatment of wood also leads to reduced fungal degradation and to some extent to reduced degradation induced by termites.

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