GREENER POWDER

Polyester made from renewable and recycled raw materials reduce the CO_2 footprint of powder coating technology. Reduced curing temperatures further improve the environmental friendliness of this coating technology. By Dietmar Fink, Allnex Germany and Alessandro Minesso, Allnex Italy.

Powder coatings can become more environmentally friendly if raw materials and production processes for the polyester are formulated without substances of very high concern (SVHC) in accordance with EU legislation (Reach Chemicals Ordinance). In addition, the content of monomers in resins and hardeners can be reduced through optimised production processes. With improved polyester resins, the powder coating manufacturer can formulate powder coatings that enable paint shops to handle powder coatings more safely.

New polyesters have also been developed that can enable lower curing temperatures or permit the powder-coated objects to run faster through the ovens. In addition, the novel polyester resins can improve the quality of applied powder coating films and can also help open new areas of application for powder coatings, such as for heat-sensitive substrates or for coating of large and heavy parts which are slow to heat.

POWDER OR WET PAINTS

Powder paint coatings have advantages over liquid paint coatings. This includes almost no emission of volatile organic compounds (VOC) from powder coatings during the curing process. This is based on the use of non-volatile organic compounds and the possibility of applying thicker layers without sagging. In addition, there is a higher transmission efficiency and the reuse of the over spray (almost 100 % use). In addition, powder coating creates less hazardous waste.

To reduce the carbon footprint, renewable bio-based monomers (*Figure 1*) are used in combination with certain recycled plastics. This creates suitable solid polyester resins via the polycondensation process, which can then be used for powder coatings. This process from allnex can be used to produce polyesters for both indoor and outdoor industrial applications.

INDOOR AND OUTDOOR

Polyester No. 1 is a hybrid 70/30 COOH polyester for use with epoxy resins, having a glass transition temperature of 60°C, a viscosity at 200°C of 6,000 mPa.s and an acid number according to ASTM D 1613 of 35. It has better overall film properties than a conventional 70/30 hybrid polyester (*Figure 2*). The most important advantage is the non-blooming effect of the resin. Even if the film is exposed to a temperature of 120°C for more than a week, the gloss reduction of the loaded paint film is small (delta of 1 unit). Another difference is the better resistance to solvents. At 100 double rubs with methyl-ethyl-ketone (MEK), the film remains intact, whereas the film of conventional quality is completely dissolved. Polyester No. 1 is also flexible, and even after

RESULTS AT A GLANCE

→ New polyester powder coating resins are based on renewable and recycled building blocks.

→ With new polyester resins, curing temperatures can be reduced, thus improving the efficiency of polyester production and energy consumption.

→ They do not contain substances of very high concern (SVHC).

6 months of aging, the paint film on a 0.8 mm steel sheet is elastic with a T-bend of 0.

Polyester No. 2 is a 95/5 COOH polyester for use hydroxyalkyl amide, HAA, resistant for industrial outdoor applications, with a glass transition temperature of 59°C, a viscosity at 200°C of 4000 mPa.s and an acid number according to ASTM D 1613 of 33. It has acceptable film properties compared to conventional outdoor resistant COOH polyesters 95/5 HAA. Such properties include good mechanicals, high gloss, acceptable smoothness and good adhesion to metal substrates. In white and light shades, the new resin technology has so far delivered less colour-stable powder coating films, however additional antioxidants can reduce this problem.

The lower UV resistance of polyester No. 2 only allows industrial outdoor applications (*Table 1*). To achieve a higher UV resistance, certain raw materials in the polyester matrix would have to be removed or reduced, since only other glycols and acids offer better weathering properties.

TIN-FREE POLYESTER

Tin-free polyesters are resins that are manufactured in compliance with EN 71 [1] and Ikea's IOS MAT 0066 [2]. Only catalysts that contain neither tributyltin oxide (TBTO) nor dibutyltin oxide (DBTO) may be used for this purpose (*Figure 3*). TBTO and DBTO are organotin substances that are introduced as impurities from the catalyst used in polyester production. TBTO is today classified as a strong marine pollutant and a substance of very high concern (SVHC) by the EU [3]. Ikea's requirements for tin-free and organotin-free powder coating films are below 1 ppm for TBTO and below 2.5 ppm for TBTO + DBTO. *Table 2* shows a selection of tin-free Polyesters for combination with epoxy resins in various ratios, with HAA for standard and super durable qualities and for combination with Isocyanate for direct food contact. The tin-free pair of COOH polyesters for dry matting technology (matte dry-blend, MDB) offer the same film properties as conventional organotin polyester for dry matting technology. The matting effect achieved is at a similar level (*Table 3*).

TIN-FREE UNSATURATED RESINS

Unsaturated resins can be used for UV curing. The advantage is that they react in a short time (within seconds) and are therefore suitable for heat-sensitive substrates. The UV-cured powder films offer excellent hardness and chemical resistance. For applications with direct food contact and requirements according to EN 71 and IOS MAT 0066 from Ikea, special unsaturated resins have been developed that contain neither organotin catalysts nor acrylic monomers. (*Table 4*).

NPG-FREE HYDROXYL POLYESTER

The polyester raw material Neopentyl glycol (NPG) is not suitable for powder coating applications with direct food contact, including alcohol (*Table 5*). Also, no organotin catalysts nor other raw materials that are unsuitable for direct food contact may be used for these applications. The hydroxylated polyesters described offer the possibility of formulating suitable powder coating qualities with different chemical resistance.

LOW BAKING TEMPERATURE POLYESTER

The hyphened number 6 in "Crylcoat XXXX-6" indicates a suitable polyester which allows low baking temperature for a ten-minute curing time. These types of polyester can save energy during application, increase productivity and / or expand powder application options. The following types of polyester are possible:
COOH polyester for epoxy (hybrid) at curing temperatures below 140°C are suitable for

- heat-sensitive non-metallic substrates such as MDF, HDF, plasterboard, plastics, paper labels
- pre-assembled goods with temperature-sensitive parts such as electric motors and
- products with limited temperature acceptance such as aluminum-magnesium car rims

COOH polyesters for hydroxyalkyl amide (HAA) at curing temperatures from 160°C are suitable for

- heavy substrates with very long heating times such as steel beams and
- heat-sensitive products such as metal profiles combined with plastic, such as aluminum windows with insulating properties.

Other types of polyester are COOH-polyester for glycidyl esters at curing temperatures of up to 160°C and COOH-polyester for triglycidylisocyanurate (TGIC) at curing temperatures of up to 160°C.

INDOOR APPLICATIONS

For indoor applications without or with low UV exposure, polyesters ("Crylcoat 15XX-6", 50/50 hybrid) were developed, for application onto metal substrates or heat-sensitive goods. More than eight different polyesters with acid numbers of approx. 70 mg KOH / g offer a few properties, including:

- glass transition temperatures (TG's) between 50°C and 66°C
- viscosities (at 175°C) between 4000 and 10.000 mPa.s
- type and amount of catalyst
- reactivity for curing within 10 minutes at low temperatures from 125°C. to 160°C or for very rapid
- curing at 180°C from 1 minute to 5 minutes

- application features such as smoothness, textures or improved scratch resistance and degassing.

OUTDOOR APPLICATIONS

For the industrial exterior coating, for architecture and for class 2 of the association for quality control in the painting and coating industry (Qualicoat) or the master quality of the quality association for the piece coating of components (GSB), polyesters ("Crylcoat 26XX-6" or "Crylcoat 46XX-6 ", HAA polyester) were developed to coat massive substrates or heat sensitive goods.
There are more than ten reactive polyesters to combine with HAA with properties like:

- acid numbers between 18 and 90 mg KOH / g
- TGs between 52°C and 66°C
- viscosities at 200°C. between 2,000 and 8,000 mPa.s
- reactivity for slow curing at 20 min. 150°C to 10 min. 160°C or for quick curing at 180°C with 3 to 5 minutes in the oven
- application features for smoothness, textures, matting (MDB), Tribo, non-blooming optimized, easy to degas, water stain resistant, gas-oven and overbaking resistant.

POLYESTER SERIES FOR OTHER OUTDOOR RESISTANT HARDENERS

The following reactive, exterior-resistant polyesters enable shorter dwell times in the curing oven or an efficient curing of the paint films on solid substrates or heat-sensitive goods. In total, more than eight reactive COOH polyesters have been developed for various outdoor-resistant hardeners.
The reactive polyesters of the "Crylcoat 25XX-6" or "Crylcoat 45XX-6" series for cure with aromatic glycidyl esters, such as "Araldite PT 910" from Huntsman, are designed for three quality levels in combination with glycidyl esters for outdoor use. These include: industrial qualities, Qualicoat class 1 and Qualicoat class 2 or GSB standard and GSB master qualities.
The reactive polyesters "Crylcoat 24XX-6" or "Crylcoat 44XX-6" with Triglycidyl-Isocyanurate (TGIC) are also designed for three quality levels in combination with TGIC for outdoor use. These include: industrial qualities, Qualicoat class 1 and Qualicoat class 2 or GSB standard and GSB master qualities. These reactive polyesters offer properties that are cured at low temperatures for 10 minutes from 130°C to 10 minutes at 160°C or for rapid curing at 180°C with 1 minute to 5 minutes in the oven, depending on the binder system used.

REFERENCES

[1] European standard EN 71: standard for toy safety.
[2] Ikea of Sweden AB, IOS MAT 0066: General requirements for surface coatings and coatings.
[3] European Chemicals Agency (Echa): substance of very high concern (SVHC).

Figure 1: Combination of bio-based raw materials to produce suitable polyester for powder coatings.

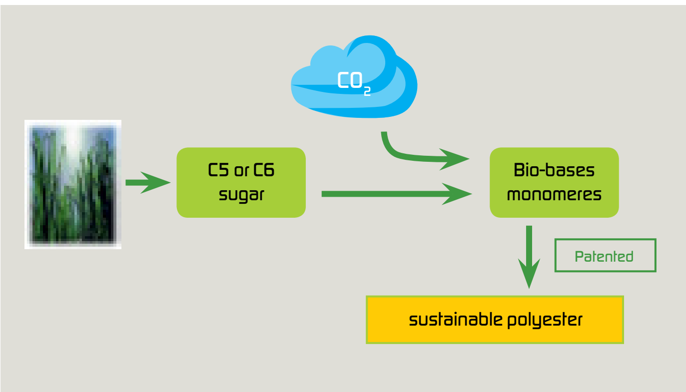
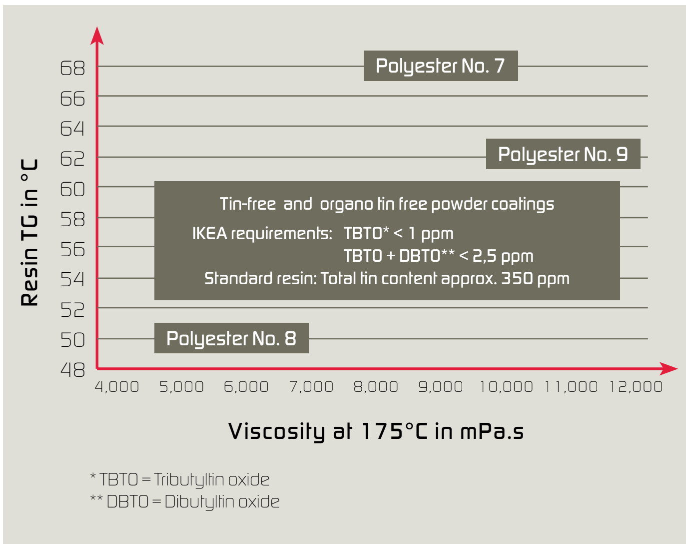


Figure 3: Tin-free, 50/50 hybrid polyester for low baking temperatures.



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"The new polyesters are totally based on renewable monomers and recycled materials."

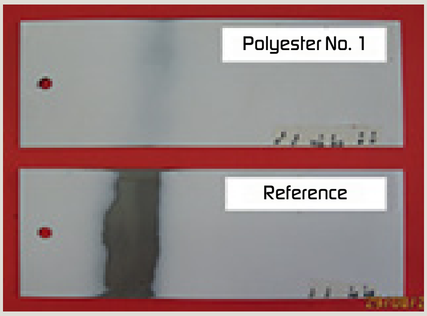
2 questions to Dietmar Fink

Are the new polyester powder coatings 100 % renewable and recycled building blocks? *The new polyesters are promoted as 100 % sustainable resins because they are totally based on renewable monomers and recycled materials, with no uses of traditional oil-based monomers. This patented platform was developed in order to fulfil the increased need for environmentally friendly and sustainable technologies, with coating producers more and more looking for alternative sources for the chemical ingredients derived from petroleum or other fossil sources. During the last years the renewable feedstocks availability has grown and become more and more important also in the paint and coating areas, while the price of recycled polymers has become competitive towards that of virgin resins.*

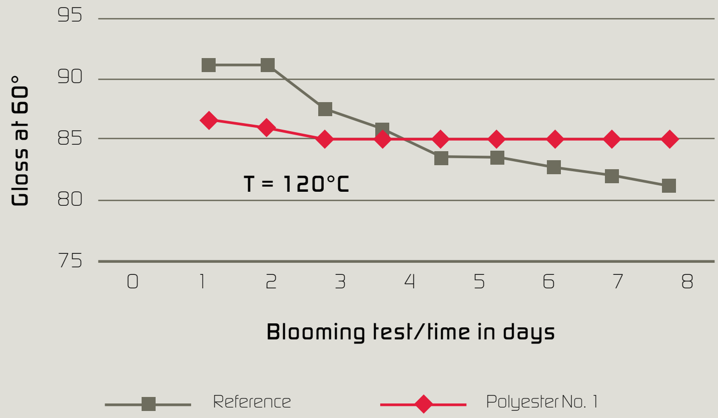
For which applications are the new resins better, for which less suitable? *Based on this technology, we have already developed different polyester resins targeting all necessary finishing effects (glossy & matte) with all key technical performances required for being used in the different market segments of powder coatings, covering indoor and outdoor applications by thermosetting or radiation curing. Interesting to notice that some coating performances of the new polyesters are even exceeding the expectation and this will give possible technical advantages in comparison with conventional resins (coating flexibility for instance), which should permit to penetrate alternative coating segments where today the powder coating technology is not fitting so well because of some technical limitations.*

Figure 2: Results with renewable polyester No. 1 compared to a conventional 70/30 hybrid polyester.

Polyester No. 1 - 100 double rubs MEK



Blooming resistance



Mechanical properties

6 months ageing of cured film	Curing schedule 10 min at 180°C	
	DI/RI	T-bend
Conventional 70/30 PE white formulation	120/120	1-T
Polyester No. 1 white formulation	160/160	0-T

Improvements:

- T-bend
- Ageing of cured film (6 months)
- Solvent resistance
- Non-blooming (120°C, 7 days)
- Boiling water resistance (2 hrs)

Table 1: Technical properties of a white high-gloss formulation with a sustainable, exterior-resistant COOH polyester 95/5 HAA for industrial applications.

Test description	**Test method**	**95/5 HAA PE Nr 2 industrial**	**95/5 HAA reference PE B architecture**
Gel time at 200°C in (sec)	PCI #6	150	200
Pill Flow at 180°C in (mm)	PCI #7	45	45
Impact resistance 10 Min 200°C in (inch/pound) at 70 µm (F/R) on AL-36	ASTM D2794	70/70	70/70
Gloss (G 60°/G 20°) in units	ASTM D523	92/78	95/85
Smoothness (PCI)	PCI #20	5	6-7
QUV B 313 (0,75) RAL 6005 gloss retention after 150 hrs		23%	80%
Florida, 5°South RAL 8014 gloss retention after 12 months		4,5%	62%
Adhesion (Cross-cut 2 mm)	ASTM D3359	GT0	GT0
Initial b-value (yellowing) 10 Min 180ºC (white)	ASTM D2244-16	5,8	3,4

Table 2: Tin-free polyester.

Polyester	Glas transition T [°C]	Viscosity at 200°C [mPa.s]	AV ASTM D 1613	Characteristics
No. 7	66	8,200	72	50/50 Hybrid 10 Min 130°C high TG
No. 8	50	5,200	72	50/50 Hybrid 10 Min 130°C excellent flow
No. 9	62	10,000	73	50/50 Hybrid 10 Min 130°C for textures
No. 10	62	4,000	62	60/40 Hybrid 10 Min 200°C
No. 11	59	5,100	36	70/30 Hybrid 10 Min 180°C
No. 12	58	5,500	28	95/5 HAA 15 Min 160°C
No. 13	59	8,000	23	97/3 HAA 10 Min 180°C for MDB
No. 14	59	5,800	48	93/7 HAA 10 Min 180°C for MDB
No. 15	59	3,700	33	95/5 HAA SD 10 Min 190°C
No. 16	52	2,600	OHV 180	NPG-free OH-PE for direct food-contact
No. 17	46	3,300	OHV 240	NPG-free OH-PE for direct food-contact

Table 3: Technical properties of a white semi-matt formulation with polyester No. 13 and polyester No. 14, tin-free HAA resins for semi-matt dry blends.

Test description	Test method	MDB PE 1/PE 2	Tin-free PE Nr 13/PE No. 14	Reference PE D/PE E
Gel time in [sec]	PCI #6	PE1 at 200C/ PE2 at 180C	185/130	243/94
Pill flow 180°C x 20 min in [mm]	PCI #7	PE 1 / PE 2	51 / 28	47 / 31
Smoothness [PCI]	PCI #20	MDB	4	4
Impact resistance 10 Min 200°C at 70 µm [F/R] in [inch/pound]	ASTM D2794	MDB	70/70	70/70
Gloss G 60°/ G 20° PE 1/PE 2	ASTM D523	MDB	34/9	37/10

Table 4: Tin-free series of unsaturated resins according to EN 71 and IOS MAT 0066 from Ikea.

Unsaturated resins	Glass transition T in [°C]	Viscosity at 200°C in [mPa.s]	Characteristics
F	48	4000	Amorphous unsaturated polyester resin
Nr 15	48	3700	Tin-free version of resin F
Nr 16	56	4200	Tin-free, higher TG version of resin F
G	55	55000 at 140°C	Aliphatic unsaturated acrylic urethane polymer
Nr 17	50	5500 at 140°C	Tin-free, acrylic monomer-free version of polymer G

Table 5: NPG-free hydroxyl polyester series for direct food contact including alcohol with aromatic anhydride or isocyanate hardeners.

Polyester	Glass transition T in [°C]	Viscosity at 200°C in	OHV ASTM E 1899	Characteristics
Nr 18	58	5500	50	NPG – free OH-PE with basic chemical resistance
Nr 19	51	3600	120	NPG – free OH-PE with good chemical resistance
Nr 20	52	2600	180	NPG - free, tin – free OH-PE with excellent chemical resistance
Nr 21	46	3300	240	NPG - free, tin – free OH-PE with best chemical resistance

* Reference: https://ec.europa.eu/food/safety/chemical_safety/food_contact_materials_en