CHEMICAL RAW MATERIALS

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Bio-based binders for high-solids two-component coatings

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Content

Bio-based binders for high-solids two-component coatings

High-quality industrial coating systems are usually based on polyacrylates or polyester polyols containing hydroxyl groups, which can be reacted with corresponding coating isocyanates. Depending on the required properties, the appropriate polyols are selected. The properties provided by the polyols can be somewhat differentiated. Polyacrylates enable coating systems with good reactivity, good drying properties, high hardness, good chemical resistance and good weather resistance. Polyester polyols are often characterised in particular by good mechanical properties, such as elasticity, scratch resistance and abrasion resistance. These products also provide good optical properties, such as high gloss and low gloss haze, good fullness and improved flow. With increasing hydroxyl content, correspondingly more lacquer isocyanate is required, which generally leads to better resistance.

Sustainability is changing the requirements for such coating systems

Whereas in the past the properties of the coating systems and the price played a very important role, today sustainability is added to the equation. The products should have the smallest possible CO2 footprint, be based on bio-based or recycled raw materials that do not compete with food production and do not consume additional land. Furthermore, the products should be water-based or contain as few solvents as possible. In addition, consumers expect at least comparable properties that they are used to from previous products.

There are now many possibilities for making products more sustainable. For example, polyacrylates can already be partly built up on the basis of bio-based monomers. In addition to the direct use of such monomers, mass-balanced approaches are also being pursued. The broad availability of these raw materials is not yet the same as for conventional monomers.

On the other hand, polyester polyols also offer very diverse possibilities. The availability of bio-based raw materials is also greater here than with the polyacrylates. In particular, the alkyd resins, which are fatty acid-modified polyester polyols, are a well-known product group that is also suitable for many systems.

Alkyd resins are a modern binder class based on bio-based raw materials

By definition, alkyd resins are based on a high proportion of bio-based raw materials. They are fatty acid-modified polyester resins produced by polycondensation and esterification reactions from polyvalent carboxylic acids and alcohols as well as vegetable fatty acids or oils [Fig. 1].

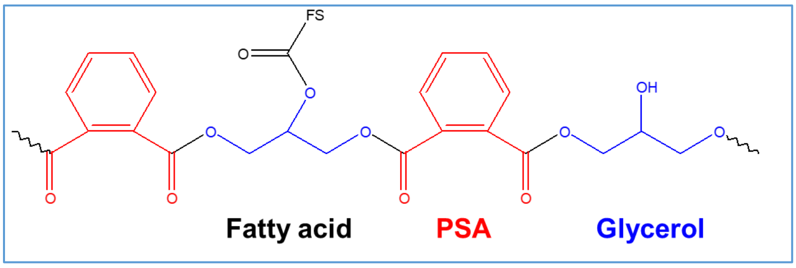

Figure 1: Structure of alkyd resins

The vegetable oils or fatty acids determine a large part of the properties

The vegetable oils or fatty acids used are essential building blocks of the alkyd resins, which is why they also influence their properties to a great extent. Vegetable oils have a specific fatty acid composition [see Fig. 2], which determines the properties of the oils in the alkyd resins. They are usually divided into non-drying, semi-drying and drying oils or fatty acids. The classification attempts to classify whether and to what extent the oils or fatty acids offer the possibility of oxidative drying with the aid of atmospheric oxygen. This property is primarily due to the presence of polyunsaturated fatty acids, such as triple-unsaturated linolenic acid.

Fatty acid	C-Atoms	C=C	Coconut oil	Palm kernel oil	Palm oil	Castor oil	Peanut oil	Cottonseed oil	Soyabean oil	Sunflower oil	Tall oil fatty acid	Safflower oil	Tall oil distillate	dehydrated Castor oil	Linseed oil	Tung oil
Caproic	C6	0	1	1												
Caprylic	C8	0	5	2												
Capric	C10	0	7	4												
Lauric	C12	0	45	50												
Myristic	C14	0	18	16	2			1								
Palmitic	C16	0	10	8	42	1	10	27	8	10	1	6		1	6	4
Stearic	C18	0	4	3	5	1	4	4	4	8	1	3	1	1	4	1
Arachidic	C20	0					1				1		4			
Behenic	C22	0					3									
Lignoceric	C24	0					3									
Palmitoleic	C16	1														
Oleic	C18	1	8	14	41	3	54	25	28	27	32	15	18	2	22	8
Linoleic	C18	2	2	2	10	5	24	43	52	54	44	75	26	85	16	4
conj.	C18	2									6		15			
Linolenic	C18	3					1		8	1	10	1	7		52	3
conj.	C18	3									2		6			
Eleostearic	C18	3														80
	C19	1									1		1			
	C20	1											3			
	C20	2											3			
	C20	3									2		16			
Ricinoleic	C18	1				90								11		
Iodine Number (IN)			8-10	12-18	51-57	81-90	83-103	103-111	124-133	127-136	130-138	138-150	155	150-165	169-196	147-242
OHZ						150-160										
Classification according to Jamieson			IN < 125 non-drying						IN 125 - 140 semi-drying			IN > 140 drying				

Figure 2: Composition of different oils

On the other hand, the oils or fatty acids naturally also determine other properties, such as yellowing, physical drying, flexibility, adhesion or even weather resistance. In many cases, a combination of different vegetable oils or fatty acids can be useful to adjust a specific property profile of the corresponding alkyd resins.

Other bio-based building blocks are available

In addition to vegetable oils and fatty acids, alkyd resins consist of polyvalent carboxylic acids and alcohols, as described above. These building blocks are also partly available on the basis of bio-based raw materials. In alkyd resins, glycerol, pentaerythritol, trimethylolpropane or dipentaerythritol are usually used as polyfunctional alcohols [see Fig. 3].

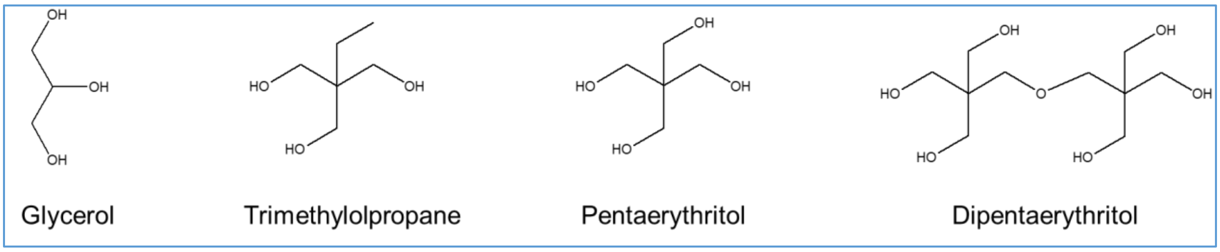

Figure 3: Polyfunctional alcohols

Glycerol has always been bio-based as a component of vegetable oils. But also the other raw materials are already chemically identical and available on a large scale on a bio-based basis.

Furthermore, alkyd resins usually contain polyvalent aromatic carboxylic acids. Raw materials such as phthalic anhydride or isophthalic acid are often used [see Fig. 4].

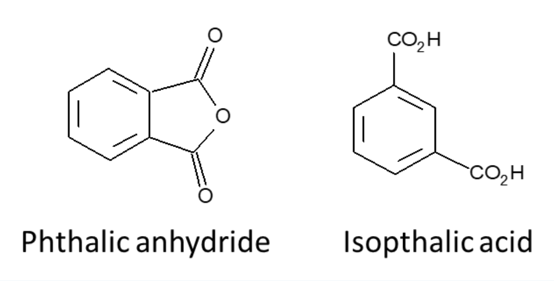

Figure 4: Polyvalent aromatic carboxylic acids

Like the other raw materials, these aromatic carboxylic acids naturally fulfil an important function within that of alkyd resins. The rigid aromatic structure provides, for example, good drying properties, good hardness, improved durability, thermal stability and chemical resistance. Dispensing with these building blocks is only possible if a large proportion of the properties mentioned are not required. At present, bio-based, polyvalent aromatic carboxylic acids are not available on a large scale. However, there are a number of interesting projects that will lead to corresponding products. In a few years, these raw materials will be available, which will enable the formulation of completely bio-based alkyd resins that achieve a property profile comparable to today's systems.

Nevertheless, there are already some bio-based, polyvalent carboxylic acids that can be used in certain applications and lead to good properties here. Here one can mention, for example, rosin, furandicarboxylic acid or succinic acid [cf. Fig. 5]. Each of these raw materials is available completely bio-based and enables specific properties in the respective alkyd resins.

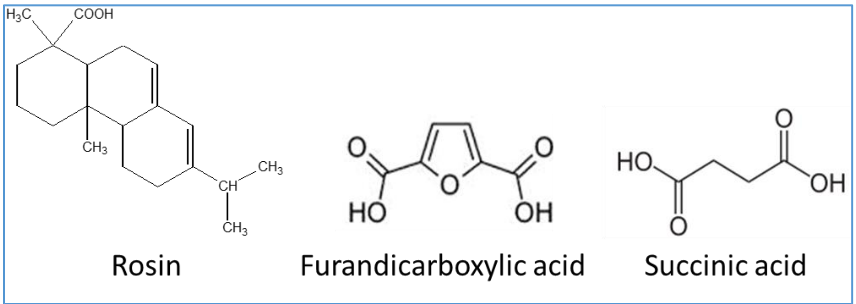

Figure 5: Some bio-based carboxylic acids

In addition to these basic raw material components, alkyd resins can be provided with various modifications that enable or improve certain properties. Table 1 gives an overview of some types of modifications and their specific properties.

Modification type	**Properties**
Vinyling	Drying, hardness, elasticity and yellowing
Siliconisation	Weather resistance, gloss and colour stability
Urethanisation	Drying, hardness, abrasion resistance, adhesion and chemical resistance
Thixotropy	Rheology, flow and stability
Epoxidation	Adhesion and corrosion protection
Phenolic resin modification	Drying, hardness, adhesion and recoatability

Table 1: Modification types of alkyd resins

All these possibilities form our basis for the development of high-quality alkyd resins for a wide range of applications.

WorléeKyd VP-W 3067/00 is a high solids alkyd resin with hydroxyl groups and conjugated double bonds.

Delivery form	80% in n-butyl acetate
Oil length	36%
Bio-based share	about 30% on solid resin
Viscosity	< 20,000 mPas
OH content	about 2% on solid resin

Table 2: WorléeKyd VP-W 3067/00

Alkyd resins can be classified according to various criteria. The simplest classification is according to the oil length, which indicates how high the oil content of the solid resin is. Here, a distinction is made between short, medium and long oil alkyd resins. If alkyd resins are used in industrial coatings, they are often divided into drying and non-drying alkyd resins. The designation suggests why this classification is made. Drying alkyd resins are based on semi-drying or drying oils or fatty acids, which can cross-link auto-oxidatively with oxygen via their conjugated double bonds (see Fig. 6).

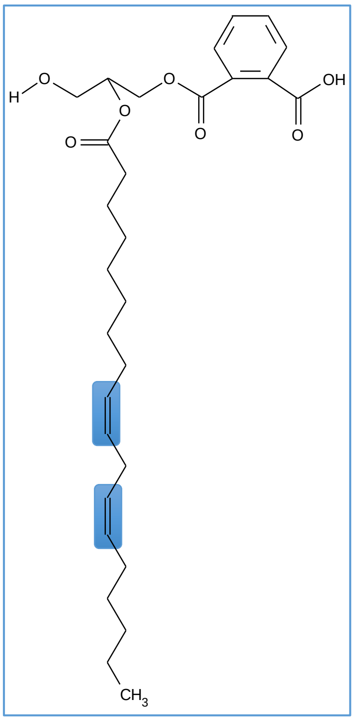

Figure 7: Alkyd resin with conjugated double bonds

Non-drying alkyd resins, on the other hand, are based on non-drying oils or fatty acids, which cannot dry oxidatively. These products often contain readily available hydroxyl groups that can cross-link with isocyanates or melamine resins (cf. Fig. 7).

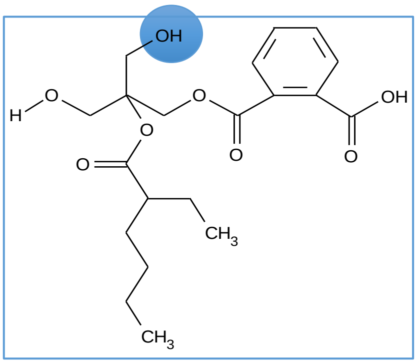

Figure 6: Alkyd resin with hydroxyl group

Both types of alkyd resins have their specific properties, advantages and also disadvantages. The possibility of auto-oxidative drying is almost exclusively reserved for alkyd resins. For this, oxygen from the air is needed as a second reaction component, which, however, does not have to be added. The alkyd resin chains thus react chemically to form resilient films. On the other hand, the reaction can be easily interrupted by stopping the oxygen uptake. Drying alkyd resins are therefore one-component systems with an infinite pot life. Non-drying alkyd resins are usually reacted with another reaction component. Here, they benefit from additional groups introduced by this component. When using e.g. isocyanates, urethane groups are formed which determine the properties. As with the cross-linking of e.g. polyacrylates, these provide excellent chemical and mechanical resistance and improved light fastness. WorléeKyd VP-W 3067/00 is based on tall oil fatty acid, which is a by-product of pulp and paper production. It therefore does not consume any additional acreage and is not suitable for human consumption. Tall oil fatty acid is one of the semi-drying fatty acids. The high content of double and triple conjugated fatty acids (see also fig. 2) enables an excellent auto-oxidative drying of the alkyd resins based on it and thus also the WorléeKyd VP-W 3067/00 (see tab. 2). In addition, the product also contains readily available hydroxyl groups, which are introduced in the synthesis.

Thus, the WorléeKyd VP-W 3067/00 can be cross-linked auto-oxidatively as well as with other reaction components. If you use both types of cross-linking at the same time, you have a so-called dual cure system.

The WorléeSin MK 223 is a modified maleic resin, which additionally improves the properties of the coating system

Delivery form	100% in pastilles
Bio-based share	about 74%
Viscosity	< 25,000 mPas @ 75% in n-butyl acetate
OH content	about 1.8%
Acid value	30-50 mg KOH/g binder

Table 3: WorléeSin MK 223

In addition to alkyd resins, maleic resins are also based on a high proportion of bio-based raw materials. These products are based on colophony, which is chemically modified with maleic acid and other raw materials. The maleic acid gives the products their corresponding name. The other raw materials are polyalcohols such as glycerol or pentaerythritol, other mono- or dicarboxylic acids such as phthalic anhydride, benzoic acid or vegetable fatty acids. The products accumulate as solids and should be dissolved in a suitable solvent.

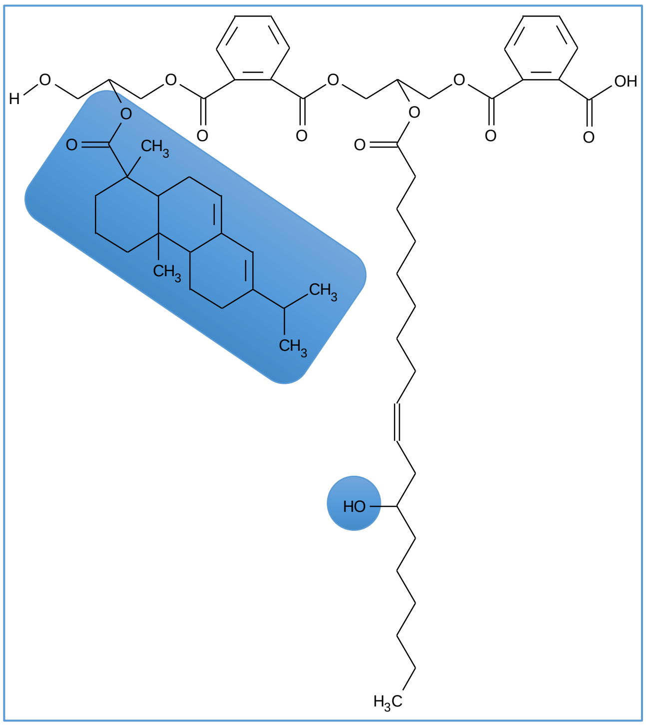

Figure 8: Structure WorléeSin MK 223

WorléeSin MK 223 (cf. Tab. 3) is a plasticised maleic resin with a melting range of 90 to 110 °C. It has a relatively high acid value and also carries hydroxyl groups (cf. Fig. 8). With 74%, it is based on a high proportion of bio-based raw materials. In the field of bio-based industrial coatings, it can fulfil various functions as a combination partner. As a maleic resin, it improves physical drying, initial hardness and, to some extent, sandability. It also frequently optimises the fullness and gloss of corresponding coating systems. The high acid value catalyses the reaction of isocyanates or melamine resins with hydroxyl groups. The low degree of thermoplasticity can also optimise recoatability, especially intercoat adhesion. The hydroxyl groups present can react with isocyanates, which improves resistance, especially to solvents.

To determine the optimum amount of WorléeSin MK 223 to be added as a combination partner, a test formulation for a high-gloss grey topcoat was chosen and different binder combinations were investigated (see Tab. 4). For easier handling, a 75% solution of WorléeSin MK 223 was used.

Master lacquer	1	2	3	4	5

Proportion of WorléeSin MK 223 of binder solids	0%	11%	23%	34%	45%
WorléeKyd VP-W 3067/00 80% in n-butyl acetate	41,25	36,50	31,90	27,20	22,50
WorléeSin MK 223 75% in n-butyl acetate	-	5,00	10,00	15,00	20,00
WorléeDisperse 8100 S	0,50	0,50	0,50	0,50	0,50
WorléeAdd 810 Paste 10% in xylene	3,00	3,00	3,00	3,00	3,00
Hi-Sil T 800	0,10	0,10	0,10	0,10	0,10
Kronos 2360	22,50	22,50	22,50	22,50	22,50
Monarch 430	0,10	0,10	0,10	0,10	0,10
Bayferrox 420	1,30	1,30	1,30	1,30	1,30
Blanc fixe micro	15,00	15,00	15,00	15,00	15,00
WorléeAdd 6236	0,50	0,50	0,50	0,50	0,50
WorléeAdd 315	0,50	0,50	0,50	0,50	0,50
Methoxypropyl acetate	2,00	2,00	2,00	2,00	2,00
Butyl acetate	13,25	13,00	12,60	12,30	12,00
Hardener					
Tolonate HDT-LV	7,00	7,00	7,00	7,00	7,00

Table 4: Test formulation 2 K PU topcoat

Various tests were carried out with the lacquers produced in this way. The VOC content achieved at the corresponding processing viscosity is important for later application. For the tests, a processing viscosity of the ready-mixed paint of 30 to 35 seconds in a 4 mm flow cup at 20°C was aimed for. In table 5 it can be seen that with increasing amount of WorléeSin MK 223 the non-volatile content decreases and the VOC increases. The viscosity of the product is higher compared to WorléeKyd VP-W 3067/00. On the other hand, the viscosity increase decreases noticeably with increasing addition of WorléeSin MK 223, which leads to longer potting or processing times.

Test varnish	1	2	3	4	5
Proportion of WorléeSin MK 223 of binder solids	0%	11%	23%	34%	45%
Quantity master lacquer	100,00	100,00	100,00	100,00	100,00
Tolonate HDT-LV	7,00	7,00	7,00	7,00	7,00
Initial viscosity DIN 4 / 20°C	52 sec	56 s	62 s	69 s	71 s
Addition butyl acetate	3 g	4 g	5 g	7 g	7,5 g
Viscosity DIN 4 / 20°C	34 sec	34 sec	33 sec	32 sec	30 sec
non-volatile content	73,3 %	72,7 %	72,1 %	70,6 %	70,4 %
Density	1.39 g/cm³	1.39 g/cm³	1.39 g/cm³	1.38 g/cm³	1.38 g/cm³
VOC content	371 g/l	379 g/l	388 g/l	406 g/l	408 g/l
Pot life /processing time					
Start	34 sec	34 sec	33 sec	32 sec	30 sec
2 h	61 sec	58 sec	52 sec	48 sec	48 sec
4 h	77 sec	67 sec	62 sec	56 sec	54 sec
6 h	90 sec	81 sec	72 sec	63 sec	63 sec
24 h	344 sec	307 sec	288 sec	227 sec	205 sec

Table 5: Technical data ready-to-use lacquers

The WorléeSin MK 223 was to have a significant influence on the drying properties and the hardness development. For this purpose, the varnishes were applied and the different tests were carried out (cf. Tab. 6). With increasing quantity, the drying time decreases significantly. If the test varnish without addition of WorléeSin MK 223 needs more than eight hours to reach drying level 4, this time is about four hours with the highest addition. The determined pendulum hardnesses also increase significantly both at room temperature and with forced drying.

Test varnish	1	2	3	4	5
Proportion of WorléeSin MK 223 of binder solids	0%	11%	23%	34%	45%
	Drying properties 100 µm wet film on glass				
Dust dry	13 min	11 min	10 min	10 min	10 min
Adhesive-free	>8h 3+	>8h 2-	5h 50min	2h 50min	2h 30min
Drying level 4	<24h	<24h	8 h	5 h	4 h
Drying level 6	>24 h	>24 h	<24h	<24h	7 h
Pendulum hardness					
after 24 h RT	22" 22"	28" 28"	36" 36"	53" 51"	65" 67"
after 48 h RT	31" 31"	35" 35"	42" 44"	60" 56"	69" 74"
after 72 h RT	40" 37"	43" 41"	46" 47"	61" 61"	75" 72"
after 1 week RT	58" 56"	48" 53"	58" 57"	75" 72"	88" 94"
after 2 weeks RT	75" 77"	74" 76"	81" 81"	100" 101"	119" 120"
30 min. 60°C + 1 h RT	17" 17"	18" 18"	25" 25"	36" 38"	55" 53"
30 min. 60°C + 24 h RT	29" 29"	32" 32"	42" 42"	58" 57"	74" 74"
30 min. 60°C + 1 week	56" 56"	49" 50"	58" 58"	75" 79"	111" 114"
30 min. 80°C + 1 h RT	28" 26"	35" 33"	46" 46"	78" 76"	84" 81"
30 min. 80°C + 24 h RT	33" 31"	37" 37"	46" 49"	88" 89"	81" 84"
30 min. 80°C + 1 week	75" 73"	50" 51"	57" 57"	107" 107"	103" 105"

Table 6: Drying properties and hardness development

On the other hand, there are also properties that are negatively influenced by too large additions of WorléeSin MK 223. A too large addition can, for example, worsen the elasticity, but also the QUV resistance. These properties were also investigated here. Table 7 shows an influence on the elasticity with increasing addition. In particular, the value of the direct impact test decreases with increasing amount. However, WorléeSin MK 223 has a much greater influence on QUV A 340 rapid weathering. Increasing quantities significantly reduce the gloss stability in the system.

Test varnish	1	2	3	4	5
Proportion of WorléeSin MK 223 of binder solids	0%	11%	23%	34%	45%
	120 µm CRS matt				
Impact direct 1kg After 4 weeks	80 cm	70 cm	40 cm	40 cm	30 cm
Impact reverse 1kg After 4 weeks	10 cm	<10 cm	<10 cm	<10 cm	<10 cm
Erichsen depression After 4 weeks	9.1 mm	8.7 mm	8.7 mm	8.5 mm	1.5 mm
QUV A 340 rapid weathering Application 150 µm wet on aluminium, 1 week drying at 20°C and 55% RF					
Test cycle: 1st UV phase; test temperature 60°C and test duration 8 hrs. average radiant intensity 0.89 W/m² @ 340 nm 2nd condensation phase; test temperature 45°C and test duration 4 hrs.					
Gloss 20° / 60					
Start	93 / 96	94 / 98	94 / 98	94 / 98	93 / 98
after 48 h	89 / 94	91 / 95	90 / 95	90 / 95	85 / 93
after 167 h	83 / 93	86 / 93	85 / 93	82 / 92	72 / 89
after 337 h	76 / 91	81 / 93	80 / 92	71 / 89	61 / 85
after 504 h	63 / 86	71 / 88	67 / 86	57 / 83	40 / 76
after 841 h	56 / 82	57 / 82	51 / 79	36 / 70	15 / 48
after 984 h	55 / 81	54 / 81	41 / 73	22 / 56	6 / 32

Table 7: Elasticity and QUV A 340 rapid weathering

Depending on the properties desired later, care should therefore be taken as to the amount of WorléeSin MK 223 used.

Siccatives also have a detectable influence on the properties

The WorléeKyd VP-W 3067/00 carries, as already described, conjugated double bonds from the tall oil fatty acid used in addition to the hydroxyl groups. These double bonds can be additionally cross-linked by auto-oxidative drying. To investigate the effectiveness, test four (about 34% WorléeSin MK 223) was selected and a usual amount of WorléeAdd 2560 was added to the basecoat. This product is a catalyst containing manganese, which is suitable for catalysing the oxidative drying of alkyd resins. First, the influence on the drying properties and the hardness development was investigated (cf. Tab. 8). The addition slightly delays the drying of the paint system. However, the addition massively improves the initial hardness at room temperature and forced drying and especially the hardness development. It therefore seems absolutely sensible to include this additional cross-linking option.

Test varnish	4	4 a
Proportion of WorléeSin MK 223 of binder solids	34%	34%
		+ 1% WorléeAdd 2560 on basecoat
	Drying properties 100 µm wet film on glass	
Dust dry	10 min	20 min
Adhesive-free	2h 50min	3 h 30 min
Drying level 4	5 h	7 h
Drying level 6	<24h	<24 h
Pendulum hardness		
after 24 h RT	53" 51"	58" 60"
after 48 h RT	60" 56"	85" 89"
after 72 h RT	61" 61"	115" 113"
after 1 week RT	75" 72"	150" 145"
30 min. 60°C + 1 h RT	36" 38"	42" 43"
30 min. 60°C + 24 h RT	58" 57"	71" 71"
30 min. 60°C + 1 week	75" 79"	147" 142"
30 min. 80°C + 1 h RT	78" 76"	88" 93"
30 min. 80°C + 24 h RT	88" 89"	106" 111"
30 min. 80°C + 1 week	107" 107"	171" 171"

Table 8: Comparison of drying properties and hardness development with siccative

As a dual cure system, the binder system can achieve similar properties to a system based on a high solids polyacrylate

As already mentioned in the introduction, high-solids polyacrylates are often used to formulate high-solids two-component coatings. It therefore makes sense to choose such a coating system as the standard for comparison.

The two products mentioned, WorléeKyd VP-W 3067/00 and WorléeSin MK 223, have relatively low hydroxyl contents of 2.0% and 1.8% respectively. Therefore, WorléeCryl VP A 2117, a polyacrylate with a similar hydroxyl content and suitable for the formulation of high solids coating systems, was chosen for comparison (see Tab. 9).

	WorléeKyd VP-W 3067/00	WorléeCryl VP A 2117
Delivery form	80% in n-butyl acetate	75% in n-butyl acetate
Oil length	36%	-
Bio-based share	about 30% on solid resin	no share
Viscosity	< 20,000 mPas	< 10,000 mPas
OH content	about 2% on solid resin	about 1.7% on solid resin

Table 9: Comparison of technical data

For the comparison, the already mentioned test four including WorléeAdd 2560 as catalyst for accelerating the oxidative drying was chosen. The test formulation already used was also transferred directly to WorléeCryl VP A 2117 (cf. Tab. 10). Due to the somewhat lower content of hydroxyl groups, the requirement for isocyanate is also somewhat lower for WorléeCryl VP A 2117.

Master lacquer	4 a	6
Proportion of WorléeSin MK 223 of binder solids	34% + Worléedd 2560	WorléeCryl VP A 2117
WorléeKyd VP-W 3067/00; 80% in n-butyl acetate	27,20	-
WorléeSin MK 223; 75% in n-butyl acetate	15,00	-
WorléeCryl VP A 2117; 75% in n-butyl acetate	-	44,00
WorléeDisperse 8100 S	0,50	0,50
WorléeAdd 810 Paste; 10% in xylene	3,00	3,00
Hi-Sil T 800	0,10	0,10
Kronos 2360	22,50	22,50
Monarch 430	0,10	0,10
Bayferrox 420	1,30	1,30
Blanc fixe micro	15,00	15,00
WorléeAdd 2560	1,00	-
WorléeAdd 6236	0,50	0,50
WorléeAdd 315	0,50	0,50
Methoxypropyl acetate	2,00	2,00
Butyl acetate	11,30	10,50
Hardener		
Tolonate HDT-LV	7,00	6,00

Table 10: Test formulations Comparison with polyacrylate

For comparison of the coatings the same processing viscosity of 30 to 35 sec flow time in a 4 mm flow cup at 20°C was chosen again. The test based on the combination of WorléeKyd VP-W 3067/00 and WorléeSin MK 223 achieves a slightly higher solids content with a very comparable VOC content. The pot life and processing time are slightly reduced in comparison (cf. Tab.11).

Test varnish	4 a	6
Proportion of WorléeSin MK 223 of binder solids	34% + WorléeAdd 2560	WorléeCryl VP A 2117
Quantity master lacquer	100,00	100,00
Tolonate HDT-LV	7,00	6,00
Initial viscosity DIN 4 / 20°C	69 s	75 s
Addition butyl acetate	7 g	7 g
Viscosity DIN 4 / 20°C	32 sec	35 sec
non-volatile portion	71,0 %	69,6 %
Density	1.38 g/cm³	1.34 g/cm³
VOC content	400 g/l	407 g/l
Potting/processing time		
Start	33 sec	35 sec
2 h	45 sec	43 sec
4 h	57 sec	48 sec
6 h	66 sec	50 sec
24 h	192 sec	82 sec

Table 11: Comparison of technical data for ready-to-use coatings

Interesting results also emerge with regard to the drying properties and hardness development (cf. Tab. 12). The basic drying is on a similar level. Drying level 4 is reached slightly earlier with WorléeCryl VP A 2117. In terms of hardness development, especially at room temperature, the system based on the binders WorléeKyd VP-W 3067/00 and WorléeSin MK 223 shows clear advantages. Only the drying at 60°C is different, here WorléeCryl VP A 2117 shows very slight advantages.

Test varnish	4 a	6
Proportion of WorléeSin MK 223 of binder solids	34% + WorléeAdd 2560	WorléeCryl VP A 2117
	Drying properties 100 µm wet film on glass	
Dust dry	20 min	17 min.
Adhesive-free	3 h 30 min	3 h 25 min.
Drying level 4	7 h	6 h
Drying level 6	<24 h	<24h
Pendulum hardness		
after 24 h RT	58" 60"	45" 43"
after 48 h RT	85" 89"	71" 68"
after 72 h RT	115" 113"	89" 92"
after 1 week RT	150" 145"	95" 102"
30 min. 60°C + 1 h RT	42" 43"	53" 52"
30 min. 60°C + 24 h RT	71" 71"	86" 88"
30 min. 60°C + 1 week	147" 142"	142" 145"
30 min. 80°C + 1 h RT	88" 93"	90" 88"
30 min. 80°C + 24 h RT	106" 111"	106" 99"
30 min. 80°C + 1 week	171" 171"	117" 121"

Table 12: Comparison of drying properties and hardness development

Both coatings can be regarded as systems with a low cross-linking density. The low content of hydroxyl groups results in a low demand for isocyanate. Thus, of course, one should not expect miracles from this type of coating system, especially in terms of resistance. Possibly, the systems based on WorléeKyd VP-W 3067/00 and WorléeSin MK 223 have advantages here, because besides the cross-linking with the isocyanate, it also dries oxidatively, which increases the cross-linking density. In terms of resistance to various substances, it certainly appears that this could offer an advantage. Against most of the tested substances, the test lacquer 4 a shows a better or at least comparable resistance (cf. Tab. 13). Particularly noteworthy here is the resistance to premium petrol, diesel, Isopar L and xylene. The resistance to brake fluid, on the other hand, was poorer. The tested brake fluid DOT 4 is based on long-chain polyglycols. Also in the test of MEK resistance, the test varnish 4 a shows slight advantages with about more than 60 double strokes compared to 20 for WorléeCryl VP A 2117. However, both values are relatively low compared to the best value of 200 double strokes, which can also be achieved with binders with higher cross-linking densities.

Test varnish	Time	4 a	6
Proportion of WorléeSin MK 223 of binder solids		34% + WorléeAdd 2560	WorléeCryl VP A 2117
		100 µm wet film on glass	
MEK test after 1 week		61 double strokes	20 double strokes
		Drying 2 weeks at room temperature	
Super petrol	30 min.	3-	5
Diesel	24 h	2-	2-3
Brake fluid (DOT 4)	24 h	5	3
Radiator antifreeze (MEG)	24 h	2-	2
Isopar L	24 h	0	2-
Ethyl acetate	5 min	5	5
Xylene	5 min	2-	5
Acetone	5 min	5	5
0 = no change 1 = very little change 2 = small change3 = medium change 4 = strong change 5 = lacquer coating destroyed			

Table 13: Chemical resistance test

Optical properties can also play an important role in certain applications. Alkyd resins usually offer further advantages here compared to e.g. polyacrylates. In addition, the WorléeSin MK 223 used can also have a positive effect on these properties. The results in Table 14 confirm this very clearly. The test varnish 4 a, based on WorléeKyd VP-W 3067/00 and WorléeSin MK 223, achieves, in the chosen formulation, a significantly higher gloss and lower haze compared to WorléeCryl VP A 2117. The differences are even more noticeable with forced drying at 80°C. In this case the brilliance of the coating suffers. Here, the brilliance of the polyacrylate-based varnish clearly suffers compared to the alkyd resin-based varnish. The wetting properties of alkyd resins are usually very good due to their chemical structure. With a binder system such as the one tested here, it may be possible to achieve significantly higher filler contents, while at the same time achieving very high gloss levels and low gloss haze. This makes it possible to formulate coatings with a higher solids content and lower solvent content.

Test varnish	4 a	6
Proportion of WorléeSin MK 223 of binder solids	34% + WorléeAdd 2560	WorléeCryl VP A 2117
	100 µm wet film on glass	
Gloss 20°/60°/Haze		
after 24 h RT	90 / 94 / 14	87 / 92 / 30
after 1 week RT	91 / 95 / 16	84 / 92 / 48
30 min 60°C + 1 week RT	91 / 96 / 30	85 / 92 / 49
30 min 80°C + 1 week RT	91 / 96 / 22	75 / 89 / 100

Table 14: Gloss level and gloss haze

The paint systems formulated here can also be used outdoors. For this, of course, it is necessary that they have the best possible resistance to light irradiation and possibly also to water condensation. To get a basic idea of the resistance, comparative quick tests can be carried out. For the results in Table 15, the paints were applied, conditioned and loaded in the QUV A 340 rapid weathering device. The coatings are exposed to an alternating climate test consisting of an irradiation phase and a condensation phase. This test has already been used to classify the optimum proportion of WorléeSin MK 223. To classify the differences, the values of test varnish 4 were also listed in the table. The difference between test lacquer 4 and 4 a is only the use of WorléeAdd 2560 as catalyst for the oxidative drying of the double bonds of the fatty acid used. It can be clearly seen that gloss retention during rapid weathering is significantly improved when the varnish is additionally equipped with WorléeAdd 2560. The improved cross-linking density also seems to have a very positive effect here. The more important comparison is of course between the test varnish 6 based on WorléeCryl VP A 2117 and the test varnish 4 a based on the combination of WorléeKyd VP-W 3067/00 and WorléeSin MK 223. When comparing these varnishes in the QUV A 340 rapid weathering test, we measured not only the change in gloss level but also the change in colour shade (Delta E) compared to the unloaded surface. As in the previous tests, the initial gloss of the test varnish 4 a is clearly higher. The gloss stability of the test varnish 4 a is also significantly better in the course of the load test. Concerning the colour stability, WorléeCryl VP A 2117 shows its advantages and achieves a better stability. Alkyd resins and also maleic resins tend to yellow more due to their chemical structure. This is primarily due to the use of aromatic polycarboxylic acids and the oils or fatty acids that carry double bonds. Depending on the selected colour tone, in this case a grey tone, a shift of the colour tone takes place when exposed to UV light and also heat, which may become noticeable in a larger measurable colour tone deviation.

Test varnish	4	4 a	6
Proportion of WorléeSin MK 223 of binder solids	34%	34% + WorléeAdd 2560	WorléeCryl VP A 2117
QUV A 340 rapid weathering Application 150 µm wet on aluminium, 1 week drying at 20°C and 55% RF			
Test cycle: 1st UV phase; test temperature 60°C and test duration 8 hrs. average radiant intensity 0.89 W/m²@ 340 nm 2nd condensation phase; test temperature 45°C and test duration 4 hrs.			
Gloss 20° / 60° / Delta E			
Start	94 / 98	93 / 97	81 / 92
after 48 h	90 / 95	88 / 95 / 0,17	76 / 90 / 0,06
after 167 h	82 / 92	83 / 93 / 0,33	68 / 88 / 0,06
after 337 h	71 / 89	77 / 91 / 0,42	50 / 81 / 0,15
after 504 h	57 / 83	73 / 89 / 0,55	36 / 75 / 0,14
after 841 h	36 / 70	64 / 85 / 0,64	26 / 68 / 0,21
after 984 h	22 / 56	59 / 83 / 0,77	27 / 68 / 0,20
after 1129 h	-	53 / 80 / 0,86	26 / 67 / 0,40
after 1247 h	-	45 / 76 / 0,94	17 / 59 / 0,39
after 1486 h	-	30 / 64 / 1,11	20 / 62 / 0,62

Table 15: QUV A 340 rapid weathering

The binders used make it possible to formulate coatings with relevant bio-based components.

The bio-based share can be specified in different ways. Table 16 gives an overview of the summarised components of the formulation, which serve as the basis for calculation. For ease of consideration, the additives used were considered as if they were solvents.

Component	Quantity	Polymer content solid	inorganic portion	VOC	organic fraction	bio-based portion
WorléeKyd VP-W 3067/00	27,20	21,80	-	5,45	27,20	6,50
WorléeSin MK 223	15,00	11,20	-	3,75	15,00	8,30
Pigments / Fillers	39,00	-	39,00	-	-	-
Additives and solvents	18,80	-	-	18,80	18,80	-
Base paint	100,00	33,00	39,00	28,00	61,00	15,00
Hardener	7,00	7,00	-	-	7,00	-
Dilution	7,00	-	-	7,00	7,00	-
ready-to-use paint	114,00	40,00	39,00	35,00	75,00	15,00

Table 16: Summarised ingredients of the formulation

On the basis of this, the corresponding bio-based shares result depending on the approach (cf. Tab. 17). For the total formulation, the bio-based share is about 13%. Of course, this approach is extremely dependent on the selected formulation. The test varnish chosen here is a pigmented and relatively highly filled topcoat. As the degree of filling increases, the organic content and especially the polymer content is reduced accordingly. This would mean that the corresponding bio-based content is further reduced. Calculated only on the total organic content, the bio-based content is about 20%. All organic components, especially the polymers and solvents, were considered here. The main adjusting screw for a manufacturer of binders is, of course, the corresponding polymers. Solvents can certainly be replaced by available bio-based variants or, in principle, by water. Therefore, if one considers the bio-based share in relation to the polymer share, it is already possible to achieve a share of about 37% of bio-based raw materials in the ready-to-use coating in the selected formulation.

	Bio-based content in the ready-to-use coating
on the overall formulation	about 13%
on the organic portion	about 20%
on the polymer content	about 37%

Table 17: Bio-based shares considered differently

An outlook - the development is very dynamic

The coatings industry is already doing its part to improve sustainability. Coatings protect goods from a wide range of stresses such as water, sun or even mechanical and chemical stress. On the other hand, it also makes the world a little more colourful, and usually with comparatively small application quantities. In addition, the systems must continue to show improved sustainability in the future. The term sustainability is not precisely defined and encompasses many aspects. Certainly, one aspect is the move away from petrochemicals and the increased use of bio-based raw materials. However, factors such as land consumption, the plate-tank discussion or the deforestation of rainforests also play a role here. Other factors can be, for example, durability, danger to humans and the environment or regionality. In addition, the raw materials contained must be available and the product must also fit into a corresponding economic framework.

Already today there are possibilities to develop products that combine many of these factors. The WorléeKyd VP-W 3067/00 is suitable for formulating coating systems with a good property profile. It is based on a relevant proportion of bio-based raw materials and allows the formulation of high-solids systems. Tall oil fatty acid is a major part of the bio-based raw materials. It occurs as a by-product of paper and pulp production, is not suitable for human or animal consumption and does not occupy any additional cultivation area.

On the other hand, the development in the markets is very dynamic. There are many efforts to develop more sustainable products and technologies, as well as to improve the measurability of sustainability, not only by the carbon footprint.

Worlée-Chemie accompanies this path very intensively. In cooperation with customers, the development teams from research and development as well as application technology can develop new products, modify them and adapt them to the customers' needs. With many of their own ideas, new technologies and possible prototypes, they answer questions on current topics and are already thinking about future issues.