

## Resins and additives for powder coatings and alkyd paints, based on renewable resources

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**Abstract** Due to limited fossil resources and an increased need for environmentally friendly, sustainable technologies, the importance of using renewable feedstocks in the paint and coatings area will increase in the decades to come. This paper highlights some of the perspectives in this area. Alkyd resins for high-solid paints and reactive diluents, completely based on commercially available renewable resources, were prepared and characterized. Alkyd resins based on sucrose and unsaturated fatty acids or oils showed a

low intrinsic viscosity, making them suitable to be used in high-solid alkyd paints. Reactive diluents based on similar starting materials showed excellent properties with regard to thinning behavior and effect on drying characteristics. Powder coating polyester resins were synthesized, starting from isosorbide and diacids. Polyester resins with glass transition temperatures up to 70°C were obtained. Incorporation of small amounts of other diols and trifunctional components was found to improve color and coating properties. In order to create completely renewable resin systems, the development of renewable drying agents for alkyds and crosslinkers for powder coatings is in progress.

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### Introduction

Faced with current crude oil price hikes, the emerging economies of China, Brazil, and India, and the limited success in finding new vast crude oil reservoirs, the perception is growing among the masses that the end of the cheap oil era has arrived, and that prices for crude oil and transportation fuels are much more likely to increase than to decrease in the coming years and decades. This, combined with the desire to become less dependent on the countries of the Middle East with regard to feedstocks and the desire for more sustainable technology, drives society to develop alternative sources for energy and chemical feedstocks. At the same time, prices of renewable feedstocks have dropped continuously over the last few decades as a result of increased yields of biomass per acre.<sup>1</sup> Consequently, there is, in all respects, a growing opportunity to price effectively use of renewable feedstocks in nonfood products such as paints and coatings.

Many items in our everyday life are coatings, with the coatings having either a protective, signal, or decorative function. In addition to their aesthetic function, coatings obviously aim at enhancing the *durability* of a product. In addition, the increased *sustainability* of coatings is required today as well, with demand increasing for coatings with properties such as “solvent-free,” “easy-to-apply,” “recyclable,” and “produces less waste.” As long as such coatings contain resins and additives that are based on *undepletable*, *renewable* resources, they will contribute to enhanced sustainability.

In the “Biobased Products” Department of Wageningen University and Research Centre, various research programs are being carried out in co-operation with universities and industries that aim to develop both durable and sustainable coatings based on renewable resources. Current research projects cover the four principal components of coatings (i.e., binders, pigments/fillers, additives, and solvents). With regard to binders, products have been obtained that are suitable as paper coatings, floor coverings, high-solid alkyd resins, or resins for water-based systems. These products are based on new fatty acid or carbohydrate technology using combinations of carbohydrate and fatty acid technology,<sup>2,3</sup> or are based on microbial polymers (e.g., polyhydroxyalkanoates or polypeptides).<sup>4</sup> Microbial production of solvents and the production of reactive diluents is also under study.<sup>5</sup> Patented alternative technology in the area of additives is under development, leading to cobalt-free drying catalysts for alkyd-based paints and inks.<sup>6</sup> In contrast, the development of renewable crosslinkers for powder coatings has only recently begun.

### Towards sustainable paint and coating resins

To develop safer working conditions for those who produce or apply paint, and to reduce the environmental burden, there has been a drive over the last few decades toward the development of coating technologies using less, or even no, volatile organic solvents. This has led to the development of powder coatings, as well as UV-curing and waterborne paint technologies. Solvent-free powder-coating systems have already become a commodity and are especially suited for the industrial coating of metal surfaces. New and improved technologies will make powder-coating systems also increasingly more suitable for protecting wood-based products.<sup>7</sup>

Next to the industrial use of solvent-free systems, the use of solvent- or waterborne paints that are applied by brush will remain very important. Most likely, alkyd resins and alkyd resin-based paints will also remain of utmost importance for the decorative coatings industry. Currently, alkyd resins are being produced annually in quantities of approximately 400,000 tons in Western Europe. Traditionally, alkyd

paints are organic and solvent-based, using up to 50% of volatile organic carbon-based (VOC) solvents in a paint formulation. These types of coatings are especially popular because of their ease of application and high gloss characteristics. New, existing, and anticipated legislation aiming at reducing VOC levels is the current driving force for the coatings industry, especially for decorative paints. Manufacturers of solvent-based paints have to respond to these forces, which will lead to three main options:

- Switch to water-based systems, making use of alternatives to alkyd technology
- Switch to water-based alkyd systems
- Switch to high-solid systems containing less or no VOCs

Another environmental issue connected with the use of current alkyd resin-based paints is the use of cobalt-based drying catalysts for this type of paint. There are indications that cobalt aerosols are potentially carcinogenic.<sup>8</sup> Consequently, there is a driving force to move away from cobalt-based drying catalysts and toward effective and more environmentally acceptable drying catalysts.

In this paper, activities in the development of renewable-based powder coating resins, high-solid alkyd resins, reactive diluents, and cobalt-free drying catalysts are described.

## Results and discussion

### Powder coating resins and crosslinkers

Whereas alkyd resins have low melting points and glass transition temperatures ( $T_g$ ), powder coating resins need to have a sufficiently high glass transition temperature in order to provide good storage stability and processing ability. The resins should have  $T_g$  values above 45°C.

To synthesize renewable-based powder coating resins, combinations of renewable-based diacids and carbohydrate derivatives can be used. To create systems with a high  $T_g$ , the polyester backbone should be rigid, suggesting the use of rigid carbohydrate derivatives in combination with short chain diacids.

Such rigid carbohydrate derivatives can be obtained by the dehydration of sugar alcohols. The use of isosorbide, in this respect, is of special interest. The use of isosorbide has already been given some attention in polyester synthesis, because it is easily obtained from sorbitol. Terephthalic acid-based polyesters containing isosorbide have been described,<sup>9</sup> as well as polyurethanes and poly(ester carbonate)s. Coating, and especially fiber, applications of polymers containing isosorbide have been described in the literature, including polyesters cured with styrene.<sup>10</sup> Powder

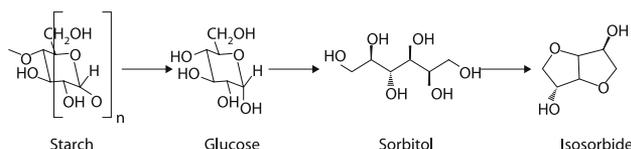
coating applications using isosorbide are not specifically mentioned or described. Isosorbide can be obtained from sorbitol, which is commercially produced from starch through hydrolysis and subsequently hydrogenating the glucose into sorbitol (see Fig. 1). In Europe, over 400,000 tons of sorbitol are produced by companies such as Cerestar, Roquette and Tate & Lyle.

A series of renewable isosorbide-based copolyesters were synthesized by direct esterification of isosorbide with short-chain diacids such as succinic acid, using  $Ti(OBu)_4$  as a catalyst. Next to isosorbide, varying amounts of other diols such as 2,3-butanediol, 1,3-propanediol (potentially obtained by fermentation of sugars) and/or neopentyl glycol were built in (see Fig. 2). Reaction temperatures of 150–240°C and further polycondensation under reduced pressure ( $P < 5$  mbar) led to polyesters with number-average molecular weights of a few thousand Daltons, and polydispersities between 1.6 and 2.0.

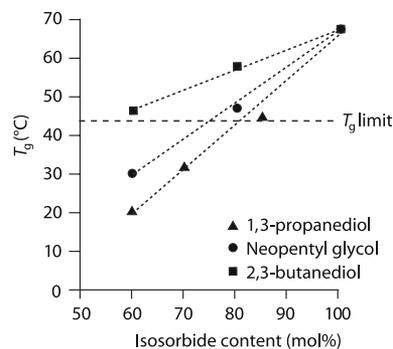
Figure 2 shows the effect of incorporating isosorbide on the  $T_g$  values of the resulting terpolyesters. Upon incorporation of 60–80% of isosorbide, the  $T_g$  is high enough to insure a good processing and storage stability of the polyester resin. It was also found that incorporation of other diols had a beneficial effect on the color of the resin. The introduction of small amounts of trifunctional acids (citric acid) or triols (trimethylol propane) in the resins resulted in improved coating properties.

Polyesters with either carboxyl or hydroxyl end groups were cured using different commercially available curing agents. Hydroxyl-functionalized resins were cured with (blocked) isocyanate groups containing petrochemical-based crosslinkers, whereas acid-functionalized resins were cured with crosslinkers having epoxy groups (TGIC—triglycidyl isocyanurate, Aldrich Chemicals) or activated hydroxyl groups (Primid XL-552; *N,N,N',N'*-tetrakis(2-hydroxyethyl)adipamide, EMS Chemie). Depending on the specific crosslinker used and the functionality of the resin, films were obtained that can withstand full impact testing and show good-to-excellent solvent resistance (see Table 1).

Table 1 shows that, after crosslinking, interesting coating properties can be obtained with these renewable-based polyester resins and conventional petrochemical-based crosslinkers. All films showed König hardnesses values above 200 s. Good solvent resistance and impact resistance could be obtained. The best



**Fig. 1: Conversion of starch and glucose into sorbitol and isosorbide, respectively**



**Fig. 2: The effect of incorporating different amounts of isosorbide on the  $T_g$  values of terpolyesters:  $\blacktriangle$  = 1,3-propanediol,  $\bullet$  = neopentyl glycol,  $\blacksquare$  = 2,3-butanediol**

performing crosslinker (TGIC), nonetheless, is also the least desired from a health point of view. Therefore, to develop crosslinkers with an increased sustainability profile and less negative impact on health and environmental issues, it is desirable to evaluate renewable-based crosslinking agents.

Epoxidized linseed oil has already been known for several years as a bio-based crosslinker for powder coating resins,<sup>11</sup> but although it effectively crosslinks numerous powder coating formulations and is commercially applied to some extent, its application scope is limited because it has a tendency to severely lower the  $T_g$  of powder coating formulations, and thereby has a negative effect on storage ability and the processing window.

**Table 1: Coating properties for renewable polyesters crosslinked with conventional crosslinkers**

Resin functionality	Curing agent	Impact test (1 kg, 100 cm)	Solvent resistance <sup>a</sup>
<i>OH-functional</i>			
Linear	VB	–	–
Linear	DN	+	+/-
Branched	DN	+	+
Branched	VB	+/-	+
<i>COOH-functional</i>			
Branched	TGIC	+	++
Branched	P552	+/-	+

*Note:* Coatings were prepared by applying a film (polyester and crosslinker dissolved in *N*-methylpyrrolidone) (NMP) of approximately 250  $\mu$ m thickness onto an aluminum panel. After drying, the films were cured at 200°C during 30 min under nitrogen. Branched OH-functional resins contain small amounts of triols. Reverse impact test was carried out according to ASTM D 2794.

DN = Desmodur N3600 (hexamethylene diisocyanate-based polyisocyanate, Bayer), VB = Vestagon B1530 (polyisocyanate based on isophorone diisocyanate, Bayer), P552 = Primid XL-552.

<sup>a</sup> Acetone rub test.

The authors, therefore, recently started to explore the potential of using more rigid renewable building blocks to produce tri- or tetra-functional crosslinkers suitable for both hydroxy- and acid-functionalized resins.

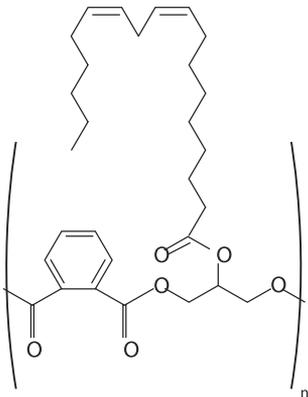
### **High-solid alkyd resins based on renewable resources**

Conventional air-drying paints usually utilize alkyd oligomers as binders. These alkyds used in coating formulations are suitable for applications at ambient temperature and are synthesized by a polycondensation reaction of polycarboxylic acids, polyhydric alcohols, and unsaturated fatty acids or oils (see Fig. 3). Highly suitable polycarboxylic acids are, for instance, phthalic acid anhydride, terephthalic acid anhydride, trimellitic acid, adipic acid, and maleic acid.

The polyalcohols commonly used in the alkyd synthesis are, among others: (di)pentaerythritol, glycerol, ethylene glycol, trimethylolpropane, and neopentylglycol. Whereas the fatty acid or oil component is derived from renewable resources, the majority of the aforementioned polyacids, and polyalcohols are alkyd building blocks derived from petrochemical resources.

Conventional synthesis of alkyd resins leads to polycondensates with a rather high polydispersity, in which case the high molecular-weight part contributes to a high intrinsic viscosity, and the low molecular-weight part has a negative impact on drying properties. To obtain high-solid paints, it is important to decrease the intrinsic viscosity of the alkyd resin. This might be achieved by developing an alkyd oligomer with a suitable average molecular mass and a narrow molecular-weight distribution (low polydispersity).

Alkyd resins completely based on renewable resources have thus far been the subject of a few studies. Hoechst's patent<sup>12</sup> describes waterborne alkyd emulsions based on renewable resources. The patent describes the use of sorbitol (easily derived from starch) as the polyhydric alcohol and the use of succinic



**Fig. 3: Structure of a typical alkyd resin**

acid anhydride as the polycarboxylic acid. Hájek<sup>13</sup> described the use of sorbitol and xylitol in alkyd resin synthesis, whereas, Bagchi and Malakar<sup>14</sup> described the partial replacement of conventional polyols (i.e., glycerol and pentaerythritol) by sorbitol.

A US patent assigned to the Research Corporation in New York,<sup>15</sup> discloses oil-modified sucrose resins obtainable by reaction of a partial esterified sucrose ester with a cyclic dicarboxylic anhydride and a diepoxide.

Although this work mentions alkyd resins based on renewables, it is not specifically aimed at deriving high-solids alkyd paints based on resins with a low intrinsic viscosity. Within the framework of a research project, together with paint producer SigmaKalon, an attempt was made to develop alkyd resins with low intrinsic viscosity. To achieve this, the authors explored the potential of two types of different renewable carbohydrate-derived resources such as sucrose and inulin.

Sucrose, in particular, is an interesting starting material because it is produced worldwide from crops such as sugar beet and sugar cane at over 140 million tons per annum, and at prices below those for common synthetic polyols used in alkyd-polyester resin synthesis.

### **Synthesis of alkyd resins**

Conventional alkyd resins are synthesized by mixing the appropriate amount of polyhydric alcohol, polycarboxylic acid (anhydride), and fatty acid or oil. Subsequently, a polycondensation reaction at an elevated temperature is carried out (usually at about 250°C), with the use of an appropriate catalyst, resulting in a polycondensate mixture with a relatively high polydispersity. This method is not directly applicable to carbohydrates such as sucrose and inulin because these carbohydrates decompose at such high temperatures, and are not easily miscible with fatty acid methyl esters or oils.

An alternative synthesis procedure was developed by dissolving (nonmodified or partially acetylated) sucrose or inulin in DMAA (*N,N*-dimethylacetamide), adding sunflower oil or methyl linoleate, and reacting the mixture at 140°C. Catalysts such as potassium carbonate or lithium hydroxide were found to be the most effective.

Derivatization of inulin with unsaturated fatty acid methyl esters or oils directly results in products with alkyd-type characteristics. In the case of sucrose, the use of renewable dicarboxylic acids (or polycarboxylic acids) is required in addition to sucrose and fatty acid methyl esters to synthesize oligomers. Examples of such renewable dicarboxylic acids are dimethyl suberate, dimethyl sebacate, or dimerized (un)saturated fatty acids. In the case of sucrose, these result in structures of alkyd resins, as shown in Fig. 4. This type of alkyd resin was synthesized by using either sucrose or sucrose acetate as the starting material.

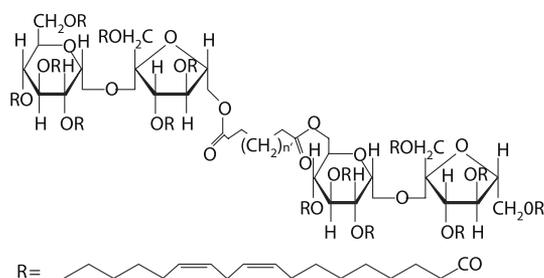


Fig. 4: Structure of an alkyd resin based on sucrose

### Characterization of alkyd resins

After synthesis and a work-up, the characteristics of the alkyd resins were determined by techniques such as nuclear magnetic resonance spectroscopy (NMR) and gel permeation chromatography (GPC). The hydroxyl value, acid value, and viscosity of the resins were also determined. Table 2 shows the characteristics of a typical sucrose-based alkyd resin at varying ratios of dimethyl adipate/methyl linoleate. Some effects of the type and amount of crosslinker on properties such as molecular weight, polydispersity, OH-value, and acid value were found, but from the limited data obtained, no clear relation could be established.

### Characteristics of paint formulations

Table 3 shows some favorable properties of the paint formulations derived from the sucrose-based alkyd resins such as fast through drying and also at lower temperatures, very good leveling, and good compatibility with (standard) color pastes. Gloss retention, determined via QUV/A measurements, can be regarded as an indication for durability. It was found that the gloss retention (see Fig. 5) of the best performing systems equals that of commercial systems suitable for outdoor applications.

In summary, it can be concluded that high-solid alkyd paints can be formulated containing the sucrose-based alkyd resins, and that the paints possess favorable properties. Given the attractive price of sucrose as a starting material, it might be expected that more

Table 3: Paint formulation containing a sucrose-based alkyd resin (OVN 299); methyl linoleate was used as the fatty acid component

Test	OVN-299	Commercial paint reference
Low shear viscosity (dPa·s)	9.4	
High shear viscosity (dPa·s)	4.8	
Solids content (% w/w)	80.2	
Solids content (% v/v)	65.3	
VOC (g/L)	262	
Specific weight (g/mL)	1.27	
Whiteness 1 day (Cie)	76.9	71.2
Whiteness 15 days (Cie)	78.0	73.0
Yellowing NH <sub>4</sub> OH ( $\Delta$ Cie)	77.9/48.4	72.5/50.9
Yellowing 5 days 50°C ( $\Delta$ Cie)	78.6/67.0	73.7/64.3
Yellowing 1 day 80°C ( $\Delta$ Cie)	78.5/54.6	73.4/55.8
Drying recorder 23°C/50% RH	+	0
Drying recorder 5°C/90% RH	0/+	0
Gloss 20°/60° 1 day	75.1/85.3	71.2/87.0
Gloss 20°/60° 15 days	62.1/80.5	47.2/78.4
Water sensitivity 15 days 1 h/8 h	+/-	+/+
Leveling	++	++
Hiding power	+	+
Paste compatibility (standard paste)	+	+
Wrinkling BA60	0	0
Elasticity (Erichsen mm)	7.5	7.7
König hardness 1 day(s)	16.6	12.6
König hardness 15 day(s)	22.4	25.2
Scratch resistance	-	+/-

solvent-free routes to sucrose-based alkyds will offer a commercial perspective.

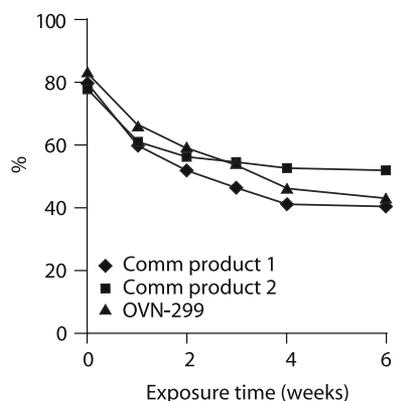
### Reactive diluents

High-solid alkyd resins completely based on renewable resources could result (except for pigments and fillers) in completely renewable-based paints, in which case the additives and solvents could also be based on renewable resources. Attractive solvents for high-solid alkyd paints consist of so-called reactive diluents: upon

Table 2: Influence of the ratio crosslinker dimethyladipate/methyl linoleate on the resin properties

Ratio dimethyl adipate/ methyl linoleate <sup>a</sup>	GPC analysis		Hydroxyl value	Acid value	Viscosity (dPa·s)
	Mn	Polydispersity			
2.4/5.6	$4.2 \times 10^3$	1.6	54	11	18
4.8/5.6	$7.7 \times 10^3$	6.9	41.8	9.6	123
5.6/5.2	$9.7 \times 10^3$	21.4	n.d.	3.2	56 (27% solvent)
7.0/4.5	$4.2 \times 10^3$			Gelation	

<sup>a</sup> Interesterification.



**Fig. 5: Gloss retention of a paint formulation containing a renewable resin as a function of exposure time (Gloss retention was established in a QUV-A cabinet according to ASTM G53; the paint film was applied on aluminum Q-panel, aged for 3 weeks under ambient conditions, and afterwards exposed to a cycle of 4 h of UV-A light and 4 h of condensation with demineralized water in the absence of UV-light. Gloss readings at an angle of 60° were monitored for 6 weeks)**

drying, these solvents react with the alkyd resins and therefore are nonvolatile.

Reactive diluents partly based on renewables have been described before. WO 97/02326, for example, discloses the use of octadienyl maleates, fumarates, and succinates as reactive diluents in high-solid paints.<sup>16</sup> EP 0 685 543 A2 describes the use of alkyl esters derived from the acid of an unsaturated vegetable oil in a coating composition containing an alkyd and a reactive diluent.<sup>17</sup>

Reactive diluents that are based on combinations of unsaturated fatty acids and carbohydrates, however, have not to our knowledge been systematically studied. Within the framework of the authors' research, they explored reactive diluents based on sorbitol, methylglucoside, sucrose, and 1-kestose.

All these components showed the properties of reactive diluents. The best performance was found for those reactive diluents that consisted of at least two saccharide units (e.g., sucrose). These reactive diluents had the best overall performance with regard to cutting behavior, compatibility with commercial binders and pastes, and drying performance. Their drying performance equals that of a commercial reactive diluent with a much higher molecular mass. Reactive diluents based on monosaccharides such as sorbitol or methylglucoside showed some negative influence on drying properties. Table 4 shows the behavior of a sucrose-based reactive diluent [sucrose octalinoleate (SOL)] in a commercial paint formulation.

The results of Table 5 demonstrate that the overall performance of the sucrose-based reactive diluent in the paint formulation is very comparable with that of a commercial reactive diluent with three times the molecular mass. Viscosity is a little lower and gloss

**Table 4: Test results of an alkyd-based paint formulation containing a sucrose-based reactive diluent and a commercial reference reactive diluent (RT = room temperature, RH = relative humidity). Water sensitivity, Leveling, Hiding power, Wrinkling and QUV-A are relative measurements with 0 = excellent performance and 5 = very poor performance**

Test	Formulation based on commercial reactive diluent	Formulation based on sucrose octalinoleate reactive diluent
Viscosity (dPa·s)	13.1	11.4
ICI-viscosity	6.8	6.6
Solids content (% w/w)	83.3	83.3
VOC (g/L)	222	222
Whiteness	73.0	72.2
Yellowing NH <sub>4</sub> OH	-29.9	-33.8
Yellowing 5 days 50°C	-12.6	-14.6
Yellowing 1 day 80°C	-8.75	-19.0
Drying recorder RT	0	0
Drying recorder 5°C/90% RH	0	0/-
Gloss	87.5	88.7
Water sensitivity 1 day	0	0
Leveling	1	1
Hiding power	1	1
Color strength	98.7	97.0
Wrinkling	0	0
QUV-A	0	0
Adhesion on old alkyd layers	Pass	Pass
Adhesion on bare spruce	Pass	Pass
Erichsen (mm)	8.6	8.3

somewhat higher compared with the paint formulation containing the commercial reference reactive diluent.

### Cobalt-free drying catalysts

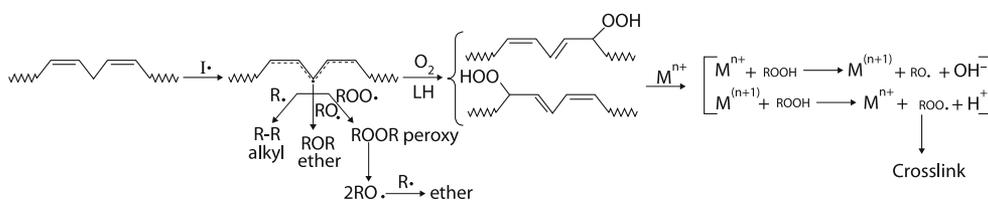
Next to volatile organic solvents, there are other environmental issues related with the use of alkyd-based paints. A quick drying of alkyd paints is of enormous commercial importance. Common solvent-borne alkyd paints contain, besides the main constituents, alkyd resins (binders), pigments and solvents, also small amounts of cobalt-based driers (e.g., cobalt-2-ethylhexanoate). The cobalt salts increase the oxidative crosslinking rate of the unsaturated fatty acids that are present as constituents of alkyd resins (see Fig. 6).

As a result of the fatty acid oxidation during air drying, hydroperoxides are formed. Their decomposition into free radicals, catalyzed by metal ions, gives rise to crosslinking reactions, leading to the hardening of the film. Despite their important role in the drying process of alkyd paints, cobalt driers, however, are potentially carcinogenic in aerosol form (shown in

**Table 5: The effect of incubation time on the Fe/IM/AsA6p systems as a drying catalyst for high gloss white paint based on Setal 16 LV WS 70 (Nuplex Resins)**

Drier	% of active drier	Incubation time (days)	Dust free drying (h)	Tack-free drying (h)	Total drying time (h)	Hardness (s/K) 5 days	Skin formation	Whiteness Index
Fe/IM/AsA6p 1/4/1	0.07 Fe	12	5.06	3.8	10.8	56	N.O.	80.6
Fe/IM/AsA6p 1/4/2	0.07 Fe	12	2.0	4.9	11.3	56.4	O.	80.8
Fe/IM/AsA6p 1/4/3	0.07 Fe	12	8.6	4.2	17.3	68.6	O.	81.5
Fe/IM/AsA6p 1/4/4	0.07 Fe	12	—	—	>20	59.7	N.O.	81.2
Co + Exkin 2	0.07 Co	12	3.3	4.2	14.1	73	N.O.	82.8
Mn	0.04 Mn	12	0.66	6	12.5	52	O.	83
Mn	0.07 Mn	12	0.66	4.76	9.9	51.3	O.	82.1
Fe/IM/AsA6p 1/4/1	0.07 Fe	18	0.7	2.66	4.5	73.6	N.O.	80.6
Fe/IM/AsA6p 1/4/2	0.07 Fe	18	0.63	0.43	2.2	80.6	O.	80.8
Fe/IM/AsA6p 1/4/3	0.07 Fe	18	0.6	1.53	5.8	85	O.	81.5
Fe/IM/AsA6p 1/4/4	0.07 Fe	18	1.16	1.53	6.6	80	N.O.	81.2
Co + Exkin 2	0.07 Co	12	3.3	4.23	14.1	73	N.O.	82.8
Mn	0.04 Mn	12	0.66	6	12.5	49	O.	83
Mn	0.07 Mn	12	0.66	4.76	9.9	51.3	O.	82.1

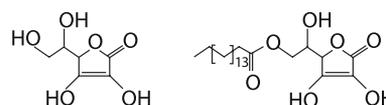
As Co-based catalyst Nuodex WEB 6 (obtained from Elementis, formerly Sasol Servo Delden) was used. NO = not observed. O = observed. Exkin; antiskinning agent.

**Fig. 6: Fatty acid oxidation by radical pathway and crosslinking reactions**

animal testing). Therefore, finding substitutes for this cobalt-based catalyst is of high importance to the alkyd-producing and using industry.

Several substitutes for cobalt-based drying agents are in development. Most of these are based on either manganese<sup>18</sup> or vanadium salts.<sup>19</sup> Manganese–bipyridine complexes have especially been promoted as alternatives.<sup>18</sup> Although these alternatives can be applied in specific systems, their overall performance does not match up to that of cobalt-based driers; the paint films usually remain too soft, and manganese can have a negative impact on the film color. Bipyridine is potentially harmful as well. More recent research has been carried out on other manganese-based catalysts.<sup>20,21</sup>

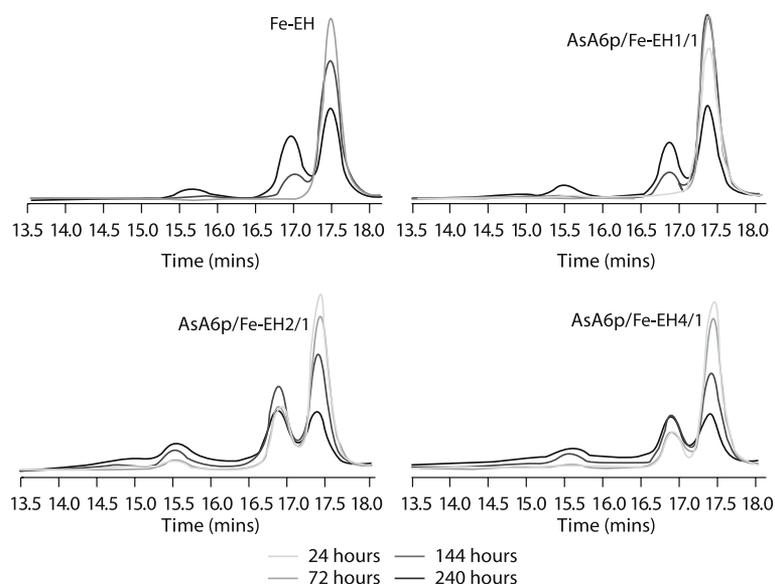
An innovative biomimetic approach was being followed to develop alternative cobalt-free drying catalysts using combinations of iron salts and reducing agents that are known to oxidize unsaturated fatty acids in nature. This concept has been translated and adopted for usage in both waterborne and solvent-based alkyd systems; the reducing agents evaluated in this study, namely ascorbic acid and ascorbylpalmitate, are both derived from renewable resources.

**Fig. 7: Structures of L-ascorbic acid (Asa) and 6-O-palmitoyl-L-ascorbic acid (AsA6p)**

The oxidative and crosslinking ability of iron salt combinations with reducing agents was studied for model systems consisting of either neat ethyl linoleate or methyl linoleate, in the case of diluted aqueous emulsions.<sup>22</sup> (See Fig. 7)

For both systems, it was found that the combination of iron salts and ascorbic acid palmitate (AsA6p) as the reducing agent was, depending on the ratio of iron to reducing agent, capable of generating hydroperoxides. In neat ethyl linoleate (EL), however, crosslinking is also induced<sup>23</sup> (see Fig. 8). Ascorbyl palmitate appeared to be more suitable than ascorbic acid, especially for nonaqueous systems.

From Fig. 8 it is clear that within the first 100 h, Fe-eh (Fe-ethylhexanoate) induces almost no crosslinking at

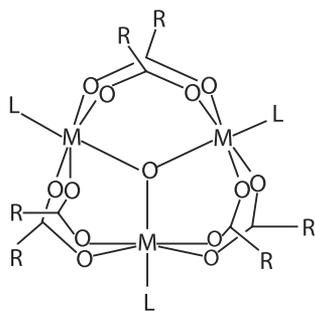


**Fig. 8:** Size exclusion chromatograph of ethyl linoleate (EL) at different periods of oxidation in the presence of various catalysts. Peak at retention time 17.5 min; EL, 17 min; ROOH + epoxy derivatives, 15.5 min; dimers, 15 min and lower; higher oligomers

all at room temperature, whereas most crosslinking occurs at an AsA6p/Fe-eh ratio of 2:1.

To understand better the mode of action of the Fe-based catalysts, both the structure of Fe-eh and that of the system formed upon addition of AsA6p were studied using a wide array of different techniques. Using ElectroSpray ionization mass spectrometry (ESI-MS), it was found<sup>24</sup> that Fe-eh, in solution, consists of trinuclear oxocentered Fe(III) clusters of formula  $[\text{Fe}(\text{III})_3(\mu_3\text{-O})(\text{eh})_6]^+$  (see Fig. 9). Mössbauer's studies revealed that the trinuclear iron was not symmetric as two equivalent Fe(III) sites and one unique Fe(III) site were identified. Upon addition of AsA6p to the Fe-eh complex, a new species was formed that was a mixed valence complex with a similar iron core.

Structural details of these complexes are not yet fully known and attempts to crystallize the complexes have so far failed. From NMR measurements it can



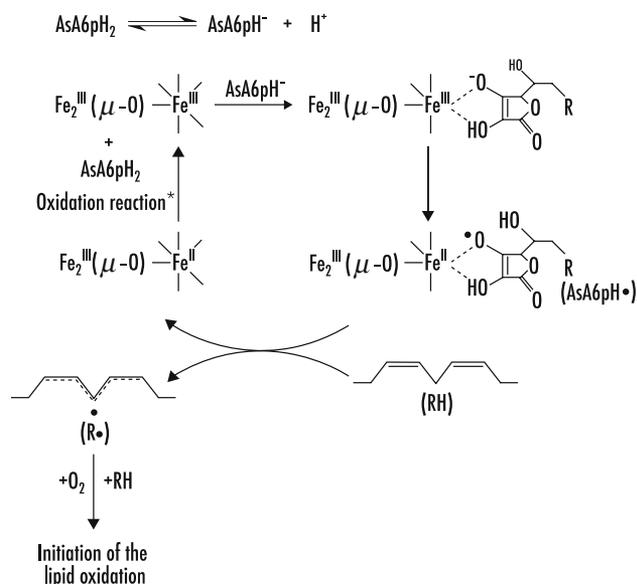
**Fig. 9:** General structure of the cluster unit  $[\text{M}_3\text{O}(\text{O}_2\text{CR})_6\text{L}_3]^{n+}$ ; M = metal ion; L = solvation molecule or free coordination site; R = carboxylate chain

nonetheless be concluded that the AsA6p most probably is coordinating to the iron via the C3 (and C4)-OH group of the AsA6p molecule. This enabled the authors to draw up a mechanism through which the combination AsA6p/Fe-eh most likely oxidizes unsaturated fatty acids such as ethyl linoleate (see Fig. 10). The ability of AsA6p to reduce Fe(III) to Fe(II) drives the catalytic cycle.

Besides model systems, the AsA6p/Fe-eh combination was also further evaluated in different waterborne and solventborne (commercial) varnish and paint formulations. From these evaluations, a rather complex pattern appears. The effectiveness of the Fe/AsA6p system as a drying catalyst was tested in a high gloss white paint based on Setal 16 LV WS-70 (linseed fatty acid-based alkyd resin) and good results were obtained. Results were further improved by the addition of Imidazole (Im) as a ligand.<sup>25</sup> The results in Table 6 show that the catalyst is not immediately effective after mixing iron and ascorbic acid palmitate, but that it needs some standing or incubation time after mixing to become active.

After an incubation time of 14 days, interestingly in the absence of auxiliary driers, the drying activity is higher than that of cobalt-based drying catalysts. Hardness development is comparable with cobalt and better than for manganese. Another very interesting feature is that the system, at various Fe/AsA6p ratios, does not show skin formation. This implies that the system will either not need antiskinning agents or will need much less than cobalt-based systems.

Similar results, with respect to drying time and hardness development, were found upon using a varnish based on Uralac AD 142 W-50 (based on



**Fig. 10: Proposed mechanism for the oxidation of ethyl linoleate by the AsA6p/Fe-eh combination; R = -OC(O)-C<sub>15</sub>H<sub>31</sub>; \*induced by oxygen or hydroperoxide decomposition reactions**

linseed oil). Very interesting results in regard to drying times and hardness development were also obtained using solventborne alkyd paints based on specially processed soy bean oil. As conventional solventborne alkyd paints will gradually be substituted by either high-solid alkyds or alkyd emulsions, these systems were also evaluated.

Few experiments so far have been carried out on high-solid paints, but the results show a less efficient drying than in the case of conventional alkyds. To date it is unknown whether this results from a decreased compatibility of the drier with these systems, from the different structure of the alkyd resins in such paints, or because of other factors.

For waterborne alkyd emulsions, the system was found to be very effective. It was found that the system could be made more effective with regard to the results previously obtained by additional water-soluble metal ion-coordinating ligands. This way, very short drying

times were obtained for Uradil AZ 554 Z-50 (based on special processed soy bean oil) emulsions (see Table 6).

From the results of Tables 5 and 6, it can be concluded that the combination of iron-ascorbic acid (palmitate), in the presence or absence of additional ligands, can be a powerful system for the drying of alkyd paints. Drying capacity is dependent on the ratio of Fe to ascorbic acid palmitate, and the drying capacity obtained so far is larger for specific systems (e.g., solvent-based or water-based alkyds containing special processed soy bean oil) than other systems (e.g., high solids). Hardness development is improved compared to manganese-based systems. More research will be needed to develop iron-based systems that are more widely applicable and also show effectiveness in high-solid systems.

### Conclusions

The results shown in this paper clearly indicate that both resins and additives for non or low-VOC paint formulations can be based on those raw materials that are the least disputed from an environmental point of view (i.e., renewable resources). High-solid paints based on alkyds containing sucrose—the world’s most produced pure chemical—with a performance equal to modern high-solid paints were obtained. Lower molecular-weight sucrose fatty esters were found to be excellent reactive diluents. It may be expected that sucrose-based alkyds will become highly attractive from a commercial point of view once effective synthesis procedures, starting from the free fatty acids or without the use of polar solvents, have been established.

Very promising results have also been obtained with regard to powder coating resins based on isosorbide. Further research is needed to determine and broaden the application scope.

With regard to renewable-based additives, the alternative iron-based catalysts demonstrate their potential for use in important types of alkyd paints. More research will be needed to broaden and fine tune their application scope.

**Table 6: Drying times of a DSM waterborne (WB) paint based on Uradil AZ 554 Z-50 (based on special processed soy bean oil)**

Catalyst		Drying stages		
Composition	Concentration (% Fe, w/w)	Basic trace (end; h)	Ripped film (end; h)	Surface trace (end; start total dry; h)
No catalyst		0.15	>10.7	
Nuodex WEB Co 6DP Cobalt-drier (225 μl)	0.08	0.17	1.1	>10.7
Fe[gluc] <sub>2</sub> [Hasc] <sub>1</sub>	0.04	0.15	0.23	4.6
Fe[EDTA] <sub>0.5</sub> [Hasc] <sub>1</sub>	0.04	0.17	0.23	4.0
Fe[citrate] <sub>0.67</sub> [Hasc] <sub>1</sub>	0.04	0.17	–	2.0

Given the continued interest in developing more sustainable technology and the fact that the prices of fossil feedstocks are destined to increase, the coming decades inevitably will see an increase in renewable-based coatings and paints components, combining economics with unique properties.

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