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Towards sustainability

Alkyd resins and alkyd drying agents based on renewable resources.

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Coatings based on undepletable, renewable resources are increasingly desirable. Alkyd resins based on inulin or sucrose and unsaturated fatty acids or oils, showed a low intrinsic viscosity, making them suitable to be used in high-solid alkyd paints. A new concept has been used to prepare effective, cobalt free, drying catalysts for both solvent and waterborne alkyd systems. Iron, in combination with ascorbic acid derivatives and optionally other ligands, was found to be a very effective drying catalyst.

Besides their aesthetic functions, paints and coatings aim to enhance the durability of a product. Moreover, nowadays sustainability of coatings is required as well. This asks for properties such as being solvent free, easy to apply and producing less waste. In this sense, coatings containing resins and additives based on renewable resources can make an important contribution to enhanced sustainability. Alkyd paints contain resins that are already partly based on renewable resources. Depending on their oil length these resins constitute approximately 50 to 80% weight of renewable (vegetable oil based) resources. Alkyd resin based paints are of utmost importance for the decorative coatings industry.

Environmental pressures

Traditionally, alkyd paints are organic solvent borne, using up to 50% of volatile organic solvents (VOC) in a paint formulation. Legislation aiming at reducing VOC levels is currently the driving force for coatings industry, especially for decorative paints. Manufacturers of solvent-borne paints have to respond to these forces, leading to basically three main options:

- Switch to water based systems, making use of other than alkyd technology
- Switch to water based alkyd systems
- Switch to high-solid systems containing less/no VOC.

Another environmental issue connected with the use of current alkyd resin based paints, is the use of cobalt based driers. Studies on mice and rats have shown that exposure to cobalt sulphate in aerosol form is related to the formation of cancer [1]. Consequently there is a move away from cobalt based driers towards more environmentally acceptable driers.

With regard to environmental and sustainability issues, renewable resources can be regarded as the most undisputed source for (raw) materials. Activities at the Agrotechnology & Food Innovations research institute aim at developing high-solid alkyd resins and cobalt free driers.

Synthesis of alkyd resins

Conventional alkyd resins are synthesised by mixing the appropriate amount of polyhydric alcohol, polycarboxylic acid and fatty acid/oil. Subsequently a polycondensation reaction at about 250 °C is carried out, resulting in a polycondensate mixture with a relatively high polydispersity. Suitable polycarboxylic acids include phthalic acid anhydride, terephthalic acid anhydride, trimellitic acid, adipic acid and maleic acid. Polyalcohols used in the alkyd synthesis include (di)pentaerythritol, glycerol, ethylene glycol, trimethylolpropane and neopentylglycol. The fatty acid or oil component is derived from renewable resources but the majority of the aforementioned polyacids and

polyalcohols are derived from petrochemical resources.

Conventional synthesis of alkyd resins leads to polymers with a rather high polydispersity. In these the higher molecular weight part contributes to a high intrinsic viscosity and the lower molecular weight part has a negative impact on drying properties. In order to obtain high-solid paints, it is important to reduce the intrinsic viscosity of the alkyd resin. This might be achieved by developing an alkyd oligomer with a suitable average molecular mass and a low polydispersity. Alkyd resins completely based on renewable resources have been the subject of a few studies [2,3,4,5].

Renewable resources for the polyhydric alcohol

Although this work mentions alkyd resins (partly) based on renewable resources, it is not specifically aimed at deriving high-solid alkyd paints based on resins with a low intrinsic viscosity. The development of alkyd resins with low intrinsic viscosity was the aim of a project with paint producer SigmaKalon. The potential of two types of renewable resources, sucrose and inulin, as the polyhydric alcohol part of alkyd resins was explored.

Inulin is an oligomer of (2>1)- β -D-fructofuranan with a terminal α -D-glucopyranosyl group (Figure 1). It is commercially produced from chicory or Jerusalem artichoke. Because of its oligomeric nature, inulin could substitute both the polyhydric alcohol and polycarboxylic acid parts of alkyd resins. Inulins with a polydispersity lower than 1.5 are commercially available.

Sucrose is a cheap, monodisperse, easily accessible disaccharide. It is commercially produced in millions of tonnes per year from sources such as sugar beet and sugar cane.

New resources require alternative synthesis methods

The conventional alkyd resin synthesis method is not directly applicable to carbohydrates such as sucrose and inulin as these carbohydrates decompose at such high temperature and furthermore are not easily miscible with fatty acid methyl esters or oils.

An alternative synthesis procedure was developed by dissolving (non-modified or partially acetylated) sucrose or inulin in N,N-dimethylacetamide, adding sunflower oil or methyl linoleate and reacting the mixture at 140 °C.

Derivatisation of inulin with unsaturated fatty acid methyl esters or oils results directly in products with alkyd type characteristics. In the case of sucrose, in order to synthesise oligomers, besides sucrose and fatty acid methyl esters, the addition of renewable dicarboxylic acids (or polycarboxylic acids) was also required. Examples of such renewable dicarboxylic acids are dimethyl adipate, dimethyl sebacate and dimethyl esters of dimerised unsaturated fatty acids.

In the case of sucrose this results in structures of alkyd resins as depicted (Figure 2).

Characteristics of alkyd resins

Characteristics of the alkyd resins were determined by techniques such as NMR and GPC. Hydroxyl value, acid value and viscosity of the resins of typical sucrose based alkyd resins are shown in Table 1 [6].

Characteristics of formulations based on renewable alkyds

The most promising binder systems were used to prepare paint formulations. The inulin esters exhibited a low polydispersity (1.2 - 1.3), favouring a low intrinsic viscosity. Drying times of the paints formulated on the renewable

inulin based alkyd resins [7] were comparable to commercial products. Wrinkling, elasticity, hardness and gloss were also comparable.

In an accelerated yellowing test (6 hours in NH_4OH), paints containing alkyd resins based on inulin tended to yellow more quickly than conventional alkyd resins. This, however, was probably related to the presence of small amounts of reducing sugars in the unreacted inulin. In the presence of NH_4OH this would lead to Maillard reactions and result in yellowing/browning. Water sensitivity, adhesion and gloss retention upon QUV-A weathering appeared to be strongly dependent on the hydroxyl value of the inulin esters; lower OH-values drastically improved these properties.

Characteristics of high-solid alkyd paint formulations containing sucrose based alkyd resins are shown in Table 2.

Sucrose-based paints have attractive properties

Paint formulations containing sucrose based alkyd resins showed very attractive properties [6], including fast (through) drying, very good levelling, good water resistance, good adhesion to wood and good hiding power. A minor disadvantage, which needs adaptation, was the tendency to have a relatively high viscosity at high shear rates. Furthermore, results of QUV-A tests showed that the gloss retention of paint formulations containing the sucrose-based alkyd resins is just as good as commercial products. This is a strong indication that alkyd paints containing sucrose-based alkyd resins will be as durable as conventional alkyd paints. In addition, there are interesting options for a price effective production for the sucrose based products.

Besides alkyd resins suitable for high-solid paints, effective reactive diluents completely based on renewable resources have also been prepared and evaluated [8].

Removing cobalt from the drying catalyst

A quick drying of alkyd paints is of enormous commercial importance. Common solvent borne alkyd paints, contain besides the main constituents alkyd resins, pigments and solvents, also small amounts of cobalt based driers (e.g. cobalt- ethylhexanoate). These cobalt salts increase the oxidative cross-linking rate of the unsaturated fatty acids, which are present as constituents of alkyd resins (Figure 3).

As a result of the fatty acid oxidation during air drying, hydroperoxides are formed. Their decomposition into free radicals, catalysed by metal ions, and subsequent cross-linking, contributes to the hardening of the film.

Cobalt based driers are facing environmental pressure and several substitutes are under development. Most of these are based on either manganese [9] or vanadium salts [10]. Manganese-bipyridine complexes have particularly been promoted [11]. Although these alternatives can be applied in specific systems, their overall performance does not yet match up to that of cobalt based driers; the paint films usually remain too soft and manganese has a negative impact on the film colour.

Biomimetic approach yields cobalt-free catalysts

At A&F, a biomimetic approach is being followed to develop alternative cobalt free drying catalysts [12]. Mechanisms by which - in vivo - unsaturated fatty acids are oxidised by the action of oxygen, iron and ascorbic acid, have been translated and adopted for both solvent borne and water borne alkyds.

After verifying the principle by studying aqueous emulsions of methyl linoleate more real water borne and solvent borne paint systems were evaluated. Ascorbic acid (AsA) and 6-O-palmitoyl-L-ascorbic acid (AsA6p) have been used as reducing agents. The latter derivative is more compatible

with the alkyds after evaporation of the solvents.

Iron based catalysts, at different Fe/AsA6p ratios, were tested at their ability to serve as driers in varnishes and complete paints formulations. 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; Table 3). Even in the absence of auxiliary driers, the drying activity was higher than that of cobalt based drying catalysts.

Hardness development was comparable to cobalt and better than for manganese. Another very interesting feature is that the system, at a Fe/AsA6p 1:1 ratio, does not show skin formation. This implies that the system will probably need less antiskinning agents than cobalt based systems.

Iron drier is also effective in waterborne alkyd emulsions

As a result of more stringent VOC regulations, water borne alkyd emulsions will increase in importance coming years. Therefore the iron based catalyst system was also evaluated in an alkyd emulsion (Table 4).

Results indicate that the Fe/AsA6p system is also an effective drier for a water borne alkyd emulsion. An effective drying could be obtained at iron concentrations as low as 0.04% weight. Further results (not shown) demonstrated that addition of Imidazole as a ligand for the iron, even further enhances the drying capacity of the iron/ascorbic acid palmitate based system in a Setal 16 LV WS 70 paint system.

Hardness development was improved compared to manganese based systems. Colour formation is less than in case of manganese but this might be solved by choosing an appropriate ligand or reducing the amount of iron in the system.

A confocal Raman spectroscopy study on short oil-based alkyd films showed the change in intensity of C=C double bonds as function of time throughout the layer of films (Figure 4). Striking is the enhanced activity of the iron/AsA6p driers in the deeper layers of the film (improved through drying), with respect to the conventional cobalt catalyst.

Ongoing studies indicate that complex formation between iron and AsA6p is taking place, an iron-AsA6p 1:2 complex probably being the catalytically most active species. Further results indicate a slightly different mechanistic pathway and byproduct formation for iron than in the case of cobalt.

An important contribution

Both resins and driers for alkyd paints can be based on raw materials which are the least disputed from an environmental point of view. After further R&D work, both high-solid or water borne alkyd paints based on renewables therefore can make an important contribution to a sustainable decorative coatings industry.

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Results at a glance

- Paint formulations based on inulin esters had a low intrinsic viscosity. Drying times, wrinkling, elasticity, hardness and gloss of the paints were comparable to commercial products.
- Paint formulations containing sucrose based alkyd resins showed very attractive properties, including fast (through) drying, very good levelling, good waterfastness, good adhesion to wood and good hiding power. A minor disadvantage was the tendency to have a relatively high viscosity at high shear rates.
- A Fe/AsA6p system in a High Gloss White paint was not immediately effective as a drying agent but, after an incubation time of 14 days, its drying activity was higher than that of cobalt based drying catalysts.
- The Fe/AsA6p system was also an effective drier for a water borne alkyd emulsion. An effective drying could be obtained at iron concentrations as low as 0.04% weight.

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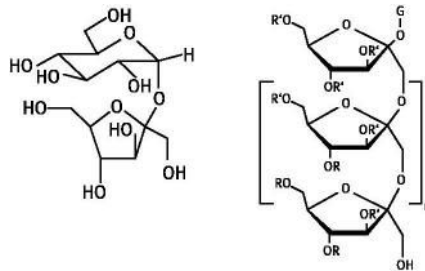


Figure 1: Structures of sucrose (left) and inulin (right)

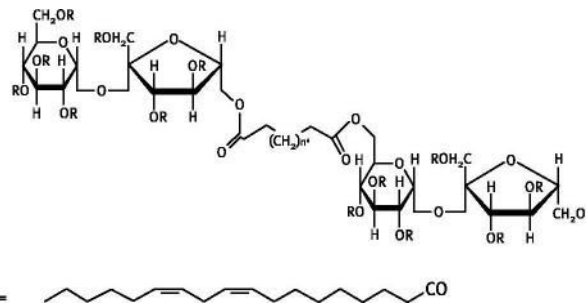


Figure 2: Structure of an alkyd resin based on sucrose and methylololeate

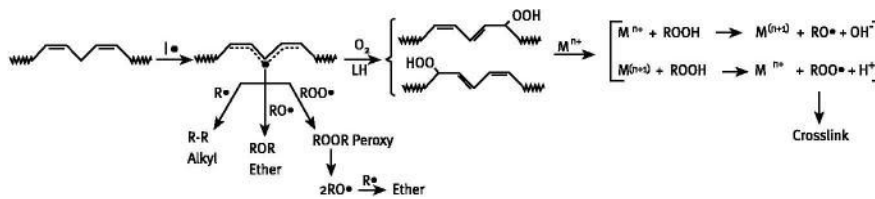
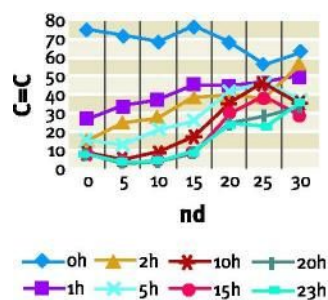


Figure 3: Unsaturated fatty acid oxidation in alkyds by radical pathway and crosslinking reactions



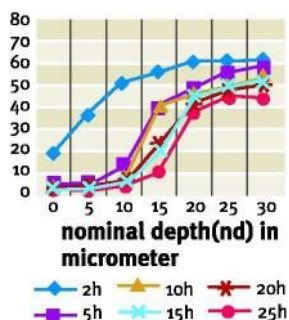


Figure 4 (a-b): Intensity of C=C peaks versus thickness of short oil-based alkyd films determined by confocal Raman spectroscopy at 1 h time intervals

Table 1: Influence of the type of chain extender on sucrose based resin properties

Dimethyl ester	Equiv. Methylinoleate	GPC-Analysis M_n	Polydispersity	OH value	Acid value	Viscosity (dPa.s)	
Adipate	4.8 equiv.	6.0 equiv.	6.8×10^3	3.8	68.2	7.8	51 (10% solvent)
Azelate	3.0 equiv.	6.0 equiv.	5.4×10^3	2.9	45.8	0.9	62.5
Sebacate	3.0 equiv.	6.0 equiv.	4.2×10^3	1.9	59.8	1.4	55
Pripol 1017	2.0 equiv.	6.0 equiv.	4.9×10^3	2.1	64.4	4.2	58 (15% solvent)

Table 2: Paint formulations containing sucrose based alkyd resins; methylinoleate was used as the fatty acid component

Test	OVN-227	OVN-228	OVN-231	Comm. product
Low shear viscosity (dPa.s)	14.0	14.0	13.8	
High shear viscosity (dPa.s)	9.8	> 10	9.6	4.6
Solids (%)	89.6	93.7	85.7	80.5
VOC (g/l)	134	83	180	260
Whiteness	77.1	75.4	74.8	76.5
Drying (RT; 50% RV)	+	+	+	+
Drying (5°C; 90% RV)	+	+	+	+
Gloss	98.8	88.9	83.5	85.9
Water sensitivity (4 days) ³⁾	0	0	0	0
Levelling ³⁾	0 - 1	0 - 1	0 - 1	1 - 2
Hiding power ³⁾	1	1	1	1

**Table 3: The Fe/AsA6p system as a drying catalyst for a high gloss white paint based on "Setal 16 LV WS-70".
As Co-based catalyst "Nuodex WEB 6" was used**

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/AsA6p 1/1	0,07 Fe	14	0.6	2.0	8.8	76	N.O.	80.2
Fe/AsA6p 1/2	0,07 Fe	14	0.7	1.8	10.0	69	O.	80.3
Fe/AsA6p 1/3	0,07 Fe	14	0.8	0.7	7.0	74	O.	80.1
Fe/AsA6p 1/4	0,07 Fe	14	2.1	0.9	6.6	68	O.	80.0
Co + Exkin 2	0.07 Co	14	3.3	4.2	14.1	73	N.O.	82.8
Mn	0.04 Mn	12	0.7	6.0	12.5	52	O.	83
Mn	0.07 Mn	12	0.7	4.8	9.9	51	O.	82.1

Table 4: Results obtained with DSM alkyd emulsion "Uradil AZ 554-Z-50" (medium oil alkyd emulsion based on soybean fatty acids). A Co catalyst containing no auxiliary driers was used

Drier	% of active drier	Total drying time (h)	Hardness (s/K) 24 h	Colour L*	A*	B*
Fe/EH/AsA6p 1/2/1	0.08 Fe	3	30.3	96.5	0.1	5.3
Fe/EH/AsA6p 1/2/1	0.04 Fe	4.5	26.1	96.6	0.0	4.9
Fe/EH/AsA6p 1/2/1	0.016 Fe	6.2	25.7	96.7	0.0	5.0
Fe/EH 1/2	0.017 Fe	»24	27.5	96.9	0.1	4.8
Fe/EH 1/2	0.008 Fe	»24	18.5	96.6	0.1	4.8
	0.0 Fe	»24	--	--	--	--
	0.06 Co	»24	42	96.4	0.0	4.3

1) Low shear viscosity was measured with a "Haake VT 500" viscometer using a cylindrically shaped E30 spindle at a rotation speed of 179 rpm and at 23 °C ; 2) High shear viscosity was measured in accordance with the ICI cone & plate method (ASTM D 4287) at a shear rate of 20.000 s⁻¹; 3) 0 = excellent performance, 5= very poor