Routes to VOC-compliant alkyd coatings

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Alkyd resins are typically produced by the condensation polymerisation of natural oils or fatty acids with polyhydric alcohols such as pentaerythritol, glycerol or trimethylolpropane, and dibasic acids such as phthalic anhydride and isophthalic acid. Since natural oils and fatty acids are renewable raw materials and polyhydric alcohols can be produced fully or partly from renewable raw materials, alkyd resins represent a very 'green' binder selection compared with acrylic binders, whose building blocks are currently derived from mineral oil.

Pentaerythritol can easily be made from renewable resources, as it is made from the aldehydes of methanol and ethanol (see Figure 1). The main environmental problem with alkyd resins is therefore that they are typically used in diluted form in organic solvents.

Organic solvents can be hazardous at many levels, both locally during the manufacture of the solvent and paint, and when the paint is applied and dried. Globally, volatile solvents can cause harm to the environment in the form of ozone depletion. It is therefore very important to minimise the use of volatile content in coatings. Such a shift of technology is also enforced in the EU countries by the provisions of the VOC (or 'Decopaint') directive. These provisions limit the amount of solvents that can be used in various decorative paints. The limits for different applications are given in Table 1.

The suggested routes to VOC-compliant coatings, high-solids resins and alkyd emulsions, present a number of technical challenges such as drying performance, final hardness or solvent resistance. Some findings are presented from work aimed at improving the properties of resins for these applications by the use of technologies such as:

- molecularly tailored resins;
- reactive surfactants for internal stabilisation;
- urethane alkyd emulsions;
- alkyd-acrylic hybrids.

Examples of resin formulation and paint performance are given.

High-solids alkyds – molecular engineering

High-solids alkyds are reported to have been produced by various methods, for example by using special molecular design and reactive diluents. The classical method is to reduce the molecular weight and/or increase the oil length, but this will give inferior coating properties.

Over the years, many reactive diluents have been proposed but have had limited success because they have not met performance requirements or because of environmental considerations. Reactive diluents based on allyl ethers, for example, are unsuitable for oxidative drying alkyds due to the emission of acrolein.

Linear polymers create viscous products through chain entanglement, and the viscosity rises smoothly in proportion to their molecular weight, according to the Mark-Houwink equation (see Figure 2 and Equation 1).

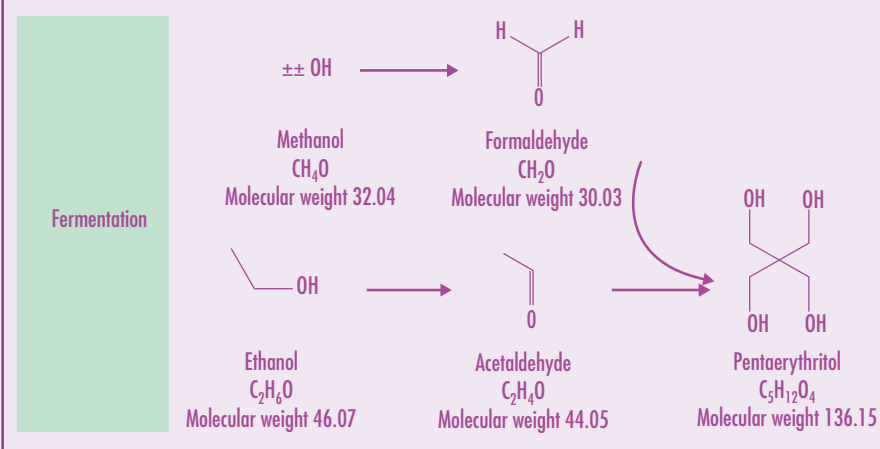Figure 1: Biochemical route to pentaerythritol

Fermentation

Methanol CH_4O Molecular weight 32.04

Formaldehyde CH_2O Molecular weight 30.03

Ethanol C_2H_6O Molecular weight 46.07

Acetaldehyde C_2H_4O Molecular weight 44.05

Pentaerythritol $C_5H_{12}O_4$ Molecular weight 136.15

Table 1: Selected provisions of the EU VOC directive

Product subcategory		Type	Phase I (g/l) (from 1.1.2007)	Phase II (g/l) (from 1.1.2010)
A	Interior matt walls and ceilings (Gloss ≤25@60°)	WB	75	30
		SB	400	30
B	Interior gloss walls and ceilings (Gloss >25@60°)	WB	150	100
		SB	400	100
C	Exterior walls of mineral substrate	WB	75	40
		SB	450	430
D	Interior/exterior trim and cladding paints for wood and metal	WB	150	130
		SB	400	300
E	Interior/exterior trim varnishes and wood stains, including opaque wood stains	WB	150	130
		SB	500	400
F	Interior and exterior minimal build wood stains	WB	150	130
		SB	700	700

$$[\eta] = K*[Mw]^a \qquad \text{Equation 1}$$

Where η = viscosity, K is a constant and MW the molecular weight.

Hyperbranched and dendritic polymers deviate from this proportionality and have a lower viscosity than anticipated at higher molecular weights due to reduced entanglement and a low hydrodynamic volume.

The viscosity of an alkyd resin is also a function of free volume availability. The free volume of a material is the sum of the spaces or holes that exist between the molecules of a material resulting from the impact of one molecule or one molecule segment striking another. These holes open and close as the molecule vibrates.

At temperatures above the glass-transition temperature (T_g), the holes are large enough and last long enough for molecules or molecular segments to move into them, resulting in a low viscosity. Free volume increases as the temperature increases, and the rate of volume increase is higher above the T_g or if a solvent is used.[1]

Alkyds made from glycerol are very linear in nature and it is difficult to build up high molecular weights with oil lengths suitable for decorative paints so as to provide high levels of coating properties. This is overcome by using a higher functional polyalcohol such as pentaerythritol. These penta alkyds have improved drying and coating properties, but their viscosity increases due to their higher molecular weight and broad molecular weight distribution.

One option for designing a high-solids alkyd involves, for instance, replacing pentaerythritol with di-pentaerythritol (di-penta). Di-penta is a unique polyol with a high functionality, six primary hydroxyl groups, and with good heat and UV stability. The highly branched, dense structure of di-penta facilitates the formulation of alkyds with high solids content in combination with good drying characteristics.

Another option is to use the hydroxylic acid dimethylol propionic acid (Bis-MPA) that will self-condense to produce branched structures with a lower viscosity at the same molecular weight compared with more linearly formulated counterparts.

The example in Table 2 shows a pure aliphatic alkyd, but partial application of this technique could also be considered in normal formulations. The second approach

Figure 2: Viscosity of dendrimers departs from the Mark-Houwink equation at high molecular weights
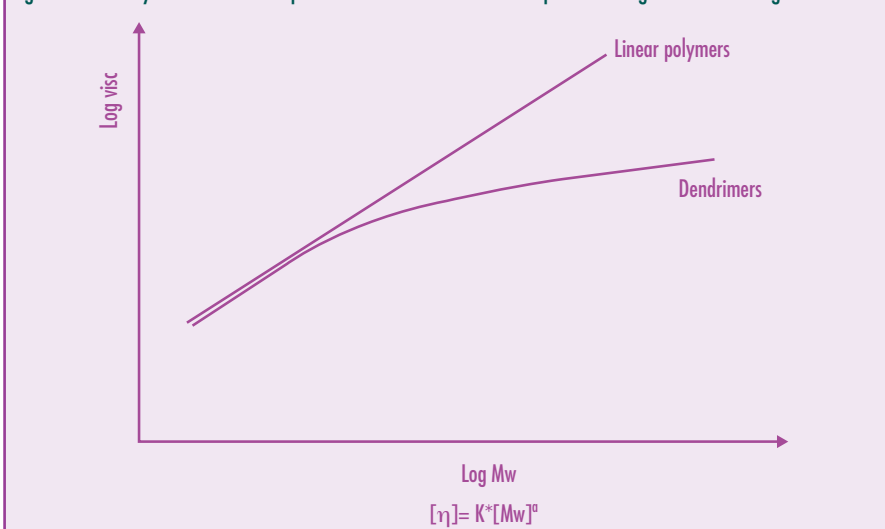
Log visc

Linear polymers

Dendrimers

Log Mw

$$[\eta] = K*[Mw]^a$$

Table 2: Bis-MPA, di-penta and 'concept' alkyd formulations

Ingredient	Standard alkyd	Bis-MPA alkyd	Di-penta alkyd	Concept alkyd
Tall oil fatty acid	62.20	69.91	62.25	75.04
Phthalic anhydride	23.88	–	14.13	9.89
Pentaerythritol mono grade	20.42	–	–	
Di-pentaerythritol	–	–	21.84	16.62
Benzoic acid	–	–	8.38	
Bis-MPA	–	39.56	–	4.48
Total charge	106.50	109.47	106.60	106.03
Water of reaction (g)	6.50	9.47	6.60	6.03

can be taken to an even higher level to produce hyperbranched alkyds in which most of the molecular weight is contained within the globular structure of the molecule (see Figure 3).

In practice, such a hyper-branched alkyd can be made by modifying the commercial hyperbranched product Boltorn H20 with fatty acids. Such a product is available as Boltorn U3000. In Table 2, alkyd formulations are presented where di-penta and bis-MPA replace penta and other alkyd components to produce high-solid alkyds.
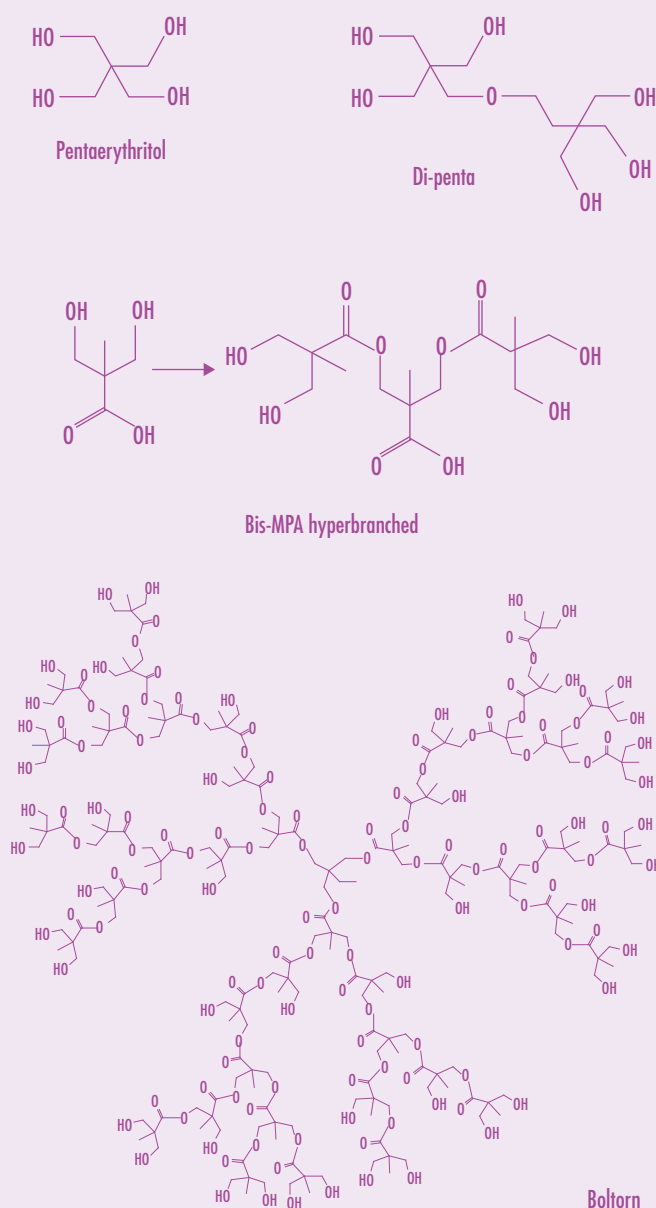
Alkyd synthesis

Except for the standard alkyd, which was produced by the fusion process, the alkyd syntheses were carried out according to the standard alkyd process at 240°C, with xylene as the azeotropic solvent, which was ultimately distilled off in a vacuum. Calculated and measured characteristics of the alkyds are given in Table 3. From the table, it is clear that alkyds with very low viscosity can be obtained by using speciality polymers in alkyd formulations.

Paint and paint performance

The alkyds shown in Table 3 were used in different white high-gloss paint formulations, as shown in Table 4. However, the di-penta alkyd has so far only been evaluated as a clear coat. The paints were then evaluated for drying performance and gloss. The di-penta alkyd and the hyperbranched version met the VOC requirement for 300g/l max for trim paints.

The paint performance study is also presented in Table 4 and shows that high-gloss paints can be formulated using bis-MPA, di-penta or Boltorn alkyds. In all of these cases, the paints are softer than the comparable alkyd, but gloss hold-out on weathering was better on the bis-MPA and the Boltorn alkyds than the standard. The di-penta alkyd exhibited very good drying and hardness development, closer to the standard alkyd, although still only measured as a clear coat.

Figure 3: Some molecules that will yield branching and dense structures

Pentaerythritol

Di-penta

Bis-MPA hyperbranched

Boltorn

High-solids alkyds – reactive diluents

The findings above indicate that it is possible to produce alkyds having very low viscosity with a low solvent content. The hyperbranched alkyds can be used as reactive diluents in a standard alkyd to meet the VOC requirement regarding trim paints. However, due to their aliphatic nature, they create soft films, which is why some applications definitely require different formulations to meet the requirements. Can it be possible to design an alkyd giving fast drying, hard films and low viscosity when mixed with a standard alkyd?

One possible method of improving hardness and physical drying might be to incorporate hard segments with a reasonable T_g shielded by softer segments and still maintaining a high molecular weight (see Figure 4). The shielding is necessary to provide the low viscosity, while the architecture itself must allow for a free volume sufficient to give a reasonable application viscosity.

One approach involves the combined use of di-penta and bis-MPA in the same alkyd. By applying a smart molecular design and

step-by-step synthesis, where the di-penta is partly fatty acid-functionalised and the bis-MPA is used to make hard segments that are primarily linearly spaced, together with phthalic anhydride between the partly fatty acid-functionalised di-penta molecules, a low viscosity resin is produced that is very well suited for use as a diluter for high-solids resins. The formulation of such a resin is presented as the 'concept alkyd' in Table 2.

Alkyd synthesis

The alkyd synthesis was carried out according to the normal method for alkyds, with xylene as the azeotropic solvent. For the concept alkyd, the reaction was carried out in three steps. In the first step, the fatty acid was reacted with the di-penta to an acid number of 3mg KOH/g at 220°C. Phthalic anhydride was added in a second step and reacted at 160°C, then held until the anhydride ring opened on the core ester.

In a third step, the bis-MPA was reacted in portions at 160°C. The alkyd was then run at 200 to 210°C until the desired acid number was reached. The low reaction temperature was chosen to minimise the reaction of the tertiary carboxyl group of bis-MPA. Calculated and measured characteristics of the concept alkyd are given in Table 3. From the table, it is clear that an alkyd with very low viscosity can be obtained.

Lacquers and lacquer performance

Lacquers were produced from the standard alkyd in Table 2 and the concept alkyd, and as a resin mix where the concept alkyd and the standard alkyd were mixed. The lacquers were formulated to have the same viscosity. As shown in Table 5, the VOC of the diluted resin was considerably lower than that of the standard alkyd and met the requirement for category D in the VOC directive for 300g/l max.

Lacquer performance is shown in Table 5, which reveals that drying was just as good in the diluted alkyd as in the standard. It is our belief that this concept could be used with many conventional alkyds and it could, as such, act as a good tool for resin producers for producing binders suitable for paints that comply with the requirements for 2010.

Alkyd emulsions

Although high-solids alkyds may be used to make VOC-compliant alkyd coatings, these will, in most cases, still contain solvents. A switch from diluting with solvents to diluting with water might therefore be an even better solution from an environmental standpoint. Alkyd emulsions can be made using no, or virtually no, solvents.

A frequently recommended method for producing alkyd emulsions is the inversion process in which water is added to the alkyd until a critical volume concentration of water is reached, and a phase transfer from a water-in-oil emulsion to an oil-in-water emulsion takes place (see Figure 5).

In the emulsification processes, the alkyd droplets formed have to be stabilised by some means. This can typically be achieved using external emulsifiers (surfactants) or incorporating internal stabilising groups in the polymer chain. Examples of these are polyethylene oxide chains or ionisable groups such as carboxyl groups from trimellitic anhydride (TMA) or dimethylol propionic acid (bis-MPA). A combination of non-ionic polyethylene chains and anionic stabilising moieties is also possible.

All techniques have their benefits and drawbacks. When using external emulsifiers, there is a risk of surfactant migration within the finished film, causing surface defects such as poor gloss, tackiness or whitening due to water absorption. Migration of molecules can be reduced or avoided by choosing to incorporate internal stabilising groups, but this type of stabilisation requires extra steps during alkyd synthesis.

It has been explained elsewhere how such an internally stabilised alkyd emulsion can be produced to make high-gloss paints by first creating an adduct between TMA and MPEG.[2] These paints were rather soft due to the relatively high number of hydrophilic ethoxylate chains needed to provide the emulsion stability. Although having high water resistance, they did not have a high chemical resistance, which is why some applications could be more difficult to address with such resins. It is therefore of interest to show how internally stabilised alkyd emulsions can be improved in respect of their hardness and chemical resistance.

In solvent-borne alkyd coatings, small quantities of isocyanates are often used to improve the chemical and outdoor resistance of the alkyd. This kind of

modification can also be applied to an alkyd emulsion, although the high viscosities of these resins make the synthesis and emulsification of the resins somewhat tricky.

Another way to improve alkyd emulsions may involve the addition of small quantities of acrylic dispersions to produce physical blends. This modification will affect properties such as hardness and drying speed in particular.

Emulsifiable alkyd resins

In Table 6, the alkyd formulations of two internally stabilised alkyds are given: one without urethane modification and one

Table 3: Characterisation of the bis-MPA, di-Penta, Boltorn and 'concept' alkyds

	Standard alkyd	Bis-MPA alkyd	Di-Penta alkyd	Boltorn alkyd	Concept alkyd
Calculated					
Oil length	65	73	65	75	78.4
Acid number (mg KOH/g)	9	7	8	10	15 (15.7*)
Hydroxyl number (mg KOH/g)	43	36	30	15	32 (35*)
Mw (g/mole)	20422	8016	20739	6500	3945
Measured					
Viscosity (23°C) 100% by wt (mPas)	–	780	42000	1200	2690
Viscosity (23°C) 60% by wt (white spirit) (mPas)	5200	–	–	–	
Colour (Gardner)	6	8	9	7	8
*Experimentally determined value					

Table 4: Paint compositions and basic properties of bis-MPA, di-penta and Boltorn alkyds

Ingredients and test procedures	Standard alkyd	Bis-MPA alkyd	Di-Penta alkyd	Boltorn alkyd
Standard alkyd 60%	57.36	–	–	–
Bis-MPA alkyd 100%	–	51.04	–	–
Di-penta alkyd 100%	–	–	71.21	–
Boltorn alkyd	–	–	–	50.54
TiO2	26.90	41.47	–	40.42
Zr-Octoate, 12%	0.84	1.05	1.45	1.05
Co-octoate, 12%	0.24	0.3	0.35	0.30
Ca-octoate, 10%	0.40	0.84	0.70	0.27
Exkin 2	0.30	0.27	0.09	–
Fungicide	0.30	1.38	–	–
White spirit	13.66	–	–	–
Exxsol D40	–	3.65	26.20	7.42
Total	**100**	**100**	**–**	**100**
PVC	17%	16%	0%	17%
Viscosity, cone and plate (25°C) (mPas s)	350	380	500	350
Viscosity (23°C) DIN-cup 4 (sec)	–	–	–	–
Calculated VOC (g/l)	430	74	265	119
König pendulum hardness				
1 day	24	43	22	43
7 days	56	23	35	42
1 to 6 months	104	23	69	35
Initial gloss at 60°	90	87	NA	82
Dry film thickness (µm)	25	25	25	45

Figure 4: Concept of using a reactive diluent to combine high and low Tg segments in a molecule

High T$_g$ segment

Low T$_g$

Table 6: Formulations of alkyds for emulsification		
Ingredients	Internally stabilised alkyd	Internally stabilised urethane alkyd
Step one		
Benzoic acid	3.4	3.69
Pentaerythritol	21	23.36
Phthalic anhydride	23.46	12.5
Tall oil fatty acid	58.19	65.16
Acid number (mg KOH/g)	30	30
OH-value (mg KOH/g)	69.1	177
Calculated Mw (g/mol)	2024	709
Step two		
Dispersing adduct	11.26	10
Acid number (mg KOH/g)	20	<5
OH-value (mg KOH/g)	43.7	124
Calculated Mw (g/mol)	4648	1406
Step three		
Isophorone diisocyanate	–	11.04

with. In both alkyds, an adduct of trimellitic anhydride (TMA) and mono-methyl ether of a polyethylene glycol (MPEG 750) are used to incorporate pendant MPEG chains into the alkyd resin.

Adduct and alkyd synthesis

The adduct was prepared by reacting TMA and MPEG 750 in a molar ratio of 1.05:1 at 170°C for five hours, purely to open the anhydride ring. GPC (gel permeation chromatography) characterisations of the resulting adduct show that single MPEG 750 substitution on the TMA molecule was the most frequent substitution. Triple substitution was not observed.

The alkyd synthesis of the internally stabilised alkyd was performed by a fusion process. All step one components were added to the reactor and condensation took place at 230 to 240°C. When the acid number reached around 30mg KOH/g, the reactor was cooled to 180°C prior to adding the dispersing adduct, which was reacted into the resins at 215°C.

In the case of the unmodified alkyd, the reactor was maintained at 215°C until the desired acid number of 20mg KOH/g was reached. In the case of the urethane alkyd, the resin was reacted to an acid number below 5mg KOH/g prior to cooling it to 80°C. At that temperature, the isocyanate was added drop-wise and the reactor was maintained at 80°C until titration of the urethane content showed that the reaction

Table 5: Lacquer formulations and basic properties, including 'concept alkyd'			
Lacquer formulation	Standard alkyd	Diluted alkyd	Concept alkyd
Standard alkyd resin, 75% in white spirit	100	60	–
Concept alkyd, 100%	–	40	100
Co-octoate, 10%	0.46	0.52	0.6
Zr-Octoate, 12%	1.56	1.78	2.08
Ca-octoate, 10%	0.76	0.86	1
Exkin 2	0.14	0.12	0.12
Aromatic-free white spirit	29.8	22.08	20.38
Lacquer characteristics			
Non-volatile content, %	56.9	68.11	80.4
Viscosity, 25°C, mPas	480	480	490
Calculated VOC, g/l	391	295	178
König pendulum hardness			
1 day	14	20	18
7 days	33	42	20
14 days	53	54	28
28 days	74	65	31
49 days	88	74	40
Dry film thickness (µm)	40	40	40

Table 7: Characterisation of the alkyds prepared for emulsification

Properties	Internally stabilised alkyd	Internally stabilised urethane alkyd
Calculated properties		
Oil length (%)	55	57
Acid number (mg KOH/g)	20	0
Hydroxyl number (mg KOH/g)	44	66
Mw (g/mole)	4649	4369
Measured properties		
Acid Number (mg KOH/g)	20.4	3.1
OH-value (mg KOH/g)	44	70
Mw	16756	12500
Mn	2221	3289
Polydispersity	7.54	3.8
Viscosity (125°C) 100% by wt (mPas)	460	894
Colour (Gardner)	7.0	7.6

Figure 5: Schematic representation of the emulsion inversion process

A = alkyd
B = water droplets in oil (alkyd)
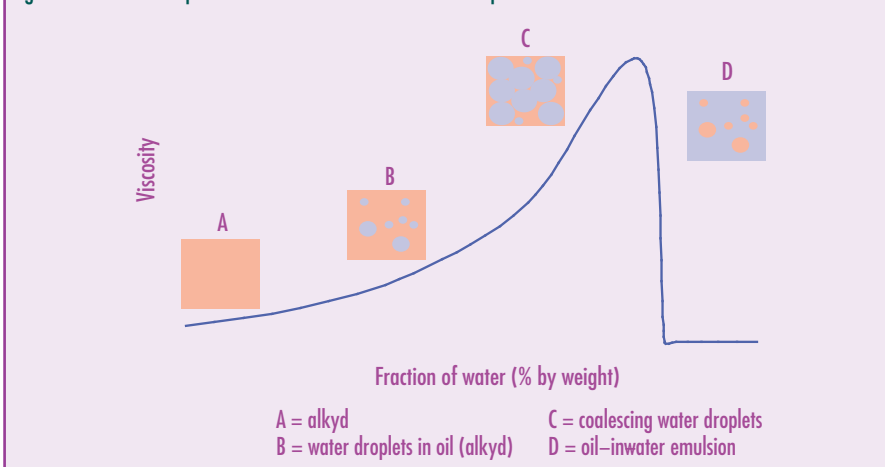C = coalescing water droplets
D = oil–inwater emulsion

Table 8: Alkyd emulsion lacquer formulations and characteristics

Formulation	Internally stabilised alkyd – emulsion	Internally stabilised urethane alkyd – emulsion
Alkyd	49.6	49
Anionic surfactant	0.3	1
Defoamer	0.5	–
Water	49.6	50
Total	100	100
Storage stability, 1 week at 50°C	OK	OK
Droplet size D(0.5) (µm)	0.8	1.1
Viscosity (23°C) (mPa s)	49	85
König pendulum hardness		
1 day	11	11
7 days	13	17
14 days	15	24
21 days	17	38
28 days	18	47
Spot testing resistance		
Water 6 hours	4	4
Water 6 hours, recovered	5	5
EtOH (48%), 30 min	1	3
EtOH (48%), 30 min, recovered	5	5

was finished. Characteristics of the alkyds are shown in Table 7.

Alkyd emulsification

Alkyd emulsions were prepared using the phase inversion process in which water is added progressively to the molten resin containing emulsifiers. A water-in-oil emulsion is formed initially which, at a critical solids content, will phase reverse forming an oil-in-water emulsion. The formulations for the alkyd emulsions produced are presented in Table 8.

Some external anionic emulsifiers were added to both emulsions because they would otherwise rely only on non-ionic stabilisation. It is generally accepted that anionic and non-ionic stabilisation should be combined for best overall performance. The alkyd emulsion characteristics are also indicated in Table 8, showing good stability, low viscosity and a reasonably low droplet size.

Lacquer performance

To the alkyd emulsions was added 1.5% by weight of the combination drier Additol VXW. Coatings were drawn down on glass using a 150µm applicator, and hardness development and covered spot resistance were tested. The hardness development shown in Table 8 reveals that the urethane-modified coating developed hardness much faster than the unmodified coating, and its ultimate hardness was also higher.

Water and chemical resistance were measured by covered spot testing on films applied to glass panels after four weeks at 23°C, 50% relative humidity, and for a dry film thickness of approximately 50µm. In Table 8 the resistance values are also presented, using the following grading scale:

5 = no visible change;

4 = minor variation in gloss or barely visible marks;

3 = weak mark;

2 = substantial mark;

1 = the structure of the surface has changed or has been partly or complete removed.

From the table it is clear that the urethane modification gave better ethanol resistance and it may be of interest to find a further application for this improved chemical resistance.

Alkyd-acrylic hybrids

Acrylic emulsions are widely used in coatings due to properties such as high hardness, fast drying and good gloss hold-

out on weathering. However, acrylics cannot always match the performance of alkyds in terms of open time, self-priming and the chemical resistance deriving from the oxidative cross-linking of the fatty acid component in the alkyd. Cost is also a factor, the alkyd being typically cheaper than the acrylics.

Alkyds and acrylics can be combined to make so-called hybrids. There are several ways to make these hybrids such as polymerising the acrylic in the alkyd emulsion, emulsifying the alkyd in the acrylic, or by simply blending the acrylic latex with an alkyd emulsion. The last will be presented here to see what synergistic features are available.

Table 9 shows some alkyd acrylic formulations. Both pure acrylic and styrene acrylic dispersions were tested. The physical blends are produced simply by mixing the acrylic latex into the internally stabilised alkyd emulsion at low shear and slow rate of addition. A suitable amount of coalescent agent has to be added in order to ensure a good film formation. The blends are very stable over time and do not vary in terms of either pH or viscosity.

A combination drier was added to the hybrids and the alkyd emulsion to obtain clearcoat formulations for evaluation. Clearcoats were applied to glass using a 200μm applicator bar and coating performance was evaluated.

Table 9 also shows the hardness development of the coatings, revealing that the hardness of the hybrids is higher than that of the pure alkyd emulsion. The drying times recorded by a Beck-Koller drying recorder also show that the small addition of acrylic or styrene-acrylic latex to the alkyd emulsion results in faster surface drying. The gloss on coated black glass at 20° and 60° is very good for the pure alkyd emulsion, whereas the hybrids both have somewhat lower gloss. This could possibly be due to a slightly excessive amount of acrylic as too high an amount may give rise to compatibility problems.

Table 9: Hybrid coating formulations and development of their physical properties over time. Drying on glass panels at 23°C and 50% relative humidity

Formulation and test procedures	Alkyd emulsion	Acrylic hybrid	Styrene acrylic hybrid
Alkyd emulsion	100	90	90
Acrylic	–	10	–
Styrene acrylic	–	–	10
Coalescing agent	–	0.7	1
König pendulum hardness			
1 day	11	10	9
7 days	13	16	16
14 days	15	30	26
21 days	17	34	31
28 days	18	41	33
Beck-Koller drying times, hours			
Dust free	1	0.5	0.5
Tack free	3	1	2
Through dry	9	2	4
Hard dry	22	6	11
Gloss at 20°			
1 day	84	72	83
7 days	84	67	82
14 days	81	71	79
21 days	82	69	77
Gloss at 60°			
1 day	91	88	92
7 days	91	87	92
14 days	91	88	90
21 days	91	87	90

Acrylic and styrene acrylic dispersions can thus be used to modify the coating properties of alkyd emulsions to address issues such as hardness or drying time. The styrene-acrylic hybrid has a much better appearance than the acrylic hybrid, and it is believed that upon film formation, the aromatic nature of the phthalic anhydride of the alkyd and of the styrene acrylic helps to produce a good blend at a

molecular level. This statement, however, requires further evidence.

Conclusions

High-solid alkyds, diluent resins, alkyd emulsions and hybrids have been described, all giving coatings with VOC levels below the limits stipulated in the VOC legislation for 2010. Thus, environmentally-friendly coatings can be produced by adapting the well-established alkyd resin technology in different ways. Alkyd resin technology is very versatile, and when combining it with other chemistry, the possible combinations to be tested are limited only by the imagination of the developer.

Acknowledgments

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