High Solids Alkyd Strategy

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Abstracts

The article presents new possible approaches for alkyd resin architecture in order to comply with market new constraints related to the VOC emissions. Examples and performance of alkyd concepts are presented with regard to VOC content and performance for "Interior/exterior trim and cladding paints for wood and metal".

Background

New regulations related to emissions/VOC content in coatings and increasing oil prices strongly recommend the shift to water borne and high solids for coating manufacturing technology.

In the Directive 2004/42/CE, from the European Parliament and the Council, limitations are established for the maximum volatile organic compounds (VOC) in decorative paints to be used within the EU. The products covered by the Directive are for use on buildings, trims, fittings and structures associated with buildings. Specific sub-categories are listed in the Directive with different limitations for maximum VOC in grams per litre of the ready to use product with two sets of limits for each sub-category. The first set of limit values will apply from 1 January 2007 and the second, stricter set, from 1 January 2010. Limits are established both for solvent-borne paints and for water-borne paints. The target levels are presented in the Table 1.

Table 1

Product Subcategory	Technology	Phase I (g/l) From 1.1.2007	Phase II (g/l) From 1.1.2010
Interior matt walls and ceilings (gloss <25@60º)	WB	75	30
	SB	400	30
Interior glossy walls and ceilings (gloss >25@60º)	WB	150	100
	SB	400	100
Exterior walls of mineral substrate	WB	75	40
	SB	450	430
Interior/exterior trim and cladding paints for wood and metal	WB	150	130
	SB	400	300
Interior/exterior trim varnishes and wood stains, including opaque wood stains	WB	150	130
	SB	500	400
Interior and exterior minimal build wood stains	WB	150	130
	SB	700	700
Primers	WB	50	30
	SB	450	350
Binding primers	WB	50	30
	SB	450	350
One-pack performance coatings	WB	140	140
	SB	600	500
Two-pack reactive performance coatings for specific applications such as	WB	140	140
	SB	550	500

floors			
Multicoloured coatings	WB	150	100
	SB	400	100
Decorative effect coatings	WB	300	200
	SB	500	200
WB= water borne SB= solvent borne			

In order to reach these targets a possibility along with the continuous development of the Water Borne systems is finding new ways for the High Solids technology.

Definitions
There is no general consensus upon defining high solids systems. However we list below some of the most commonly used:
- A system is named "high solid" when it contains max 350 grams VOC/litre of coating. (10)
- There are different regulations in U.S. e.g. max 420 g/l and max 250 g/l depending on application and state. (10)
- A paint is named "high solid" when it has a VOC content of max 420 g/l at application viscosity. (9)
- The phrase "high solid" sometimes is used for all kind of paint systems with a non-volatile content higher than average. This is very misleading because the average non-volatile content differs from application to application. (9)
- A high solids coating typically contains greater than 60% solids by weigh or 80% solids by volume (8)
- Lacquer with very high non-volatile content (>70%) (11)

Specific approach for high solids
Formulation of high solids systems requires attention with respect to the choice of all involved components. Here we have listed some of the factors to influence the selection:
- binders of high reactivity
- binders of low viscosity/low molecular weight
- molecule design
- pigments/fillers of low oil index
- wetting additives
- solvents that reduce the number of H-bonds

Table 2

High solids	Conventional
• Low or no physical drying • Tg build by cross-linking	• Intense physical drying • Tg of final coating is a sum of Tg of binder and cross-linking

Alkyds are type B polymers which exhibit a high functionality but generally have a low glass transition temperature. The Tg and hardness is a built up in the drying process.
In the oxidative process, the difficult part is that the cross-linking is not performed by reaction of the alkyd with another component (cross-linker) and

by thus removing functional groups that have a plasticizing effect, but through polymerisation of double bonds (delivered by the fatty acids). Hence, the final molecular weight is not reaching that high molecular weight of a thermoplastic polymer, and the hardness development is not always as high as expected. The phenomenon is known as the air/oxygen is kicking off the autoxidation of the alpha position from the double bond on the fatty acids in a complex process of radical polymerisation assisted by the metal dryers. This process results in the linkage between the fatty acids which bonds may be carbon-carbon, ether bond or peroxide bond. It is commonly accepted that driers only assist in the process of hydroperoxide decomposition and that higher temperatures and high double bounds conjugated fatty acids favour the formation of carbon-carbon bonds.

As well the target of low viscosity may be obtained by using groups that may act as built-in plasticizing moiety. However this approach has negative impact on the Tg of the alkyd (physical drying) and as well may increase the water sensitivity.

Basically an alkyd binder has a drying diagram as shown in figure 1, while a high solids alkyd has a by far longer drying due to a very low Tg which is built by oxidative reaction as in figure 2.
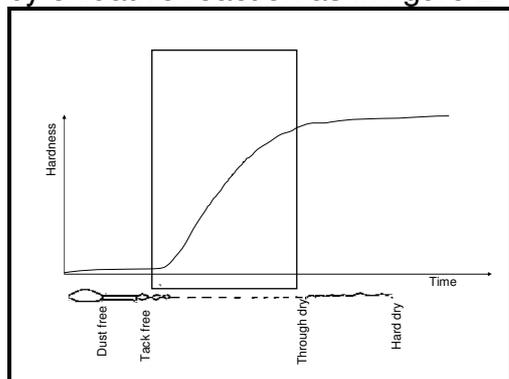

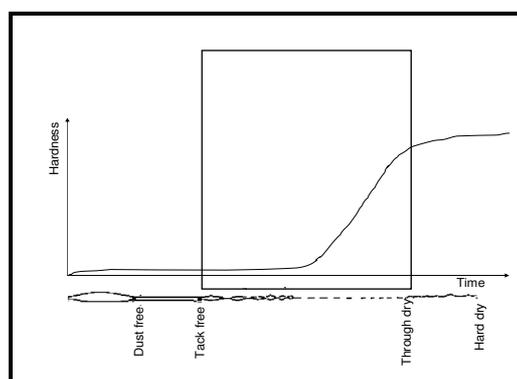**Figure 1.** Typical alkyd binder drying process

Figure 2. High Solids binder drying process

Considering the drying process itself, and defining drying as an expression of viscous behaviour, according to the Williams-Landel-Ferry equation (figure 3), the dry-to-touch performance at 25ºC (viscosity measurement temperature) is achieved at a Tg as low as lowest -29ºC.

$$\ln(vis\cos ity) = 27.6 - \frac{40.2(T - Tg)}{51.6 + (T - Tg)}$$

Figure 3. Williams-Landel-Ferry equation

This should correspond to a viscosity of 10^6 mPas (cP) while the theoretical Tg for a coating that should pass the blocking resistance at 25ºC (viscosity measurement temperature) should be of +4ºC (3).

The viscosity of an alkyd resin is a function of free-volume availability. The free volume of a material is the summation of the spaces or holes that exist between molecules of a material resulting from the impact of one molecule or molecular segment striking another. These holes open and close as the molecules vibrate. Above the glass-transition temperature (Tg) the holes are large enough and last long enough for molecules or molecular segments to move into them leading to low viscosity. Free volume increases as temperature increases, the rate of volume increase is higher above Tg or in case we use a solvent.

So the major problem is how to deal with the almost non-existent physical drying required by the desire of a larger free volume in conditions of keeping the molecular weight as high as possible!

The answer may be the design of the alkyd binder itself. Basically this means moving from low free volume to higher/high free volume (figure 4) in almost 100% non-volatile content.
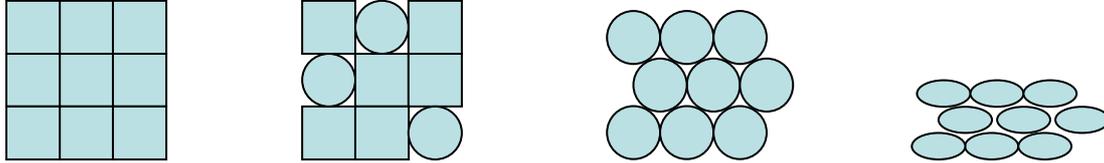

Figure 4. Generating more free volume and lower viscosity.

Allowing the alkyd binders to have a reasonable molecular weight and at the same time shielding a segment that has a reasonable high Tg, the hardness build up will be transmitted to the coating in the drying process. The shielding is necessary to provide the low viscosity, while the architecture itself must allow a sufficiently reasonable free volume leading to a reasonable application viscosity in conditions complying to the high solids definitions.

The immediate response to this problem may be found in designing the alkyd binder. It is well known that dendritical structures give lower viscosity, but as well low hardness development. This may be due to the fact that the core of the dendrimer must be a soft segment in order to secure a good mobility/reactivity for the groups intended to build further layers. However, even in the case that the core is sufficiently hard, due to the symmetry of the dendrimer and the fact that the dendrons are built by soft segments, the hard core is so strongly shielded by the branching arms, that the physical drying is almost insignificant.

Considering a dendritical structure as in figure 5, the core segment is not visible in the drying process, in order to exhibit the physical drying properties.
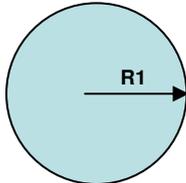

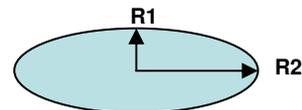Figu**re 5.** Dendritical structure   **Figure 6.** Discoid structure

The pendulum is measuring oscillations in the soft shell of the molecule. Therefore the molecule should be shaped as much as possible as in figure 6, in order to allow the hard core of the molecule to be visible in the drying process.

Therefore, the alkyd binder should be built as a discoid structure as in figure 6, allowing a higher mobility, a lower shielding of the hard core of the molecule. The core may be such shaped in order to control, by raw materials and length, the Tg. A shape as shown in figure 7 may be very suitable to comply with these requirements and is easy to synthesize using the usual raw materials for alkyds, using semi-fabricates there of, or loaded and reacted in a suitable order.
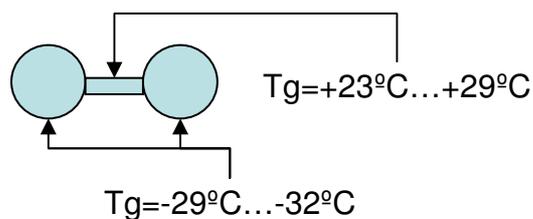
Tg=+23ºC...+29ºC

Tg=-29ºC...-32ºC

Figure 7. Dendritical moieties shielding a hard segment
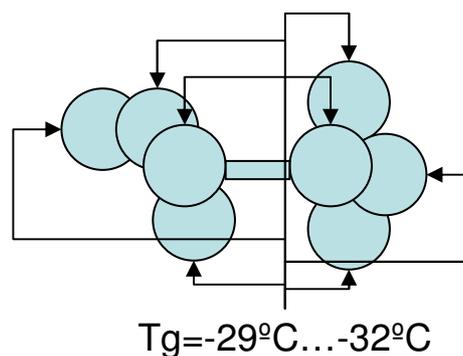

Tg=-29ºC...-32ºC

Figure 8. Further branching on the core concept structure.

Considering this architecture as in figure 7, the molecular weight may be grown on the dendritical side of the molecule, trying to preserve the architecture as shown in figure 8. This may be performed by reacting hydroxyl functional dentritical moieties of low OH number on anhydride functional moieties as will be further explained.

Thus the segment to be shielded may be generated from usual raw materials such as di-basic acids and diols, preferably 1,3-diols. The most common segment having a Tg of +26ºC may be build of phthalic anhydride and neopentylglycol as in figure 9:
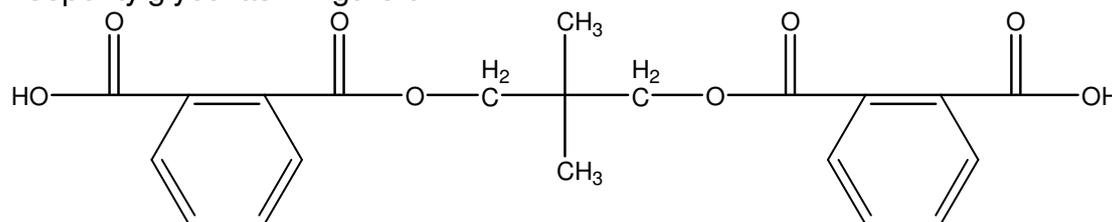

Figure 9. Hard segment obtained by reacting Neopentylglycol with Phthalic anhydride

This segment is further shielded by esters from vegetable fatty acids and high functional polyols. This results in low Tg moieties that will provide the oxidative drying. The Tg of such moieties is lower than -32ºC, depending on the acids involved.
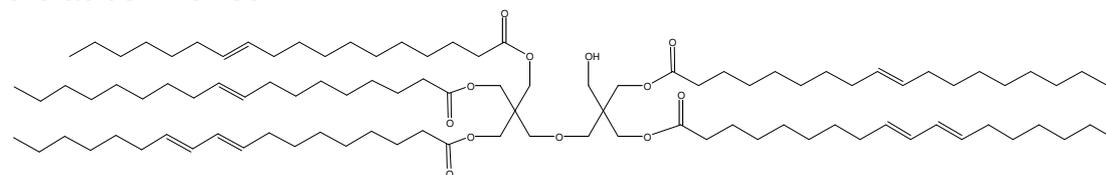

Figure 10. Hydroxyl functional dentritical moieties of low OH number

The example in figure 10 is a building block on di-pentaerythritol and tall oil fatty acids. These building blocks may be esters of pentaerythritol, trimethylolpropane, di-trimethylolpropane, etc.

The oil length of the alkyd may be controlled by changing the fatty acids for other acids. However these acids should be selected in such a way that they do not affect the desired Tg of the building block. Thus the use of benzoic acid is not recommended, while the use of an adduct from dicyclopentadiene with a diacid (figure 11) has positive result in terms of preserving the Tg, reducing the oxygen inhibition and speeding up the drying, and as well not requiring

any reduction of the spacer as defined above as offering the same shielding properties as a fatty acid.
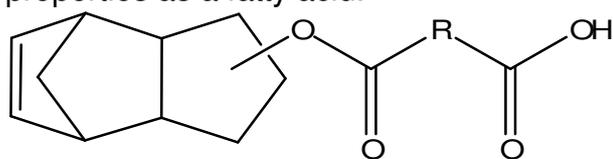

Figure 11. Carboxylic functional aduct of DCPD and a di-basic acid.

The oil length of the structures as in figure 10 are related to the length and Tg of the spacer as described above (figure 9).

The further growth of molecular weight according to the architecture in figure 8 is performed by reacting maleic anhydride on the fatty acid moieties in the dendritical structure as in figure 10 and further reaction of the said dendritical polyol fatty acid esters to those moieties. The resulting moieties from reaction of maleic anhydride on the fatty acids are presented in figure 12:
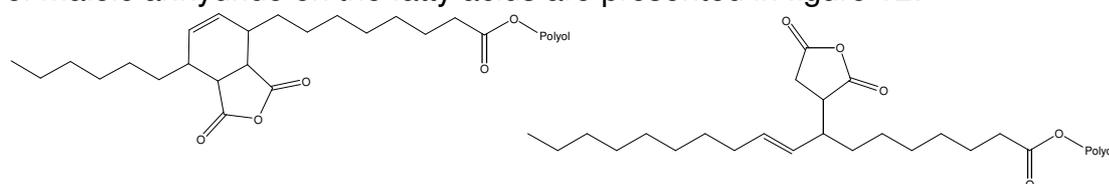

Figure 12. Dendritical fatty acid moieties modified with maleic anhydride for further molecular weight enhancement.

This allows a serious increase of molecular weight without a significant impact on the final viscosity.

Experimental and discussions

In order to make a proper evaluation of the idea a typical long oil alkyd has been done and compared to alkyd binders obtained according to the concept. Further in order to maintain some functional reactive groups on the binders according to the concept, necessary to fulfil other requirements related to coating formulation such as adhesion, pigment wetting, etc, for the 1,3-diol in the hard segment the choice went to BisMPA (dimethylol propionic acid) controlling the synthesis in such a way in order to preserve the larger part of the carboxylic group unreacted in direct or side reactions.

Table 3

	Typical Alkyd resin	Concept Alkyd Figure 7	Concept Alkyd Figure 8
Tall oil fatty acids	62.21	75.23	75.65
Pentaerythritol (mono grade) [1]	20.42		
Di-Pentaerythritol[1]		16.66	16.65
Phthalic anhydride[1]	23.88	9.71	9.71
Maleic Anhydride			1.25
BisMPA (dimethylol propionic acid) [1]		4.40	4.39
Total batch	106.51	106	107.65
Reaction water	6.51	6.0	6.00

Theoretical parameters			
Acid number, mgKOH/g	9	15	15-25
Oil length, %	65	78.4	77.5
OH number, mg KOH/g	47	32	18-30
OH excess, %	11.3	7.1	1.6
Molecular weight, g/mole	20480	3945	2967-7113
Alkyd constant	0.979	0.997	0.972
Acid number at gel, mg KOH/g	6.3	0.8	7.1
Functionality	2.042	2.006	2.058
Practical results			
Acid number, mg KOH/g	8.6	15.7	15-25
OH number, mg KOH/g	40	35	25-35
Molecular weight, Mn g/mole		2081	2132-2766
Molecular weight, Mw g/mole		4857	4766-12738
Peak Molecular weight, g/mole		2317	3636-4906
Polydispersity, GPC		2.3	2.24-4.6
Viscosity Brookfield, 100% at 100ºC mPas	860	-	-
Viscosity Brookfield, 75% in white spirit at 23ºC, mPas	8100	-	-
Viscosity Brookfield, 100% at 23ºC, mPas	-	2690	1420-2820

[1] Perstorp Specialty Chemicals AB

The typical alkyd resin has been synthesized according to the general accepted cooking protocol for alkyds, at a temperature of max 235ºC.
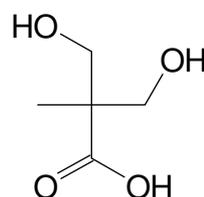

Figure 13. BisMPA (Di-methylool propionic acid)

The concept alkyds may be synthesised in steps: a first step to generate the strong segment as described in figure 9 which is further loaded to the branched moieties esters of polyol and fatty acids. However it is possible to run the synthesis in one shot carefully observing the correct order of loading raw materials to lead to the desired structure at temperatures close or slightly

higher than the melting point. Concept alkyds have been synthesised according to the following protocol:

- ✓ Charge oil fatty acid, Di-Pentaerythritol, xylene (4% on raw materials), and Fascat 4100 (0,1% on raw materials)

- ✓ Start heating. Raise the temperature with 4°C /min to 160 °C.

- ✓ Raise the temperature to 220°C with 1°C /min. Hold until the final acid number is about 3 mg KOH/g.

- ✓ Cool down to 180°C and charge the phthalic anhydride. Wait until the anhydride ring opens on the core ester.

- ✓ In case the concept alkyd is according to figure 8, drop the temperature to 120-130 °C and then add maleic anhydride

- ✓ Start heating and when the alkyd is clear at about 140-150 add Bis-MPA under stirring in small portions so it does not fall down to bottom

- ✓ Raise the temperature to 200°C. Hold until the final acid number is 15-25 mg KOH/g.

- ✓ Vacuum at 160-170°C to remove the Xylene

Drying performance evaluation of the concept
Following clear coatings have been prepared:

Table 4

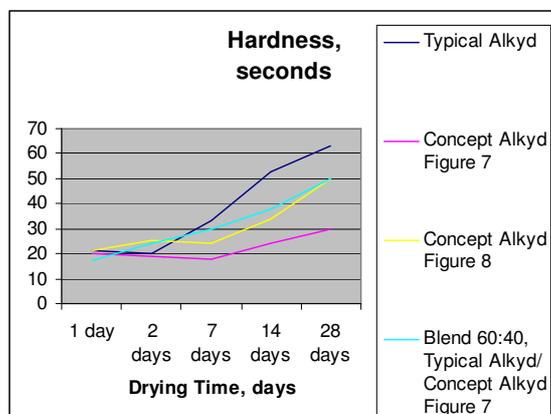| Lacquer formulation	1	2	3	4
Typical Alkyd resin, 75% in WS	100	60		
Concept Alkyd Figure 7; 100%		40	100	
Concept Alkyd Figure 8; 100%				100
Dryer Co, 10%	0.46	0.52	0.6	0.6
Dryer Zr 12%	1.56	1.78	2.08	2.08
Dryer Ca 10%	0.76	0.86	1	1
Exkin 2	0.14	0.12	0.12	0.12
Aromatic free white spirit	29.8	22.08	20.38	36.96
Non-volatile content, %	56.9	68.1	80.4	71.9
Viscosity, 25ºC mPas	480	480	490	500
VOC, g/l lacquer	417	296	196	262

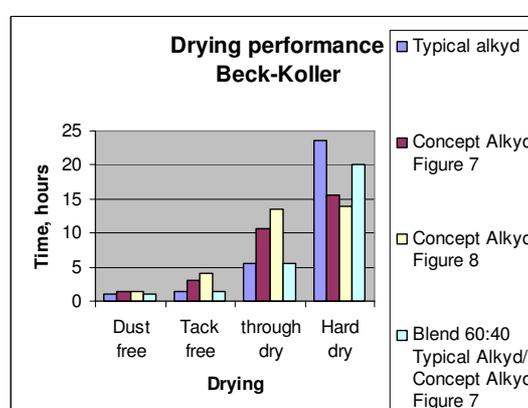**Figure 14.** Dry film thickness 38-42 μm

Figure 15. Dry film thickness 38-42 μm

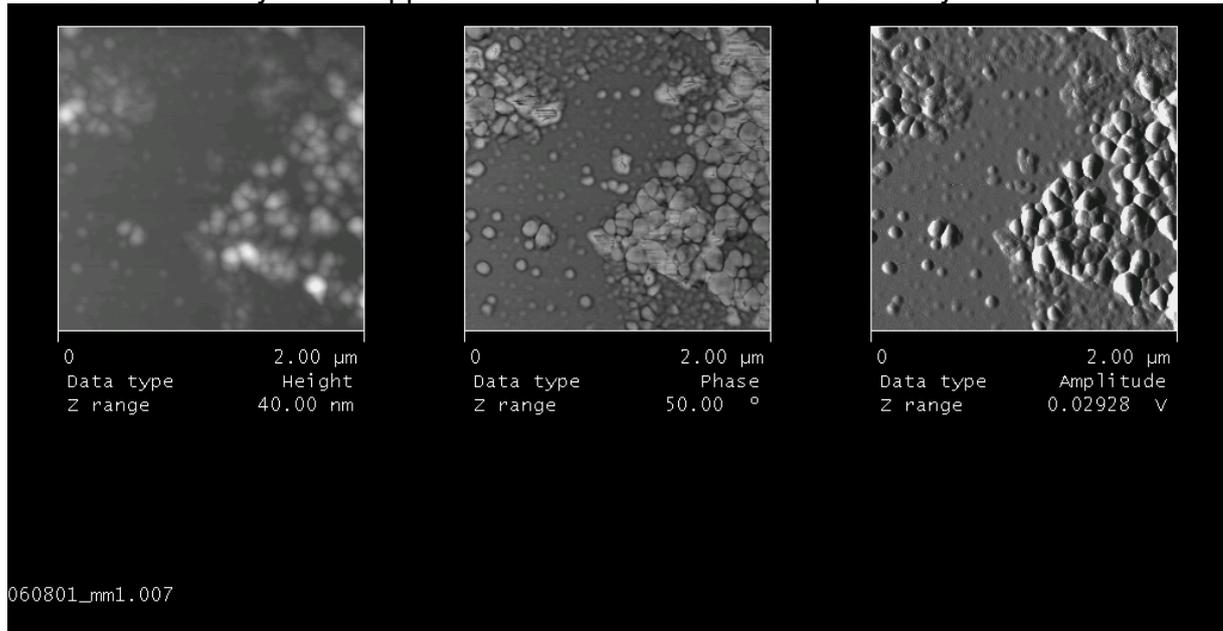Further the solidity of the approach has been tested and proved by AFM.

Figure 16. AFM image Concept Alkyd Figure 7. From left to right are representations of height, phase and amplitude.
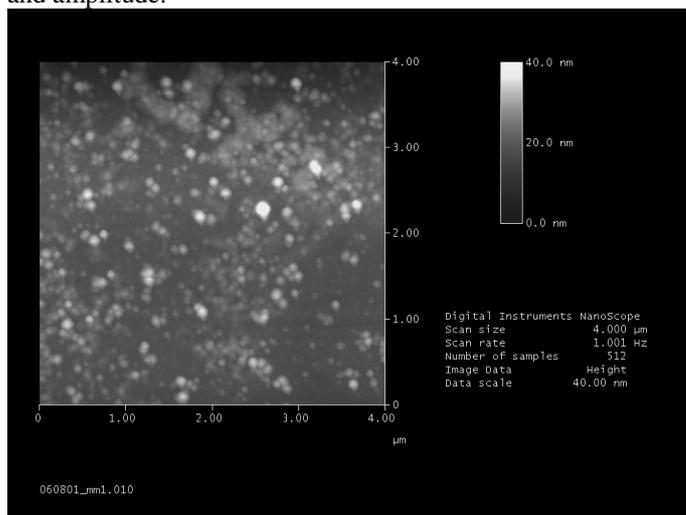

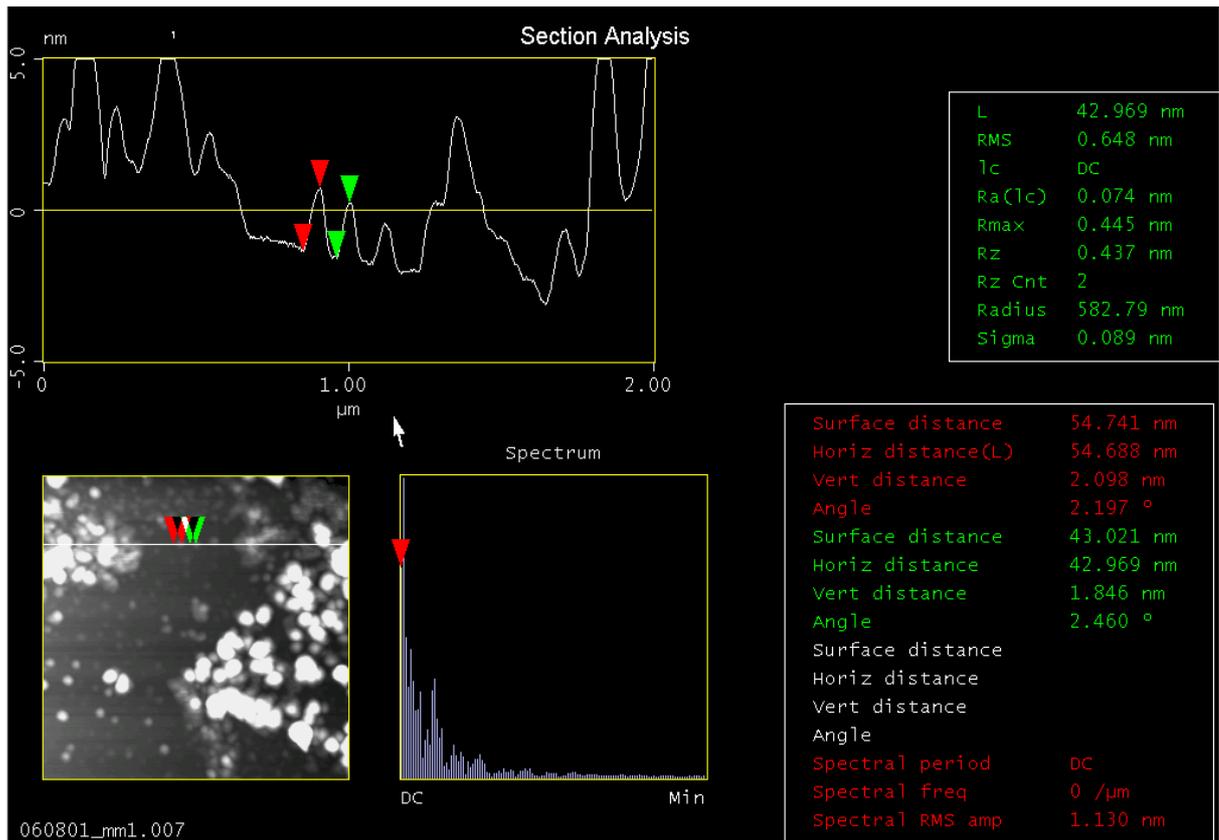**Figure 17.** AFM Height image of Concept Alkyd Figure 7.

Figure 18: AFM section analysis of Concept Alkyd Figure 7. The area analysed is 2x2 µm large.
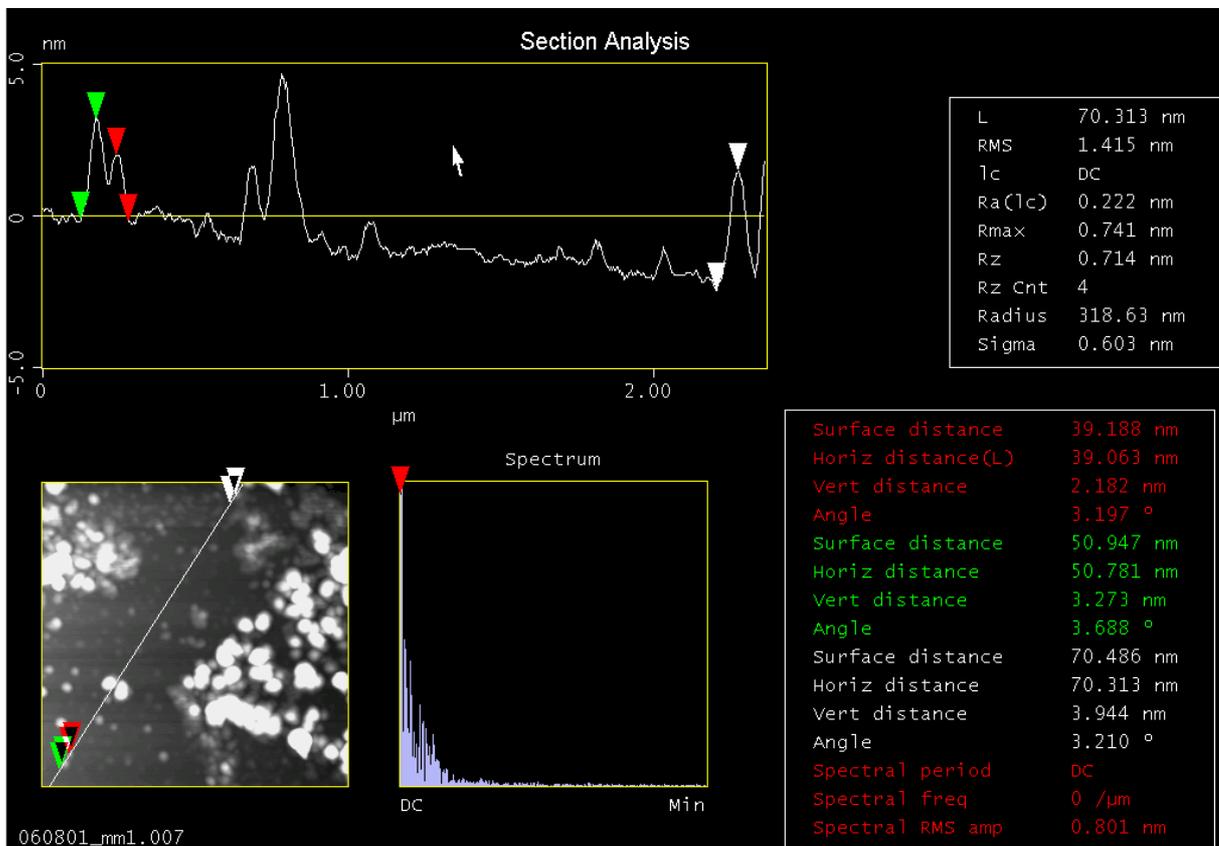

Figure 19. AFM section analysis of Concept Alkyd Figure 7. The area analysed is 2x2 µm large.
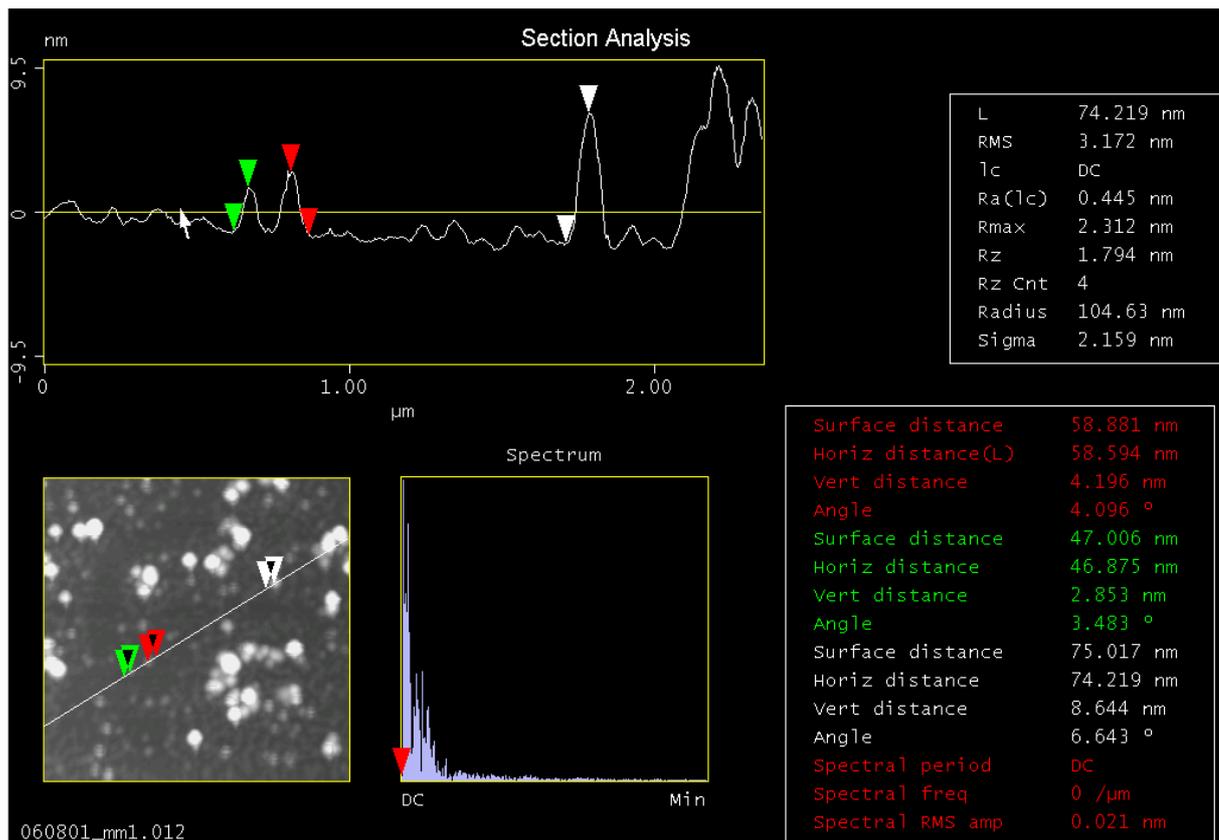
Figure 20. AFM section analysis of Concept Alkyd Figure 7. The area analysed is 2x2 µm large.

The particles in the AFM images have a large size distribution. A likely explanation is that the samples ware too concentrated. Several polymer molecules could then merge forming larger agglomerates. The large particles in figures 16 and 17 could be such agglomerates. However, when the sample was further diluted, contact between the AFM tip and the sample could not be achieved. Areas with few or no such big particles could be identified, figure 16, and size analysis of these areas were performed in figures 18-20. The section analysis of the height images give vertical sizes ranging from ca 1.8 µm to 4 µm for those small particles.

The horizontal distances as well as the vertical distance were obtained from the section analysis of the height images. These distances were a lot longer than the vertical ones, approximately 16 times longer in most cases, figures 18-20. This indicates that the particles/molecules are flat. But there is a possibility that this effect is caused by a large pressure from the tip of the AFM onto the sample which causes the particles/molecules to flatten a bit.

Conclusions

Considering the drying performance and the VOC content in formulations which are aromatic free we may assume that the approach has been successful.

The drying performance of the typical alkyd is lower than the performance of both concept alkyds as described above. The blends of the typical alkyd with any of the concept alkyds may impart both hardness and drying performance. The approach may comply with the request of VOC emissions of 2007 and

even 2010. Some trimming of the formulations may be necessary and is left to the customer latitude, but this may be considered a reasonable starting point. The binders as presented here above are filling the drying behaviour gap between typical alkyds and general high solid alkyds or simple dendritical structures. The concept binders may be used as such or in combination with typical alkyds as reactive solvents without the risk of altering the drying behaviour or other general properties.

The AFM results may show that a reasonable assumption that the discoid shape as in figure 6 for a concept as illustrated in figure 7 may have been achieved with a good impact on free volume/viscosity and typical alkyd comparable drying properties.

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