Presentation : 4th International Conference

ADVANCES IN COATINGS TECHNOLOGY (ACT 2000)

7. - 10. November 2000 - Katowice
P o l a n d

Coating Evolution with new Higher Solids Resins for 2-K Car Refinishing and Industrial Finishes

Dr. Ulrich Epple and Dr. Ulrike Kuttler

Solutia Austria GmbH
Leechgasse 21
A-8010 Graz
Austria

Tel.: +43 (316) 344 302 or 256
Fax: +43 (316) 344 349 or 350

Recent legislation (USA: different US-state regulations, Europe: UK 1998/2. stage and EU directive 1999/13/EG) about the emission of volatile organic compounds (VOC's), increasing quality consciousness, rising costs for raw materials and special solvents have set off an intensive search within the paint industry for new solutions such as high solids and waterborne coatings as more environmentally compatible concepts. The basic principles in these regulations are:

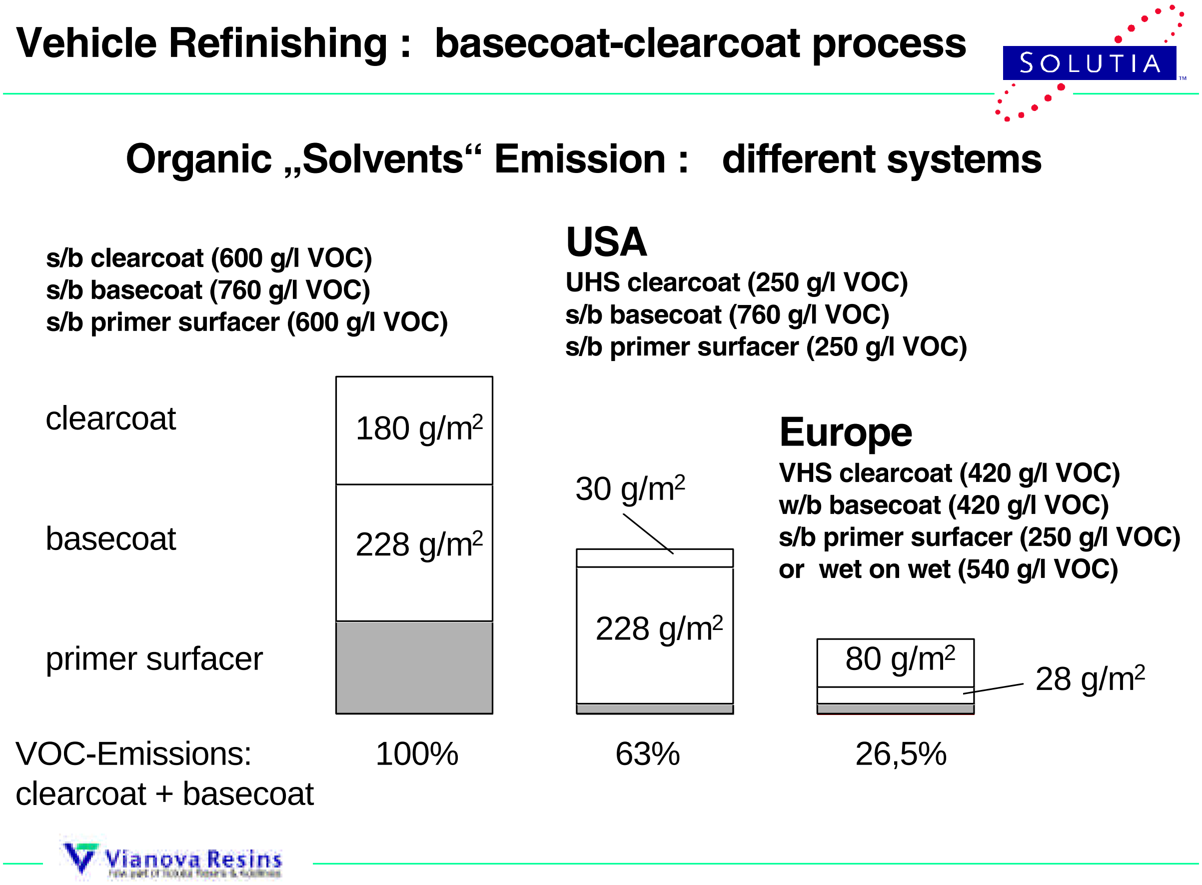
to reduce and prevent emission direct at the source.

As a consequence, paint layers will have a specified maximum emission level and paint users have to take a compliant coating system to keep the emission within the statutory limits.

For industrial finishing, based on a primer and a topcoat these limits can be fulfilled with new modified resins.

For vehicle refinishing, however, based on primer surfacer, basecoat and clearcoat, the VOC-levels in g/l are hard to fulfil (Figure 1).

Figure 1



There exist two different coating markets : USA and Europe with roughly two different coating technologies for the basecoat-clearcoat process.

USA and Europe : differences in paint technology

While in the US-market s/b basecoats are standard the clearcoat are forced to have 250 g/l. This emission limit can only be reached with reactive diluents, which are organic chemicals with different complex chemistry for crosslinkage with polyisocyanates.
Mostly, sterically hindered or capped amines (e.g. aspartic acid esters; ketimines, aldimines and oxazolidines) are used, which often causes problems:

- long drying times (decapping: moisture necessary)
- short pot life : ≤ 3 h, mostly: 1,5 h
- redissolving of the basecoat : flop problems
- less resistance to UV and harsh chemicals.

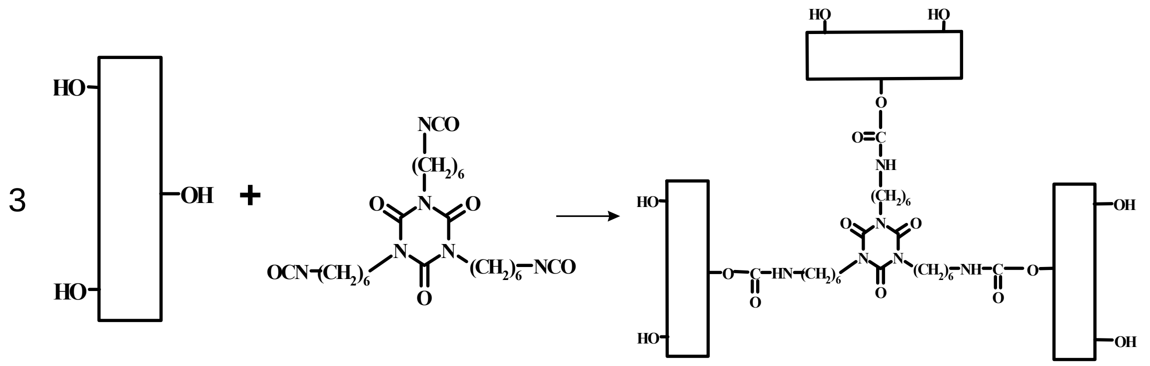
Within the European polyurethane coating market such weaknesses of "ultra high solids" clearcoats are not accepted. Futhermore, basecoats in Europe are mostly waterborne and the challenge is to develop very high solids clear coats with a VOC level of 420 g/l and a good dry time/pot life balance which are practical for use under a number of weather and application conditions. This European concept set solvent emissions for the basecoat-clearcoat process from 100 to only 27 % and is the logical evolution of systems that meet and exceed the new requirements without sacrificing performance.

Classification of clear coats

Current high quality automotive refinishing clearcoats mainly based on medium solids acrylic polyols as binder and aliphatic polyisocyanates as hardener (see Fig. 2), possess a non volatile content from 50 - 55 wt.% at spraying viscosity (4 mm cup, 21 s, 23°C), corresponding to a VOC-level ≥ 455 g/l.

Figure 2

Two Pack-Automotive Refinishing Clearcoats



Polyol
®Macrynal / ®Duroftal

Polyisocyanate

Polyurethane-Network

Medium solids
50 - 55 wt.%
VOC ≥ 455 g/l

→

High solids
56 – 58 wt.%
VOC 454 - 421 g/l

→

Very / Ultra high solids
≥ 59 wt.% / ≥ 66 wt.%
VOC max. 420 g/l
max. 350 g/l

Vianova Resins

Standard high solids systems reach 56 to 58 wt.%, which is equal to 454 - 421 g/l.

To meet the requirements for very high solids or more, coating systems with a non volatile content of at least 59 wt.% (420 g/l) are necessary. This target may be achieved by changing binders and synthesis parameters (see Fig. 3):

polyols with lowest solution viscosities or low molecular weights.

Figure 3

Approaches „very / ultra high solids"

SOLUTIA

- **reactive diluents (sole binders ?)**
- **„low molecular" polyols**
  - acrylic polyols
  - polyester polyols
  - blends

Vianova Resins

Binders : lowering molecular weight / functional groups

Low molecular polyacrylate or polyester polyols are easy to prepare :

1. for radical polymerized acrylates (via: chain reaction) using
   - high concentrations of (special) initiator or
   - high polymerization temperatures

2. for polyester via condensation process (step reaction) using
   - high levels of OH-functional monomer units (e.g. diols) or
   - short reaction times / low conversions.

Unfortunately these resins have an extended drying time (Fig. 4) due to:

1. a reduced functionality per molecule in acrylates,
2. a high amount of plasticizing diols (or dimers, trimers etc.) in polyesters,

both resulting in low film hardness and low chemical resistance.

Figure 4

Low molecular weights : polyols

Disadvantages: long tack free time
low film hardness
low chemical resistance (petrol, xylene)

Solution:

car refinish	**industrial coatings**
(cc, topcoat, primer surfacer)	(metal: topcoat)
higher functionality	flexible monomers
special bulky aliphatic monomers	price - functionality

narrow molecular weight distribution

Solvents:

high evaporation	balanced evaporation

good levelling power
good cutting power (viscosity/density)

The simple increase of the number of functional groups like OH or COOH in low molecular resins with standard monomers, alone, is not the solution of the problem, because excessive hydrogen-bonding-interaction leads to a remarkable increase in viscosity.

Binder architecture - physical relationships

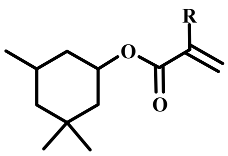
Introduction of special aliphatic monomers with bulky groups and good solvents reduces this effect. As a low molecular weight polyol behaves like a monomer in nature, simple evaporation of solvents does not leave the coating tack free because physical drying speed and tackyness strongly depend on the Tg-value (glass transition temperature) of the neat polyol and the crosslinking density, respectively. The drawback is, that each polyol has a critical molecular weight, where Tg falls rapidly and predictions with Gordon Taylor (Fox) or Gibbs DiMarzio equation's [1] fail.
So we are forced to test empirically each bulky monomer (see Fig. 5) in different concentrations at a constant low molecular weight for viscosity reduction and Tg-effectivness at an high OH-content (e.g. for acrylics: 145 mg KOH/g solid resin) [2, 3].

Figure 5

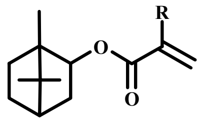
Special monomers : aliphatic monomer units

SOLUTIA

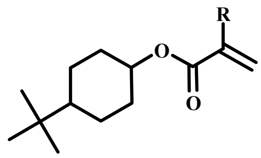
1. Acrylic resins



3,3,5-Trimethylcyclohexyl (meth) acrylate

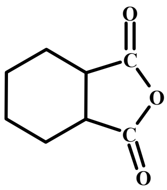


Isobornyl (meth) acrylate

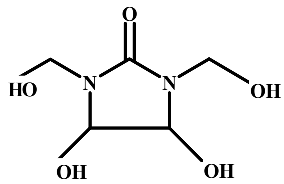


4-tert.-Butylcyclohexyl (meth) acrylate

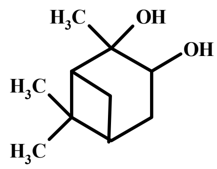
2. Polyester resins



Hexahydrophtalic acid anhydride



Dimethylol dihydroxyethylene urea



Pinane diol

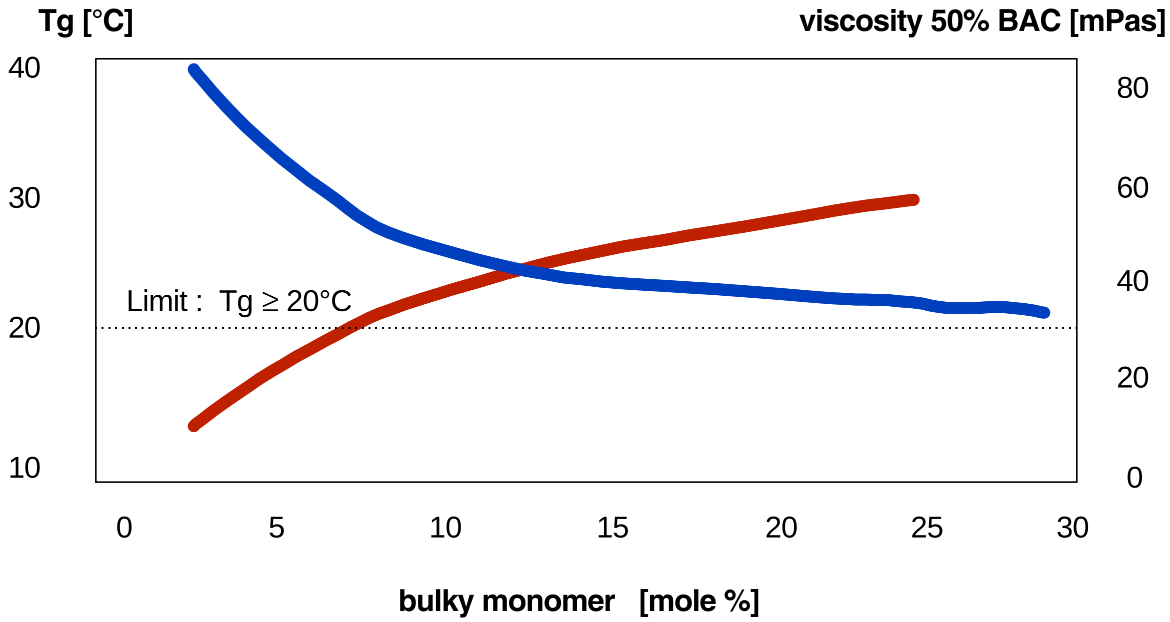
Vianova Resins

Figure 6 presents the correlation between solution viscosity (50 wt.% in butyl acetate) and Tg-value with the molar fraction of a bulky monomer in an acrylic polyol.

Introduction of approximately 7 mole% of such a monomer in an acrylic - styrene copolymer leads to a resin with a Tg-value above room temperature (20°C). Alongside this Tg-value a 35 % reduction in solution viscosity is obtained. 15 mole% incorporation results in a 55 % reduction and 25 mole% gives approximately 65 % reduction in the solution viscosity.

Figure 6

Acrylic polyol: Influence of „bulky“ monomer



So there must be a optimum balance of low molecular weight, content of bulky monomers, functional groups and price for each high solids system.

A sophisticated combination of these parameters leads to two acrylic polyols:

®Macrynal VSM 1565/70BAC and ®Macrynal VSM 2872/70BAC (Fig. 7), the latter with inherent activation for isocyanate crosslinkage.

Inherent activation means, changing the polarity of the polymer backbone (e.g. with carboxyl or tert. amino groups) to such an extent that external catalysis [e.g. Dibutyl tin dilaurate (DBTL), Zinc octoate (Octa-Solingen Zink, Borchers), Triethylene diamine (DABCO, Air Products), low volatile acids] and reactive thinners (e.g. Diethyl ethanol amine) are less important for both ambient (RT) and forced drying.

Figure 7

Acrylic resin – chemical constants

®Macrynal	VSM 1565/70BAC	VSM 2872/70BAC
Non volatile content [%]	70	70
OH-content [mg KOH/g]	145	145
acid value [mg KOH/g]	10	22
Tg [°C]	23	25
Viscosity / 23°C [mPa s] 50% BAC	45	55
Density, 20°C [g/cm^3]	1,05	1,04

The neat ®Macrynal VSM 2872 fulfils the tack free test, judged in an oven after 40 minutes / 60°C. This test simulates today's usual forced drying with IR-equipment in automotive refinishing business to increase productivity.

For further reduction in VOC it is useful to change the type of polymer formation:

<u>condensation products easily reach solution viscosities below 40 mPa s</u>.

So we synthesized "oligomers" with different bulky raw materials, with different branching levels, with high functionalities (OH and COOH groups), with high inherent polarity and hopefully low viscosities and high Tg's [4]. Our very best developments are two aliphatic polyester polyols: ®Duroftal VPI 2801/78BAC and ®Duroftal VPI 2803/78BAC with Tg-values of about 22°C (Fig. 8).

Figure 8

Polyester resin - chemical constants

®Duroftal	VPI 2801/78BAC	VPI 2803/78BAC
Non volatile content [%]	78	78
OH-content [mg KOH/g]	220	180
acid value [mg KOH/g]	22	22
Tg [°C]	24	21
Viscosity 23°C [mPa s] 50% BAC	29	31
Density 20°C [g/cm³]	1,11	1,14

Solvents: good cutting power

As coatings become higher in solids and the amount of solvents is reduced, the proper selection of solvents becomes more critical. As seen in Figure 9, butyl acetate is an excellent solvent for delivering polyols after manufacturing due to their viscosity reduction power, evaporation rate and their better odor than ketone solvents.

The ranking in viscosity with different solvents is for the acrylic polyol:

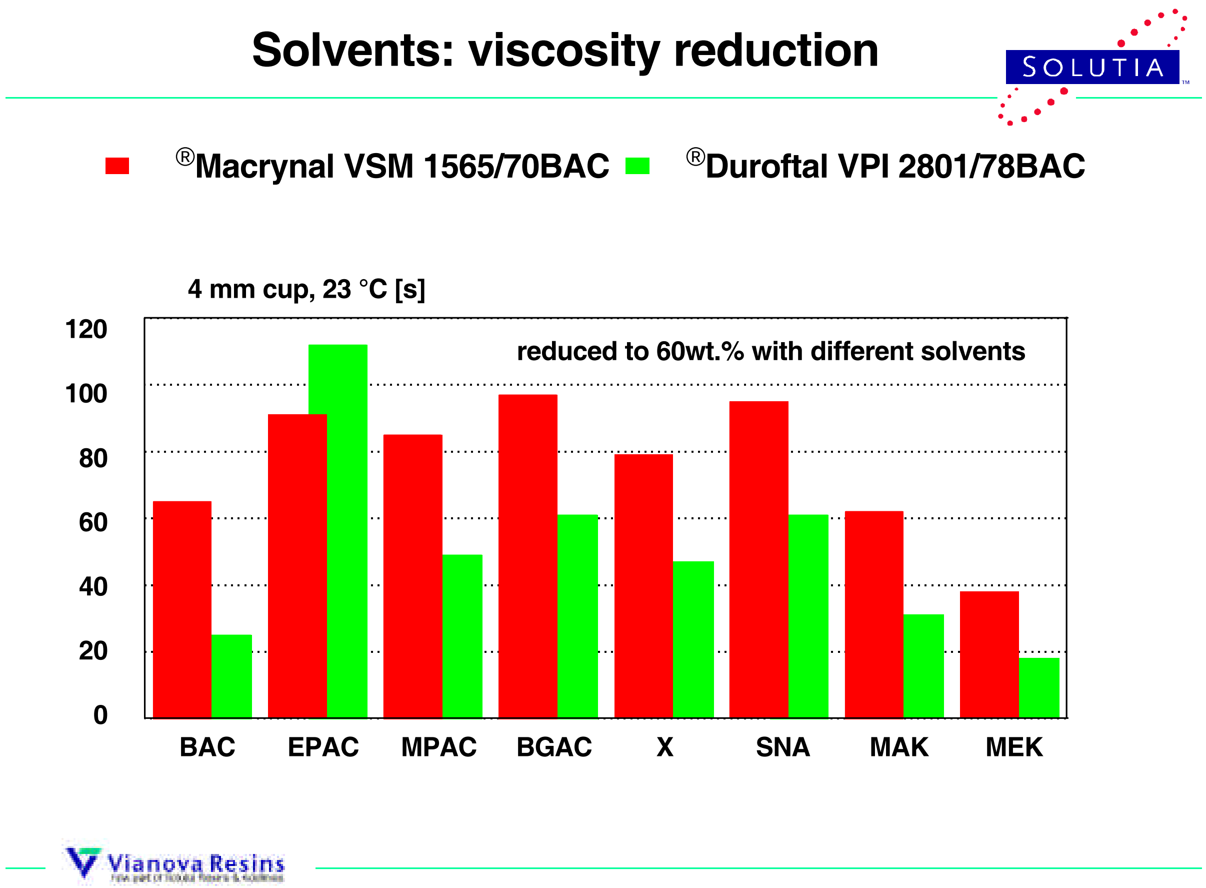
MEK << MAK ≅ BAC < X < MPAC < EPAC < SNA ≅ BGAC

and for the polyester polyol:

MEK < BAC ≅ MAK < X ≅ MPAC < BGAC = SNA << EPAC.

Nevertheless formulating very or ultra high solids clearcoats with high performance means not only to use solvents with a good cutting power (e.g. MEK), but also to use solvents ensuring good levelling and degassing: MPAC, SNA or BGAC. A sophisticated combination of these aspects directed us to the right choice and quantities of solvents in our car refinishing guiding formulations.

Figure 9



Compliance and lower VOC clearcoats

The technical performance of clearcoats based on ®Macrynal VSM 1565 or VSM 2872 and ®Duroftal VPI 2801 or VPI 2803 are presented in Figure 10.
The new polyester polyols in combination with standard polyisocyanates of the isocyanurate type provide a solids content of 66 wt.%, corresponding to a VOC level of 350 g/l, in comparison to 60 wt.% or 59 wt.% for the acrylic polyols, respectively. The features of this "ultra" high solids system are:

- good physical drying
- long pot life : ≥ 3 h
- excellent chemical resistance
- high film hardness and
- excellent weatherability.

Figure 10

Technical Performance : Clearcoats

®Macrynal / ®Duroftal	VSM 1565	VSM 2872	VPI 2801	VPI 2803
drying: RT-without Catalyst				
potlife [h]	> 8	min 6	min 3	min 6
tack free [h], 200 µm wet	6,5	5	6	5
forced drying: 20 min/ 60°C				
film hardness (König) [s] 1h	86	152	155	153
after 7 days	207	201	200	198
chemical resistance [min.]				
Petrol (lead free)	> 10	> 10	> 10	> 10
Xylene	> 10	> 10	> 10	> 10
Skydrol	> 10	> 10	> 10	> 10
weatherability				
QUV / 313 nm [h]	> 2000	> 2000	> 2500	> 1000
Florida [year]	> 2	> 2	> 1,5	in test
VOC [g/l]/[%]	410 / 60	420 / 59	350 / 66	350 / 66

So the bad image of polyester polyols in comparison to acrylic polyols has to be revised with these developments.

Compliance alternative

Blends between todays high solids acrylic resins, like ®Macrynal VSM 2800/70BAC (OH-content : 140 mg KOH/g solid resin) and the new poly-ester resins ®Duroftal VPI 2801/78BAC or VPI 2803/78BAC (e.g. 1:1 wt./wt. solid resins) have advantages (Fig. 11):

- reach VOC limit : 420 g/l and
- adjust: pot life / drying time

of the pure acrylic resin coating.

Figure 11

Compliance alternative : blend (1:1)

SOLUTIA

®Macrynal VSM 2800/70BAC + ®Duroftal VPI 2801/78BAC
or VPI 2803/78BAC

„high solid“ acrylic polyol — „ultra high solid“ polyester polyols

Advantages:	- reach	VOC-values	max. 420 g/l
	- adjust	potlife	5 - 7 h
		drying time	5 h (tack free)

reduce : system price

OH-content : 180 or 160 mg KOH/g

Vianova Resins

Industrial coatings

For industrial coatings, which are also under the EU directive 1999/13/EU, we synthesized low molecular weight acrylic polyols with different modifications: branched aliphatic side chains and polyesters. The first one: ®Macrynal VSM 2570/70BAC has an OH content of 80 mg KOH/g solid resin. The second ®Macrynal, VSM 2705/70LG, has an OH-content of 100 mg KOH/g.
The technical performance of these high solids resins in topcoats is nearly equal to standard low or medium solids products (Figure 12).

Pigmented coatings (white, ratio (binder : pigment) = 1 : 0,8) with ®Macrynal 2570 have an solid content of 67 wt.% (21 s, 4 mm cup, 23°C), a good adhesion on different metals (Fe, Zn, Al, Steel) and on plastic parts (PA, PMMA, PP (flamed), PVC h/w, ABS, GFK), good chemical resistance and excellent outdoor stability. With this resin it is possible to formulate one layer systems.

Figure 12

Technical Performance : industrial topcoats

white, ratio (binder : pigment) = 1 : 0,8 (21 s, 4 mm cup, 23°C)

®Macrynal	VSM 2570	VSM 2705	SM 500
drying: RT-with catalyst			
pot life [h]	8	6	7
tack free [h], 150 µm wet	3	6	2
film hardness (König) [s] 10 d	160	110	165
forced drying: 30 min / 80°C			
film hardness (König) [s] 1 h	101	70	130
chemical resistance [min]			
Petrol (lead free)	5	5	> 5
Xylene	1	1	5
weatherability			
QUV / 313 nm [h]	1200	800	500
VOC [g/l] / [%]	430 / 67	450 / 65	545 / 52

Pigmented coatings with ®Macrynal VSM 2705 have a solid content of 65 wt.%, good levelling power and a very good aspect. For the application of this resin we recommend a two layer system: primer (epoxy or acrylic) and the pigmented topcoat.

Summary:

For VOC compliant coatings we synthesized different low molecular binders: acrylic and polyester polyols with bulky monomers and high functionalities. An overview of the available guiding formulations: clear-coats, pigmented coatings, primer surfacers and primers (anti-corrosive) for high performance protective coatings and the commercial vehicle market are presented in Figure 13.
It's also possible to blend high solid acrylic resins with our new ultra high solid polyester polyols for emission reduction.

For industrial maintenance, like agricultural and industrial machinery, building machinery or general equipment (e.g. bridges, hydrants), we offer new high solids products with a reduced OH content (Figure 14). All products are worth their money.

Figure 13

Guiding formulations : car refinish

®Macrynal	type	clear	pigmented	primer surfacer	primer anti-corrosive
VSM 1565/70BAC	VHS	x (410)	w (415)	-	-
VSM 2872/70BAC	VHS	x (420)	w (425)	x	-
VSM 2800/70BAC	HS	x (435)	w (440) green (425) red (440)	x (430)	x (450)
®Duroftal **VPI 2801/78BAC** **VPI 2803/78BAC**	UHS	x (350)	w (350) green (350) yellow (350)	x (345)	-

HS high solids: Very, Ultra **VOC (g/l) at 21s, 4 mm cup, 23°C**

Figure 14

Guiding formulations : industrial topcoats

®Macrynal	type	pigmented white (1: 0,8)	primer	„airless“ application
VSM 2570/70BAC	HS	x (430)	x (410)	possible
VSM 2705/70LG	HS	x (450)	x (430)	possible
SM 500/60X	MS	x (545)	x (500)	possible

HS high solids, MS medium solids **VOC (g/l) at 21 s, 4 mm cup, 23°C**

References

1. Schneider, H.A., "Glass transition (theoretical aspects)" in Encyclopaedia of Polymer Materials, Editor, CRC Press, Boca Raton, Florida (1996).
2. Schmidt, H., Epple, U., Kubillus, U. and Becker, P., Proc. 21st Waterborne, High-Solids, and Powder Coatings Symp., New Orleans, LA 786 (1994).
3. Zezza, C. A. and Talmo, K. D., Journal of Coatings Technology, 1996, Vol. 68, No. 856, 49.
4. Epple, U. and Kuttler, U. 5rd Nürnberg Congress, Nürnberg (1999).