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Comparison of retarder solvents

used in high-solids automotive refinish clear coatings

Regulatory restrictions on volatile organic compound (VOC) emissions continue to impact industries that use solvents. One solution to the mandated VOC requirements in the coatings industry has been the development of high-solids (HS) coatings. Formulators choose this technology pathway because of the unmatched application versatility of solventborne coatings, i.e., suitability for shop and field conditions, precise control of evaporation rate, good tolerance for marginal surface quality, changing environmental conditions, high aesthetics, and excellent performance properties. The challenge to formulate a regulatory-compliant HS formulation that has same or better performance than previous coating technology is being addressed by creative resin chemistry and more careful solvent selection.

Global VOC trend

VOC requirements imposed upon coatings formulators and solventborne automotive refinishers have been a topic of discussion for many years in the U.S. The current VOC requirement for automotive clear refinish is 420 g/L for most of the country. However, China has recently begun to take action to improve air quality and environmental impact by following suit in limiting the amount of solvents allowed in automotive refinish clear coats. The implementation of this regulation will require Chinese automotive refinish shops to exercise more diligence when selecting a solvent for their formulation in order to avoid taxes and/or remain practicing in certain provinces.
On January 26, 2015, China's Ministry of Finance (MOF) and State Administration on Taxation (SAT) released the "Notice on Imposing Consumption Tax on Batteries and Coatings" ("Notice"). The tax took effect February 1, 2015.

Coatings discharging less than 420 g/L of volatile organic compounds during painting processes are exempt from the consumption tax. The rest are subject to this 4% consumption tax in the process of production, no matter what kind of coating (waterborne/solventborne) it is. For refinish coatings, Beijing, as capital of China, has taken the initiative to launch stricter regulation. The VOC content limits for clear coat must be lower than 480 g/L starting January 1, 2017, which means: 1) if VOC < 420 there is no need to pay the consumption tax; 2) if VOC is between 420 and 470, the consumption tax is required; 3) if VOC > 480, it is not allowed in the Beijing market whether the consumption tax is paid or not.

Since HS formulations require lower solvent loading, the criteria for selecting solvents that enable great film properties at lower solvent levels have gained importance. Methyl amyl ketone (MAK) and propylene glycol monomethyl ether acetate (PMA) are two retarder solvents that should be considered when formulating and/or applying high-solids refinish coatings. Both solvents exhibit traits that are desirable for VOC-compliant HS coatings. Some of these properties include low density, high solvent activity, and slow evaporation rate, resulting in better film formation. Xylene will be mentioned throughout much of this document as a reference due to its ubiquitous use in the industry.

Table 1. Comparison of physical and chemical properties[a]

Solvent	Evaporation rate *n*-BuOAc = 1	Functionality	Density, g/mL @ 20˚C	Vapor pressure, torr @ 20˚C	Dilution ratio[b] toluene	Hansen solubility parameters			MIR value g O_3/g VOC
						Nonpolar	Polar	Hydrogen bonding	
MAK	0.4	Ketone	0.818	2.14	2.6	16.2	5.7	4.1	2.36
PMA	0.4	Glycol ether ester	0.970	3.70	3.9	15.5	5.5	9.8	1.70
Xylene	0.7	Aromatic	0.870	6.60	—	17.6	1.0	3.1	7.64

[a] *Eastman solvent selector chart SOL-030A* [b] *Dilution ratio determined with RS ½-sec nitrocellulose.*

Challenges when developing high-solids coatings include increasing the solids content of the coating while meeting application viscosity requirements, balancing cure chemistry to achieve a suitable pot life with acceptable drying speed, and meeting or exceeding mandated coating properties (durability, chemical resistance, etc.) germane to a specific application. These challenges can be seen along the value chain from raw material and intermediate production to application.

Resin synthesis

Let-down solvent

The major binder component in a typical industrial clear coating is an acrylic, a polyester polyol, or a combination of the two. Thus their redesign represents the greatest opportunity to build solids content without appreciably increasing solution viscosity. Therefore, let-down solvent selection for high-solids coatings is extremely important, since less solvent is available for controlling paint atomization and rheology characteristics.

Table 2. Polyester resin HS-3-6T[a] viscosity profile[b]

Solvent	Brookfield viscosity, cP
MAK	808
PMA	1,930
Xylene	1,420

[a] HS polyester resin based on Eastman TMPD glycol (Eastman publication N-306). *[b] Eastman publication M-271C*

Polymerization solvent

Low-molecular-weight acrylic resins (oligomers) are prepared by free-radical polymerization of various acrylic monomers. The extent of monomer-to-polymer conversion and the molecular weight distribution (polydispersity) of the resultant polymer depend on the monomer/solvent ratio, monomer feed rate, polymerization temperature, initiator type and amount, chain transfer agents, and solvent chain transfer activity. The boiling point and chain transfer characteristics of the polymerization solvent are important variables in achieving these types of acrylic resins. Nitrogen blanketing and sparging are recommended to reduce color formation when using oxygenated solvents.

Table 3. Acrylic resin properties[a]

Property	MAK	PMA
Polymerization temperature, °C	145	145
Initiator	Lupersol 533[b]	Lupersol 533
Resin molecular weight (M_n)	3,800	4,100
Polydispersity (M_w/M_n)	1.8	1.9
Wt% solids	75	75
Viscosity	1,960	5,460

[a] Eastman publication M-271C *[b] Pennwalt*

Coating application

Solvent density

The density of a solvent has a major effect on the VOC content of a coating formulation. Lower density enables formulators to add more volume of solvent per unit weight of coating, thereby increasing free volume. The importance of this physical property is magnified by VOC regulations that limit the weight of solvent per volume of coating. Tables 4 and 5 show how VOC contribution is related to density in a sample 2K polyurethane formulation.

Table 4. Sample 2K polyurethane clear coat formulation[a]

Component	Wt%
Acrylic resin	55
Additives	2
NCO cross-linker	12
Solvent	31
Total	**100**

[a] *Eastman publication TT-70B*

Table 5. Solvent effect on VOC[a]

Solvent	Density, g/mL @ 20˚C	Coatings VOC, g/L
MAK	0.82	414
PMA	0.95	445
Xylene	0.87	435

[a] *Eastman publication TT-70B*

Solvent activity

It is essential that a VOC-compliant coating meet targeted viscosity specifications as required by the mode of application. If not met, the coating as applied will have unacceptable appearance and poor film formation. One important formulating tool for meeting paint viscosity requirements is via the selection of retarder solvents with great solvent activity across different resin families.

Table 6. Acrylic and polyester resin solubility comparison via Brookfield viscosity, cP at 25°C[a]

Solvent	Acrylic			Polyester
	Thermoset™ 70[b] Wt%	Paraloid™ B-66 40 Wt%	Elvacite™ 2010 20 Wt%	65 Wt%[c]
MAK	498	580	220	123
PMA	671	3000	275	254
Xylene	548	520	Insoluble	157

[a] *Resin Solubility Chart M-282D* [b] *Acrylic resin—80 wt% solids in MAK. The acrylic resin was then diluted to 70 wt% solids with the solvent shown. The final solvent was 58/42 wt% blend of MAK/solvent shown.* [c] *Polyester resin—85 wt% solids in PM acetate. The polyester was then diluted to 65 wt% solids with the solvent shown. The final blend was 35/65 wt% of PM acetate/solvent shown.*

The lower amounts of solvent used in high-solids coatings make them less forgiving than conventional coatings. This causes the available free volume for solvent to diffuse through the coating and decrease exponentially as the coating dries. The rate of increasing solution viscosity, as it relates to pot life, can determine any adjustments to be considered when spraying high-solids coatings. Proper solvent selection to compensate for this while allowing acceptable solution viscosity and rate is important.

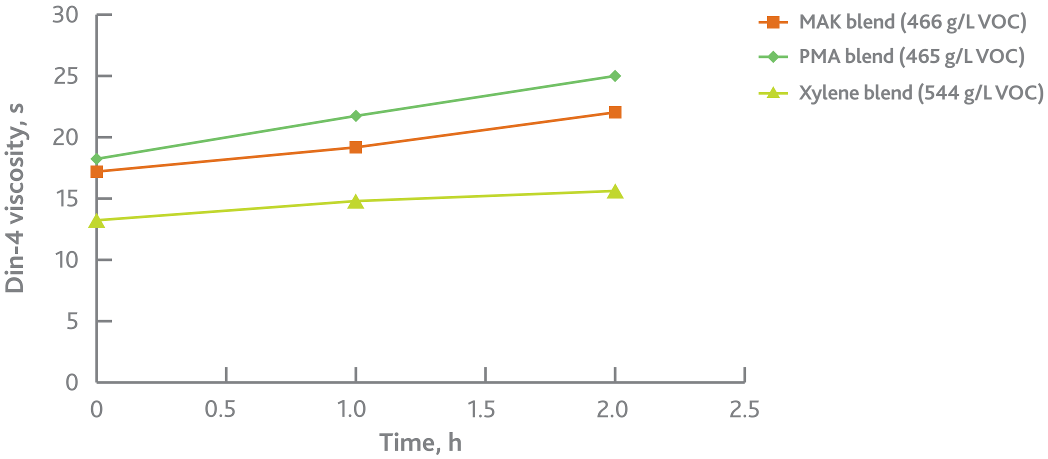
Table 7. Sample 2K polyurethane clear coat formulation[a]

Component (trade name)	MAK blend	PMA blend	Xylene blend
Acrylic resin (Setalux™ 1753)	46.94	46.94	39.52
Additives	0.15	0.15	0.13
NCO cross-linker (Desmodur™ 3300)	21.12	21.12	17.79
Thinner solvents (butyl acetate)	13.00	13.00	18.85
MAK	11.74	—	—
PMA	—	11.74	9.88
Xylene	7.04	7.04	13.83
Total, wt%	**100**	**100**	**100**
Solids, wt%	**49.98**	**49.98**	**42.08**
VOC, g/L	**466**	**465**	**544**
Test density, g/L	**982.1**	**1003.7**	**980.1**

[a] *TR-2015-18822*

Table 7 highlights differences between solids content, solution density, and VOC with respect to each retarder solvent used in the blend. Figure 1 shows viscosity increase over time for the formulations from Table 7.

Figure 1. Viscosity rate comparison for 2K polyurethane clear coat blends (TR-2015-18822)



VOC-exempt solvent—U.S. only

The aforementioned formulating principles are still valid when blending conventional solvents with VOC-exempt solvents. However, very few VOC-exempt solvents are suitable for coating applications, and all have notable properties that limit their use in high-solids coatings. Examples include acetone, methyl acetate, and *p*-chlorobenzotrifluoride. These solvents can be used to meet specified viscosity without contributing to the total VOC of the coating. Using VOC-exempt solvents is sometimes necessary in extremely restrictive regions, such as those governed by California's South Coast Air Quality Management District (SCAQMD). However, VOC-exempt solvents can have some drawbacks, particularly in undesirable or poor solvent activity. Table 8 shows how retarder solvent choice can affect the amount of VOC-exempt solvent needed to adjust to a desired viscosity and a total VOC limit of 420 g/L.

Table 8. Example of 2K polyurethane clear coat comparing VOC-exempt usage based on retarder solvent choice

Component (trade name)	MAK blend	PMA blend
Acrylic resin (Setalux™ 1907)	33	29
Polyester polyol resin (Setal™ 1603)	4	3
NCO cross-linker (Tolonate™ HDT LV)	20	18
Total solids	**57**	**50**
Additives (Tinstab™ BL 277)	3	2.5
Thinner solvents	12.5	10
MAK	27	
PMA		20.5
p-Chlorobenzotrifluoride	0.5	17
Total, wt%	**100**	**100**
VOC, g/L	**420**	**420**
Ford 4-cup viscosity, s	**20**	**20**

Conclusion

More stringent global VOC regulations are causing formulators and automotive refinishers to exercise more scrutiny when selecting solvents for each step in their process, from synthesis to application. Choosing the correct retarder solvent can:

1. Reduce the VOC content of the resin at synthesis, providing higher solids per volume to the formulator
2. Decrease shipping weight and cost for the same solids content
3. Increase the coverage per coat applied due to higher solids, which reduces the overall energy expended to apply a refinish coating

Lower energy expense is seen not only in the synthesis and application steps but also at the solvent production step, which results in lower greenhouse gas (GHG) emissions. Some preliminary life-cycle assessment (LCA) studies show that cradle-to-grave production of PMA results in more than twice the GHG emissions of MAK, which is more than twice that of xylene.

Table 9. Relative GHG impacts of solvent production

	Normalized GHG[a]/L
Solvent	MAK = 1[b]
MAK	1
PMA	3
Xylene	0.2

[a] 100-year global warming potential (GWP) is a common GHG impact assessment metric used in life-cycle analysis. [b] These values are normalized to MAK using internal calculations for GHG emission of Eastman manufacturing processes and database values, which may not represent other suppliers. The internal calculations from Eastman's LCA group have not been third-party verified and are intended to show the order of magnitude differences between the GWP of the different solvents.

When greenhouse gas impacts of solvent production, solvent efficiency improvements, and lower VOC emissions per kilogram are considered, the environmental benefits can be substantial. Regulatory constraints and global sustainability trends can impact how formulators could benefit by choosing the proper retarder solvents for HS coatings that reduce the environmental impact without sacrificing performance, quality, and color-matching excellence for HS automotive refinish clear coats. Factors, from solvent activity and density to environmental impacts, should be considered when evaluating retarder solvents. Balancing the parameters that are critical to quality to meet today's regulatory constraints in the automotive refinish industry is paramount.

Eastman methyl *n*-amyl ketone (MAK) has a high solvent activity, slow evaporation rate, low density, low surface tension, and high boiling point. These properties make MAK a very good solvent for cellulosic lacquers, acrylic lacquers, and high-solids coatings. Because regulations limit the weight of solvent per gallon of coating, formulators favor the use of low-density solvents that help reduce the VOC content of a coating. MAK is lower in density than ester, aromatic hydrocarbons, and glycol ether solvents with similar evaporation rates. The low density and high activity of MAK are significant advantages when formulating high-solids coatings to meet VOC guidelines.

For more information, visit **www.eastman.com/solvents**.

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