Reducing VOC Levels in Aerosol Hairspray Products

Various propellant options allow the reformulator to meet tightening regulations

SPRAY
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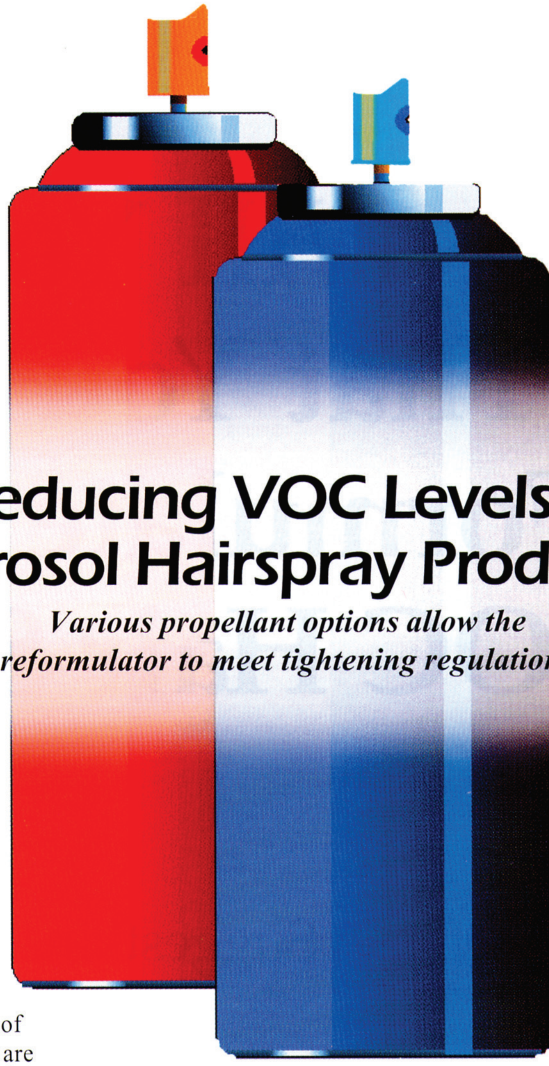

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Introduction

In recent years, concerns over ground level smog from volatile organic compounds (VOCs) have had a dramatic impact on the way aerosol products are formulated. As regulations continue to tighten, new concepts and techniques for reducing VOCs while maintaining product efficacy remain a challenge. In attempting to meet regulations limiting the VOC content of consumer products, many formulators are developing products with higher water levels.

Propellants have been a key issue in meeting VOC regulations, and over the years, new propellants and innovative ways of using these propellants have been introduced in the industry. New propellants mean different properties and characteristics that affect the basic strategies for reformulating aerosol products. And with increasing water levels, new approaches are evolving to expand available options for meeting regulations.

Dymel® Propellants

Two propellants that were brought to market to help fill industry needs in addressing environmental issues are 1,1-difluoroethane (HFC-152a) and dimethyl ether (DME). DuPont markets HFC-152a as Dymel® 152a and dimethyl ether as Dymel® A. As formulators continue to evaluate options for reducing VOCs in aerosol products, new approaches are being investigated to achieve required VOC levels while minimizing impact on product performance.

Dymel® 152a and Dymel® A offer options when used individually or together. Using Dymel® 152a and Dymel® A together has not been a widely explored possibility, but some synergies in high water systems make this combination worth considering.

VOC Reduction Strategies

Dymel® 152a and Dymel® A have been used for a number of years to help reduce the VOC content of aerosol products. Typically, they have been considered separately for reformulation to lower VOC levels.

Dymel® 152a is not a VOC, so that it can be used to simply replace a VOC component. Dymel® 152a is used in zero or low-water systems alone or blended with traditional hydrocarbon propellants.

Dymel® A, on the other hand, is a VOC, but its strong affinity for water allows increased use of water to reduce overall VOC content of an aerosol formulation. The Dymel® A/water combination is used in high water systems, and again, can be used with hydrocarbon propellants. The solubility of hydrocarbons in water is relatively low, however, so that the high water content will limit hydrocarbon additions.

As regulations continue to drive VOC levels down in aerosol products, water is becoming a larger part of modified formulations. With increased use of water, it

Physical Properties of Dymel® Propellants

Propellant	Dymel® A	Dymel® 152a
Formula	CH_3OCH_3	CH_3CHF_2
Molecular Weight	46.1	66.1
Boiling Point (°F)	-13	-13
Vapor Pressure (PSIG)		
70°F	63	63
130°F	174	177
Density (G/CC @ 70°F)	0.66	0.91
Flammable Limits in Air (VOL %)	3.3 - 18.0	3.9 - 16.9
Solubility in Water (Wt.%) @70°F & Autogenous Pressure	35	1.7

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becomes more difficult to achieve desired solubilities, and single phase propellant/solvent systems. As VOC levels become more stringent, a third approach can help: Dymel® A and Dymel® 152a combinations.

Dymel® A enhances solubility in aqueous systems because of its ability to hydrogen bond with water. Hydrogen bonding is a weak to moderate attractive molecular force that exists between a hydrogen atom and the electrons of electronegative atoms, like oxygen and fluorine.

Of the propellants used in low VOC systems, Dymel® A exhibits the strongest hydrogen bonding properties, thus its high water solubility. Conversely, hydrocarbons have no hydrogen bonding properties, and correspondingly low water solubility. Between Dymel® A and hydrocarbons, Dymel® 152a exhibits weak hydrogen bonding properties, but even these weaker forces help improve solubility in aqueous systems. Table 1 summarizes hydrogen bonding and solubility parameters for these propellants, showing the impact on water solubility. Kauri-Butanol value is a general measure of a compound's solvency characteristics; high values indicate high solubility. Note that while Dymel® 152a water solubility is low, it is still up to 30 times higher than hydrocarbons.

Triangular diagrams have been used to map solubility envelopes for multicomponent propellant/solvent systems, and can be used here to demonstrate the synergistic effect of Dymel® 152a in aqueous systems.

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Figure One
Vapor Pressures and Solubility of Dymel® A/A-31 (50/50) with Ethanol and Water at 70°F

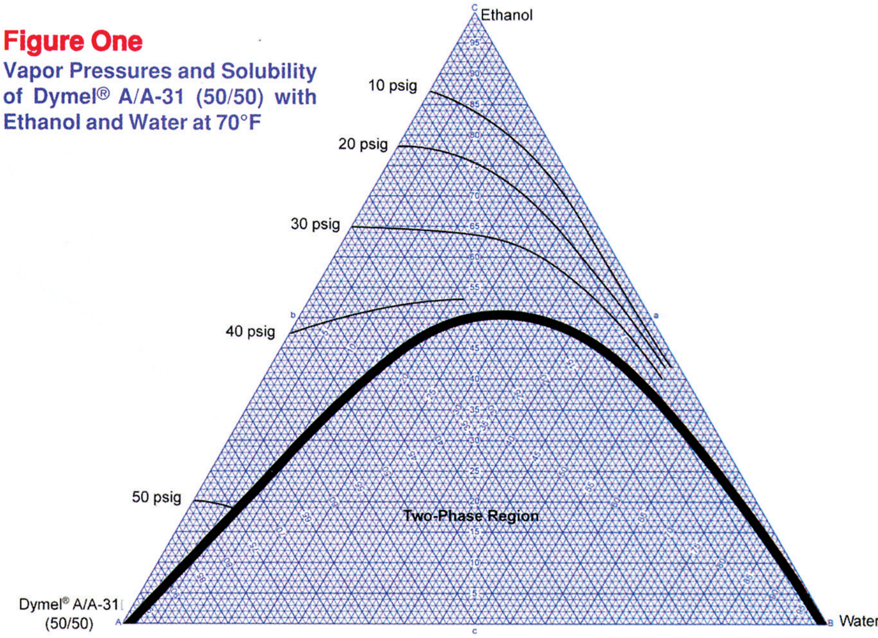


Figure Two
Vapor Pressures and Solubility of Dymel® A/152a (45/55) with Ethanol and Water at 70°F

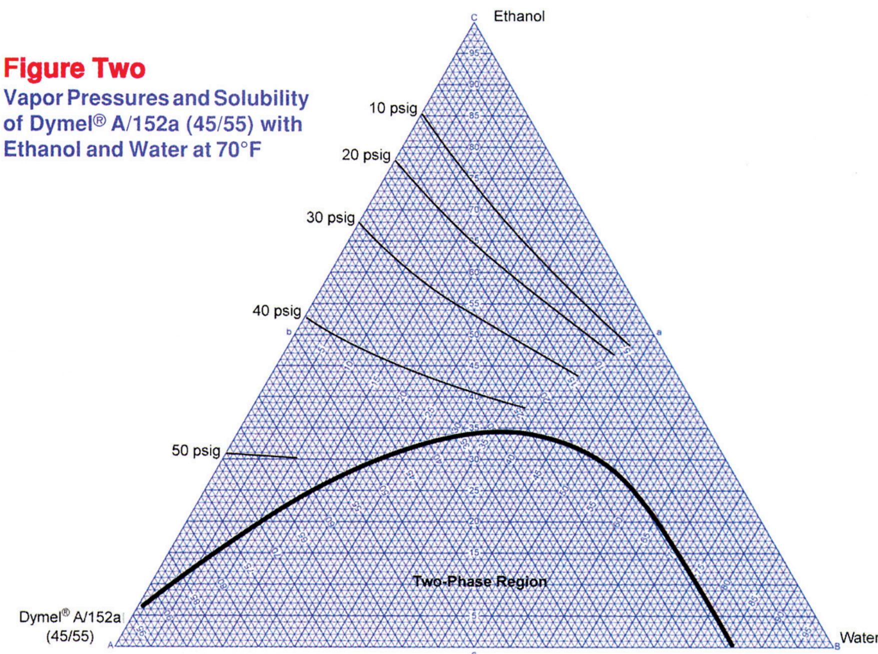


TABLE 1
Hydrogen Bonding and Solubility Properties of Aerosol Propellants

	Solubility (wt%)		Solvent Properties	
Propellant	Propellant in-Water	Water in Propellant	Hydrogen Bonding Capacity	Kauri-Butanol Value
Dymel® A	35	6	Strong	60
Dymel® 152a	.28	.17	Weak	20
Propane	.0079	.0168	None	15
n-Butane	.0080	.0075	None	20
iso-Butane	.0080	.0088	None	18
iso-Pentane	.0084	.0063	None	21

Low VOC Hairsprays

Continued from preceding page

Figures 1 and 2 show solubility envelopes for ethanol, water, and a propellant combination. In Figure 1, the propellant combination is a 50/50 mixture of Dymel® A/ A-31; in Figure 2, the propellant combination is a 45/55 mixture of Dymel® A/ Dymel® 152a. Comparing the two diagrams, note how the 2-phase region is reduced when Dymel® 152a is substituted for A-31, even with slightly less Dymel® A in the mixture.

Figures 3 and 4 show the same effect. The system again is ethanol, water, and a propellant combination. Figure 3 is a propellant mixture of 75/25 Dymel® A/A-46, and Figure 4 shows substitution of Dymel® 152a. Again, the 2-phase region is reduced with Dymel® 152a, even with lower Dymel® A levels.

This synergistic effect of Dymel® 152a with Dymel® A can be used advantageously to help improve miscibility of aqueous systems while achieving lower VOC content.

Figure Three

Vapor Pressures and Solubility of Dymel® A/A-46 (75/25) with Ethanol and Water at 70°F

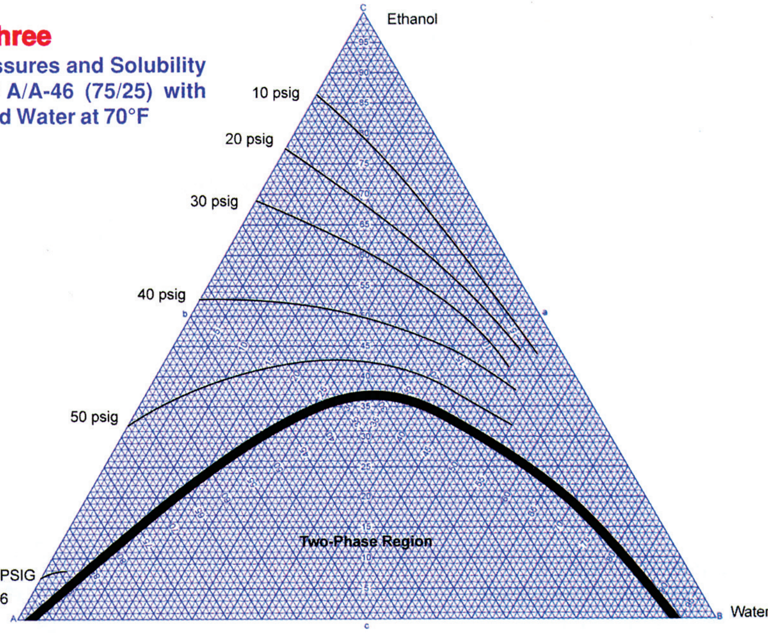
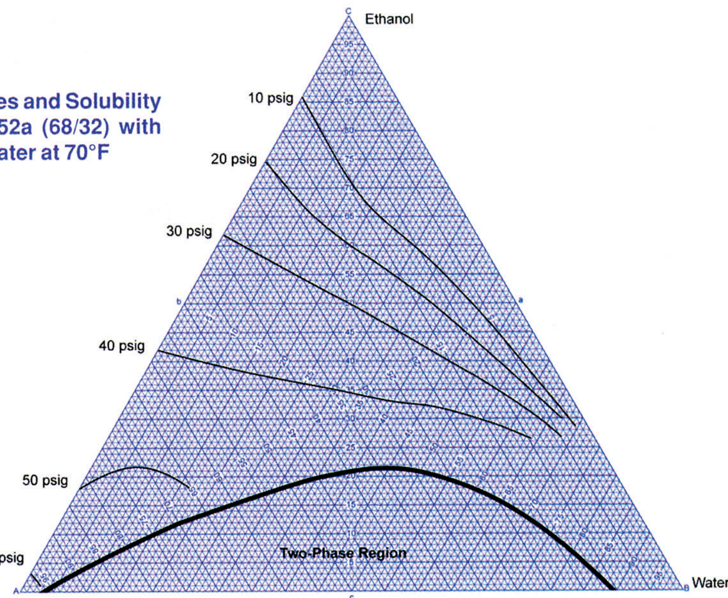


Figure Four

Vapor Pressures and Solubility of Dymel® A/152a (68/32) with Ethanol and Water at 70°F



Formulating 55% VOC Hairsprays

The current challenge for hairsprays is the 55% VOC regulation taking effect June 1, 1999. In developing low VOC formulations, the traditional approach has been to focus on anhydrous or low-water Dymel® 152a systems, or high-water Dymel® A systems. These approaches can result in a wide difference in formulation costs and performance. Taking advantage of synergies between Dymel® 152a and Dymel® A, blends of these propellants can offer a balance of cost and performance. While advances in resin technology help maintain performance with high water, Dymel® 152a/Dymel® A blends can potentially reduce the quantity of water required. Recognizing that water makes it difficult to achieve desired performance, techniques to moderate water additions bring performance value to new formulations. These intermediate water formulations are being studied to better understand the relationship of cost versus performance.

Table 2 provides hairspray formulation examples that illustrate starting points for this type of evaluation. Blends of Dymel® 152a/Dymel® A could be included in existing programs to understand what performance improvements are achievable with dryer sprays. Initial work encourages further investigation along this line.

TABLE 2
Example hairspray formulations using Dymel® A and Dymel® 152a

Component	High Water (wt. %)	Intermediate Water (wt. %)			Low Water (wt. %)
Resin	5[1]	5[1]	5[2]	7[3]	5[1]
Ethanol	25	35	33	35	55
Water	39	29	27	16	9
Surfactants/Additives	1	1	2	2	1
Dymel® A	30	20	22	20	—
Dymel® 152a	—	10	11	20	30

1. acrylate/hydroxyacrylate copolymer
2. amide/acrylate/methacrylate copolymer
3. acrylate copolymer

Conclusion

As more stringent VOC regulations drive formulation innovation, synergistic blends of Dymel® 152a/Dymel® A can provide useful benefits. Though blends increase the complexity of aerosol formulations, the trade-off can be improved performance and/or lower cost. This is especially evident for 55% VOC hairsprays. ❑