

The Exaggerated Demise of Solvents

Can solventborne systems comply with regulatory requirements without compromising performance?

Once thought to be on the verge of extinction, solvents continue to play a significant role in paint application and pretreatment. Despite more stringent regulations, solventborne coatings continue to offer the required paint performance while satisfying environmental concerns.

Myths and misconceptions

Myth No. 1 *Solvents will be completely eliminated over the next few years.*

While that may have seemed the case during the frenzy of the 1990s, government and industry have realized the need to balance environmental stewardship and business concerns. For example, poorly performing paints, though low in VOCs, require more frequent application. This actually releases more overall VOCs when compared to the less frequent application of higher performance paints that contain more VOCs. Low- or zero-VOC technology is impractical for most coating applications, making solvents an essential ingredient in coatings that meet application and performance requirements and comply with rigorous air quality regulations.

Myth No. 2 *Solvents, in general, have largely contributed to ozone formation.*

Actually, solvents emitted from coating facilities are only a minor contributor to ground-level ozone formation, the main cause of smog. In urban areas, VOCs come from numerous sources, including fuel-burning emissions from automobiles, refineries, biogenic sources and some smaller factories. Another major source of VOC's, both in rural areas and in many urban areas is biogenic emissions from natural vegetation. Furthermore, in almost all parts of the country, outside the major metropolitan areas, NOx is the rate-limiting factor in ozone creation and changes in manmade VOC emissions make little or no difference in ozone levels.

It is important to differentiate between ground-level ozone and stratospheric ozone. Ground-level ozone is produced by a photochemical reaction between chemicals and sunlight. More common during the summer months, ground-level ozone occurs in the lower atmosphere, or troposphere. Chemical emissions that contribute to this ground-level ozone formation are considered ozone-forming chemicals. Upper-level, or stratospheric, ozone protects the earth from harmful UV rays. One solvent previously used in the paint industry (1,1,1-trichloroethane), was identified as a contributor to upper-level ozone depletion and is classified as an ozone-depleting substance (ODS).

Myth No. 3 *Solvents continue to be added to the EPA's HAP and VOC list.*

No chemicals have been added to the EPA HAPs list since its inception in 1990, and we are not aware of plans to add solvents to this list. In fact, petitions have been filed requesting removal of MEK, MIBK and EB glycol ether from the list of HAP compounds. On May 30, 2003, EPA published a [Federal Register notice](#) proposing to delist MEK from the HAPs list. A ninety-day comment period followed, and we are awaiting EPA's final decision on the matter. A decision on whether or not to delist EB glycol ether is expected in late 2003 or early 2004. An addendum to the MIBK petition, including new toxicological test results was filed with the EPA in October, 2003. A decision on MIBK's HAP status is not expected until 2004-5.

Acetone and methyl acetate have been exempted from regulation as VOCs by the EPA and most states, and a petition to delist t-butyl acetate is currently under consideration by the EPA.

Myth No. 4 Solvent selection is not critical when formulating high-solids systems.

Increased use of high-solids systems has shifted emphasis toward the resin system and its role in coatings performance. However, solvents continue to play an integral role in the aesthetics and quality of an applied film. In fact, solvent selection is more critical than ever in developing low-VOC coatings because less solvent is present in the final formulation. Oxygenated solvents such as MPK and MAK, which have high activity and low density, are very useful in developing high-solids coatings with virtually no negative impact on meeting more restrictive VOC limits.

Advances in alternatives to hydrocarbon solvents

To fully comprehend the strides that have been made in solvents since the advent of the Clean Air Act of 1970 and subsequent regulation, consider solvent basics. Solvents fall into three broad categories: oxygenated (esters, alcohols, ketones, glycol ether esters and glycol ethers); hydrocarbon (aromatic and aliphatic); and chlorinated (methylene chloride and trichloroethylene, for example).

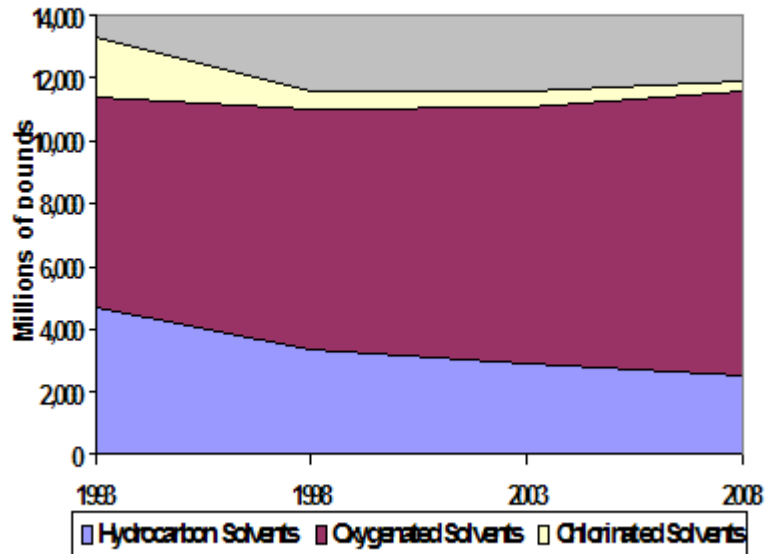
Solvents may contribute to ground-level ozone formation in varying amounts, although a few, including acetone and methyl acetate, have been ruled VOC exempt. Certain chlorinated solvents, such as 1,1,1-trichloroethane (also known as methyl chloroform), have been linked to ozone depletion and banned from use in coatings (Title VI-CAA). Toluene, xylene, methylene chloride and trichloroethylene are commonly used in cleaning and surface treatment applications and are also listed as HAPs. As a result, formulators have been using alternative solvents for cleaning and pretreatment.

Since 1993, hydrocarbon solvent demand has decreased by 36% and is projected to decrease by another 15% by 2008 (**Table 1**). Chlorinated solvent demand has decreased by 75% since 1993 and is forecasted to decrease by another 40% by 2008. Oxygenated solvents, on the other hand, have experienced a 20% increase since 1993 and are projected to grow approximately 2% annually through 2008.

Oxygenated solvents, most of which are non-HAPs, are often "guilty by association" simply because they bear the "solvent" classification and associated stigma. These solvents have demonstrated coatings performance and appearance characteristics equal to that of their HAP counterparts. Some oxygenated solvents, such as n-Butyl Propionate, have been blended with aliphatic hydrocarbon solvents to successfully satisfy HAP and VOC regulations without compromising performance or aesthetic appearance.

Table 1

Changing Demand for Solvents



Source: Eastman Chemical Co.

Reformulating with non-HAP solvents

A study conducted by Eastman Chemical Co. (Kingsport, TN) demonstrates that reformulating with oxygenated solvents can significantly reduce or eliminate solvent-related HAPs while maintaining virtually the same performance characteristics. The study included Methyl n-Amyl Ketone (MAK), Isobutyl Isobutyrate (IBIB) and n-Butyl Propionate as substitutes for xylene (**Table 2**).

Depending on the level of HAP solvent in a given formulation, the best substitution may involve blending non-HAP solvents to achieve the desired application and film formation properties while complying with environmental guidelines. Using the xylene replacement example, Eastman used a software program that enabled the use of solubility parameters to determine the miscibility characteristics of polymers and solvents. By establishing a profile for a xylene-based control blend, the software generated a non-HAP solvent blend substitution for a specific resin system.

Evaporation-rate characteristics are equally as important as solubility. To ensure that the solvent blend provided adequate flow and quality film formation, Eastman used two important rate values: relative evaporation rate and "weight % solvent composition versus weight % of blend evaporated." The software provided solvent blend composition and several weight-loss percentages, in addition to the solubility parameters at each composition level. With such information, formulators can substitute solvents and solvent blends while satisfying performance and regulatory requirements.

Table 2

Suggested Solvent Blend Replacements for Xylene

Composition, Wt %	Control	MAK/Aliph.Hydrocarbon	n-BuOPr/Aliph. Hydrocarbon	IBIB/Aliph.Hydrocarbon
Xylene	100.0	—	—	—
MAK	—	57.1	—	—
n-Butyl Propionate	—	—	63.2	—
IBIB	—	—	—	56.4
VM&P Naphtha 66*	—	42.9	36.8	43.6
	—	100.0	100.0	100.0
Solvent Blend Properties				
Evaporation Rate (n-BuOAc=1)	0.7	0.7	0.7	0.7
Hansen Solubility Parameters				
Dispersion	8.60	7.68	7.58	7.40
Polar	0.50	1.55	0.96	0.75
Hydrogen Bonding	1.50	1.11	1.73	1.55
Total	8.74	7.91	7.83	7.60
Wt/Gallon	7.17	6.59	6.91	6.75

**The aliphatic hydrocarbon of choice should have a very low HAP content and an evaporation rate similar or higher than xylene.*

Current developments in EPA regulation

It is important to note that regulatory compliance and coatings performance do not have to be mutually exclusive goals. Currently, the EPA continues to develop industry-specific regulations based on “maximum achievable control technology” (MACT).

MACT standards are already in effect for the aerospace, magnetic tape, printing and publishing, shipbuilding and wood furniture industries.

Table 3 shows the MACT rule promulgation status affecting several coatings industry segments as of August 2002. Emission standards rules generally are finalized one year after proposal and affected industries have 60 days from the proposed standard issuance date to comment. HAP limits go into effect three years after formal enactment. Visit <http://www.epa.gov/ttn/atw/coat/coat.html> for the latest on MACT rule developments.

Table 3

MACT Rules Promulgation Status

Industry	Promulgation Status	Comments
Metal Coil Large Appliance	Final rule	Existing Facilities must comply 7/2005
Paper & Other Web Coatings	Final rule	Existing Facilities must comply 6/2005
Metal Furniture Wood Building Products Misc. Metal Parts & Products (MMPP)	Final rule	Existing Facilities must comply 5/2006 Existing Facilities must comply 5/2006 Signed but not published in the Federal Register. Estimated to be published in the next few months
Fabric Coating Misc. Plastic Part & Products Auto & Light Duty Truck Metal Can	Final Rule Final Rule Correction Notice Final Rule TBA	Public Hearing & Comment Period Extension (NESHAP Metal CAN) Signed but not published

Additional developments in the use of the Incremental Reactivity (IR) approach could potentially offer more latitude to formulators and finishers. IR is based on the premise that individual solvents are not equal in their potential to form ozone. Regulators may consider developing a scale or solvent tiers ranked by IR. Thus, a formulator may be allowed to add more of a solvent with a lower IR and still comply with regulatory guidelines.

These reactivity-based rules offer better air quality control by helping predict any given solvent's ability to produce ozone. They further define the measurable impact of a VOC to produce ozone as opposed to general pounds-per-gallon or grams-per-liter across-the-board VOC limitations, which, depending on the solvent, may have very little impact on improving air quality. MIR (Maximum Incremental Reactivity, one measure of IR) rules are in effect under California's Air Resource Board (CARB) regulations for aerosol coatings.

Solvent substitution—the business case

There are obvious performance properties that only solvents can offer, particularly for industrial coatings applications. Many such requirements preclude switching to a waterborne or powder coating system. Often, in cases where a coatings system change is technically feasible, the capital investment far outweighs the cost of reformulation.

Solvent substitutions have no effect on existing capital equipment and provide the flexibility to accommodate a wider variety of application techniques and finish aesthetics. From the rich depth of furniture finishes to the high distinctness-of-image in pigmented automotive coatings, solvent substitution is a viable and cost-effective alternative.

Any capital-intensive process requires maximum throughput and capacity to ensure optimum return on investment. Solventborne systems are compatible with virtually all substrates, offering the ability to utilize capacity with a greater variety of parts. Oxygenated, non-HAP solvents are designed to help minimize process changes. This, in turn, can help maintain throughput, because operators are already familiar with the process and can use existing equipment.

Other smaller capital investments in equipment upgrades can help minimize overall emissions while increasing efficiency. For example, high-volume low-pressure spray gun technology may offer better targeting and transfer rates, which tend to reduce overspray and waste.

Abatement programs aimed at reducing emissions can also represent a lower cost alternative to major plant and equipment investments. Larger solvent users may consider installing emissions control equipment such as VOC oxidation units, which are analogous to the catalytic converter on automobiles.

Additionally, many coatings formulators have installed systems to reclaim and then reuse solvents. While more commonly reused in ink formulations, reclaimed solvent can be used to fuel heating systems in coatings applications.