# The Exaggerated Demise of Solvents

**Can solventborne systems comply with regulatory requirements without compromising performance?**

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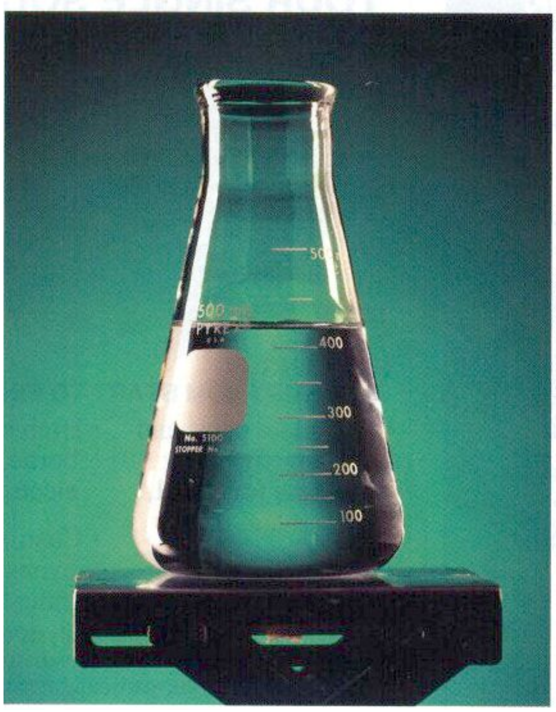
Once thought to be on the verge of extinction, solvents continue to play a significant role in paint application and pretreatment. Despite more stringent regulations, solventborne coatings continue to offer the required paint performance while satisfying environmental concerns.

### 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 contains 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.



***Solvents continue to play an important role in the coatings industry, providing both performance and regulatory compliance.** (Photos courtesy of Eastman Chemical Co.)*

**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. More prevalent in metropolitan areas, VOCs come from numerous sources, including fuel-burning emissions from automobiles, refineries, biogenic sources and some smaller factories.

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 is in the lower atmosphere. Chemical emissions that contribute to low-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-trichlorethane), 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.*

In fact, petitions have been filed requesting removal of MEK, MIBK and EB glycol ether from the list of HAP compounds. A *Federal Register* notice presenting the administrator's decision on MEK and EB glycol ether is expected in the latter half of 2002. Acetone and methyl acetate have been exempted as VOCs and t-butyl acetate is currently under consideration.

**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).

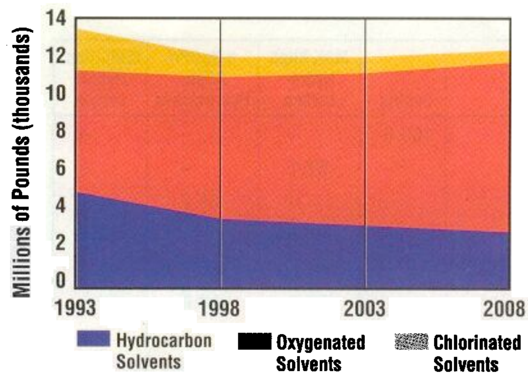
Solvents contribute to ground-level ozone formation, although a few, including acetone and methyl acetate, have been ruled VOC exempt. Certain chlorinated solvents, such as 1,1,1-trichloroethane (also known as methyl chloroform), have been linked to ozone depletion and banned from use in coatings (Title 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

**Table 1**

**Changing Demand for Solvents**




*Source: Eastman Chemical Co.*

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.

### 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.

**Table 2**

## Suggested Solvent Blend Replacements for Xylene

| Composition, Wt. % | Control | MAK/Aliph Hydro-carbon | n-BuOPr/ Aliph. Hydrocarbon | IBIB/Aliph. Hydro-carbon |
|---|---|---|---|---|
| Xylene | 100.0 | – | – | – |
| MAK | – | 57.1 | – | – |
| n-Buty 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 to or higher than xylene.*

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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 vs. 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.

### Current developments in EPA regulation

It is important to note that reducing overall emissions is the goal. Therefore, 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.

Additional developments in the use of the Maximum Incremental Reactivity (MIR) approach could potentially offer more latitude to formulators and finishers. MIR is based on the premise that individual solvents are not equal in their potential to form ozone. Regulators may consider developing solvent tiers ranked by MIR. Thus, a formulator may be allowed to add more of a solvent with a lower MIR 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 rules have been in effect (June 1, 2002) under California's Air Resource Board (CARB) for general-purpose aerosol coatings. Similar rules take effect for the specialty aerosol coatings category on Jan. 1, 2003.

### 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

**Table 3**

## MACT Rules Promulgation Status

| Industry | Promulgation Status | Comments |
|---|---|---|
| Metal Coil<br>Large Appliance | Implementation | Final rule |
| Paper & Other Web Coatings | Final rule stage | Awaiting administrator signature |
| Metal Furniture<br><br>Wood Building Products<br><br>Misc. Metal Parts & Products (MMPP) | Proposed rule stage | Review of comments submitted<br>Comments submitted |
| Fabric Coating<br>Misc. Plastic Part & Products<br>Auto & Light Duty Truck<br>Metal Can | Pre-proposal rule stage | |

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.

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