

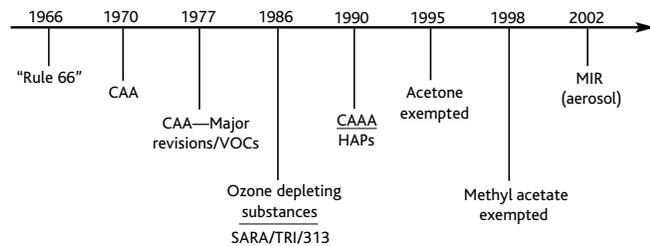
Challenges and solutions Solvent technology for present and future air quality regulations

Based on U.S. air quality regulations and definitions

Background

The process of solvent selection and blend design for coatings products continues to be dynamic. Formulators have always designed new solvent blends for performance improvements, cost reductions, alternative backup blends and product safety concerns. However, as Figure 1 illustrates, for the last 35 years, regulatory issues have been the primary driver for solvent changes. More recent regulatory requirements have imposed additional restrictions on the use of solventborne coatings.

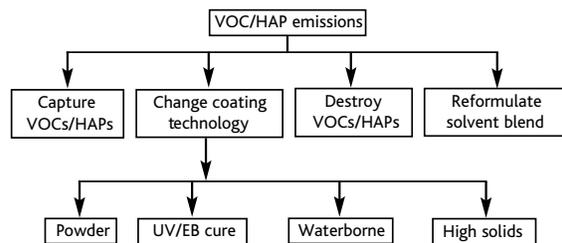
Figure 1 Regulatory timetable



Increasing regulatory demands on the coatings industry spurred the development of new formulating strategies to satisfy air quality regulations. These included:

- Continuing with the existing coating formulations and investing in emission control equipment.
- Selecting an alternative coating technology such as water based, powder, or UV cured.
- Reformulating current solventborne coatings using alternative solvents or solvent blending.

Figure 2 Developing compliant coatings strategies



The choice of alternative solvents or solvent blends can be greatly simplified by the use of computer software that allows the user to match or exceed product performance/ environmental requirements. The refinement of the solubility parameter concept in the early 1960s helped immensely in predicting resin/solvent solubility.¹⁻⁶ This concept, when combined with established evaporation rate models, enabled the development of software that allowed formulators to quickly design a solvent replacement blend for a selected coating.

This paper presents a review of the past and present regulatory changes and the evolving solvent substitution options for those who desire to optimize the performance and environmental properties of a solventborne coating.

The 1960s—Rule 66

The first air quality regulation impacting solvent selection for coatings was Rule 66, adopted by the Los Angeles Air Pollution Control District. This rule was enacted to limit the emission of a select list of solvents believed to be more photochemically reactive than others. Rule 66 included new guidelines defining the maximum allowable concentrations of the photochemically reactive solvents in a coating composition. Each listed solvent had its own maximum limit, and the total composite of all photochemically reactive solvents in the blend could not exceed 20 vol%. Table 1 lists the commonly used nonexempt solvents and their maximum allowable concentration according to Rule 66. All other solvents were classified as exempt.

Similar regulations were adopted in other regions of the country as well. In addition, federal and military coating specifications were changed to reflect the new solvent selection guidelines.

Table 1 Examples of nonexempt solvents under Rule 66

Maximum allowable concentration (vol%)		
5%	8%	20%
Isophorone	Xylene	Methyl isobutyl ketone
Mesityl oxide	Most aromatic high-flash naphthas	Methyl isoamyl ketone
		Ethyl isoamyl ketone
		Diisobutyl ketone
		Diacetone alcohol
		Trichloroethylene
		Ethyl benzene
		Toluene

Note: Aggregate volume of nonexempt solvents should not exceed 20% in formulation.

The biggest challenge that Rule 66 posed to coating formulators was determining how to reduce the aromatic hydrocarbon and branched chain ketone content of the solvent blend. The use of computer programs was invaluable in this endeavor. The most popular reformulating approach was to develop blends that contained the maximum allowable content of the nonexempt solvents while the remainder of the blend consisted of combinations of esters, alcohols, and aliphatic hydrocarbons, which were all exempt. Formulators had to work to maintain the proper balance of evaporative and solvent activity characteristics while minimizing cost increases.

Solvent suppliers assisted coating firms in this reformulation effort. For example, Eastman introduced the straight chain ketones—Eastman MAK (methyl *n*-amyl ketone) and Eastman MPK (methyl *n*-propyl ketone)—to provide similar solvent activity when replacing the nonexempt branched chain ketones.

Rule 66 restricted the amount of nonexempt compounds in a solvent blend but did not restrict the total amount of solvent emitted to the atmosphere. The solids content in the coating was not an issue, only that the coating satisfied the solvent requirements of the rule.

Rule 66 encompassed the entire finishing industry. While it represented a reasonable requirement for some, it was problematic for others, because its guidelines did not differentiate between the formulating requirements of various industries. As a result, Rule 66 placed a greater reformulating burden on some industries than it did on others.

That said, the impact of Rule 66 on solvent selection was relatively minor. The playing field was not always level, but formulators were able to make blend adjustments with relative ease, albeit at a cost premium. In the 1970s, many states adopted some type of regulation based on the format of the rule. In some states, coating firms are still required to meet these guidelines; though in most places, newer guidelines have superseded the Rule 66 requirements.

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Based on U.S. air quality regulations and definitions (Continued)

The 1970s—the Clean Air Act and the EPA

Despite the regulatory changes of the 1960s, air quality across the country was not improving. The environmental indicators chosen to help regulate solvent selection for coatings continued to evolve. For the first time, federal legislation was developed to address these changing environmental concerns.

Congress enacted the Clean Air Act (CAA) of 1970. The CAA included three principal actions:

1. Creating the United States Environmental Protection Agency (EPA) and authorizing it to establish national standards for ambient air quality.
2. Directing the states to work toward the attainment of these national standards through the development of state implementation plans known as “SIPs.”
3. Requiring that new emission sources install best available control technology (BACT) regardless of local ambient air quality.

CAA amendments of 1977—revisions focus on emissions

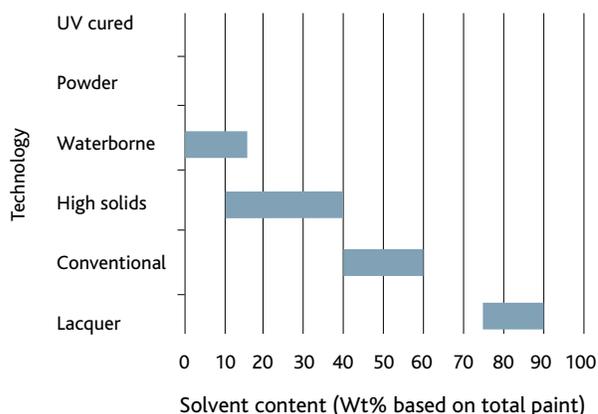
In 1977, major revisions to the CAA were implemented. They included the first federal guidelines restricting the emission of volatile organic compounds (VOCs) from coatings. A VOC was generally defined as any organic compound that participates in atmospheric photochemical reactions; however, the EPA designated some compounds with negligible photochemical reactivity as VOC exempt.

Ground-level ozone, the main ingredient in smog, was known to be a product of a series of reactions of nitrogen oxides with VOCs in the presence of sunlight. Since organic solvent emissions contributed to ozone formation, the EPA established a new objective: the reduction of solvent emissions to lower the ozone level in the troposphere to an acceptable level. To address this objective, the EPA published control technique guidelines (CTGs) for the control of VOCs within specific finishing industries.

CTGs proposed to reduce VOC emissions by limiting the pounds of solvents per gallon of coating. States were given a deadline to submit to the Federal EPA their State Implementation Plans for complying with the air quality standards. Though many states adopted regulations following the EPA’s CTG guidelines, each state was required to implement the guidelines individually, depending on the pollution situation within that state.

The CAA revisions of 1977 proposed that solvent emissions be controlled by either of two approaches: (1) process and material changes or (2) add-on engineering equipment. Coating companies responded by investing in the development of lower VOC coating chemistries and thus began to formulate coatings with reduced total solvent content (see Figure 3).

Figure 3 Coatings technology



The new regulations spurred two new developments in solventborne coatings technology: high-solids coatings and increased emphasis on reduced-density solvents.

High-solids coatings

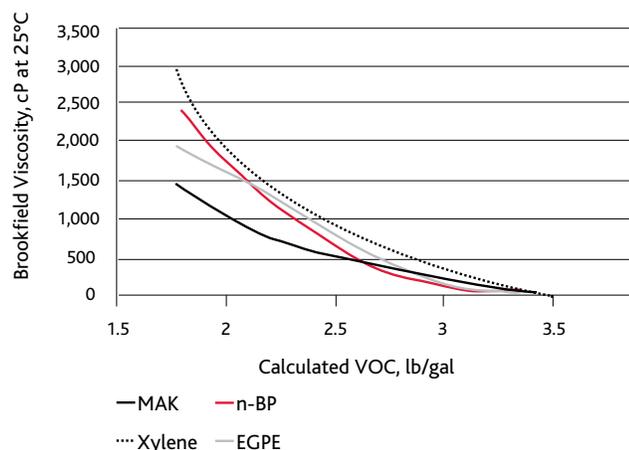
One popular approach taken by coating manufacturers to reduce solvent emissions was the development of high-solids coatings. Choosing the correct solvent balance, however, was crucial to the successful application of high-solids coatings. It required the increased use of oxygenated solvents such as ketones to achieve the proper application viscosity at the required VOC limits. These polar solvents are effective in minimizing the association of functional groups on the resin, thereby providing lower solution viscosity.

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Figure 4 provides some viscosity reduction data on a high-solids resin with selected solvents. Ketones such as Eastman MAK are particularly effective in reducing the solution viscosity of high-solids coatings while providing satisfactory application characteristics.⁷⁻⁹

Figure 4 Duramac™ HS 57-5742 alkyd resin—viscosity vs. calculated VOC (lb/gal)



Low density solvents

Because the EPA chose to reduce solvent emissions by limiting the pounds of solvent per gallon of coating, the density of the solvent also became a very important formulating parameter. As illustrated in Table 2, low solvent density can have a great influence on the final VOC content of a coating. Solvents with low density and high activity (low solution viscosity at a given VOC content) were necessary to assure suitable spray characteristics at the desired VOC level.

Table 2 Effect of solvent density on the VOC level of a white high-solids enamel

Components	Weight %
Titanium dioxide	30.0
Thermoset acrylic resin	29.9
Cymel™ 303 melamine resin ^a	10.0
Nacure™ 2500 catalyst ^b	0.1
Solvent	30.0
	100.0

Solvent	Solvent wt/gal	Enamel wt/gal	Enamel VOC, lb/gal
Hexane	5.60	9.51	2.85
Eastman MAK	6.80	10.45	3.13
Eastman EEP	7.91	11.17	3.35
DBE	9.09	11.83	3.55

^aCytec Industries

^bKing Industries

Reference method 24

Crucial to the implementation of the newly developed VOC emissions control methodology was the ability to measure VOC content. On October 3, 1980, after many discussions with industry experts in the late 70s, the EPA published Reference Method 24, "Determination of Volatile Matter Content, Density, and Volume Solids and Weight Solids of Surface Coatings." Although formulators could calculate the approximate VOC content of a coating (often reported as "formulation or theoretical VOC"), the EPA now only recognized its own measure of VOC content. Much controversy followed as to the accuracy of the test, particularly when the VOC content was being measured on a water-based coating. This latter issue is still being addressed today with progress being made on improved analytical techniques to provide a more accurate and reproducible VOC value.

Some states such as California became more aggressive in developing VOC guidelines for coating users. By the late 70s, some air quality districts in California were publishing draft regulations based on the CTGs generated by the EPA.

Throughout the 70s, the paint industry and rule developers were on a steep learning curve. By the decade's end, the

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language and acronyms of the evolving environmental regulatory framework were becoming part of coatings industry vocabulary. Terms such as "VOCs" and "RACT" (Reasonably Available Control Technology) for example, were beginning to be used by chemists and formulators.

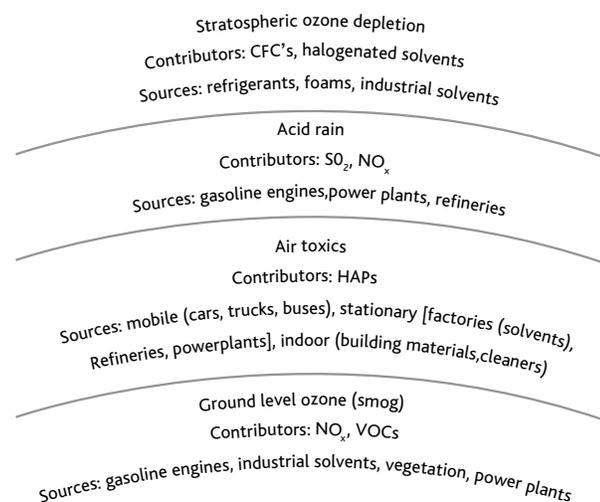
The 1980s—trial and error

Environmental issues continued to drive the paint industry to develop lower VOC coatings in the 1980s. Industry representatives and regulators, particularly at the state level, continued to strive to develop feasible, enforceable regulations.

1,1,1 Trichloroethane

The most stringent VOC regulations were based in southern California. To meet these regulations, companies there began formulating with 1,1,1 trichloroethane, a VOC-exempt solvent with satisfactory activity and a fast evaporation rate. It proved to be only a temporary solution, however. The chlorinated solvent was soon found to be an ozone-depleting substance (ODS). Because of its long atmospheric lifetime, it was shown to cause stratospheric ozone depletion (see Figure 5).

Figure 5 Overview of air pollution issues



In 1987, international parties to the Montreal protocol agreed to cease production and use of 1,1,1 trichloroethane, except for "essential" uses, by 1996. For formulators this meant exploring alternative blends without the advantage of using a VOC-exempt solvent. R&D continued at a brisk pace in the 1980s. Formulating strategies were focused on developing coatings that reduced the formation of ground-level ozone (see Figure 5). However, air quality problems persisted, particularly in urban and suburban areas. Efforts continued through the 1980s to modify the Clean Air Act and strengthen the federal statutes designed to promote public health and welfare through the control of air pollutants.

CAA Amendments of 1990—new challenges

Following much discussion in the preceding decade, the 101st Congress passed the CAA Amendments of 1990 (CAAA). The revised act enlarged the scope of the federal statutes objectives, which:

1. Substantially revised the nonattainment program, especially with regard to ozone formation.
2. Completely rewrote section 112 of the act, addressing hazardous air pollutants.
3. Created a new federal operating permit program.
4. Created a new program to protect stratospheric ozone.

Each of these programs presented a series of new challenges to the coatings industry. The following is a brief description of two key titles incorporated in the new CAAA of 1990, and guidelines on solvent selection to address the changes.

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Title I—VOC regulations

The primary objectives of these regulations were two-fold:

- To reduce ground-level ozone in nonattainment areas.
- To prevent significant deterioration of ambient air quality in attainment areas.

Regions of the country not meeting the ozone standard were called nonattainment areas. The more severe the ozone problem, the more time Congress provided for those areas to reach attainment. Section 172 (1) of the CAAA required the application of Reasonably Available Control Technology (RACT) to control VOC emissions from certain existing stationary sources in nonattainment areas. Where available, states were required to develop RACT for the various sources using CTGs supplied by the EPA. Timetables were established for the development of CTGs for many major sources in the coatings industry.

Eventually, regulations would limit VOC emissions from coating operations, though these limits would vary from industry to industry. For example, in 1998 the EPA promulgated the Architectural and Industrial Maintenance (AIM) coating rule to establish VOC limits for paints included in that surface coating category.

California takes the lead

States such as California began developing even stricter VOC emission mandates as part of their ozone reduction strategy. In 1998, the South Coast Air Quality Management District (SCAQMD) passed its own AIM Coating Rule 1113, imposing severe VOC limits on AIM paints sold in its district. Additional amendments were implemented in May 1999. The first phase of VOC content reduction limits were to become effective in 2002, with the last phase scheduled for 2006.

The National Paint and Coatings Association (NPCA) filed suit in the Superior Court in Orange County, challenging the rule on several grounds. In June 2002, the Southern Court of Appeals, Fourth Appellate District, Division Three, ruled that the May 1999 amendments must be vacated.

In December 2002, the SCAQMD readopted the VOC limits for AIM coatings, with minor revisions, but established a compliance date of January 1, 2003. Once again, the NPCA initiated litigation, and SCAQMD countered by successfully requesting that the litigation be moved to a federal district court.

The California Air Resources Board (ARB), which has overall responsibility for California air quality, has developed a draft of a suggested control measure (SCM) for VOC limits for AIM coating applications. The SCM guidelines were intended to promote uniformity in the VOC reduction limits among the air quality districts in California. The SCM reduction levels on VOC emissions were very similar to those set in phase one approved by the SCAQMD. In most categories, the VOC limits for AIM products suggested for California are significantly more stringent than the federal standards. ARB is currently developing phase two of their suggested control measure (SCM) (See section titled The New Millennium).

As VOC limits for various coating categories became increasingly stringent, formulators of solventborne coatings had to further reduce the solvent content to meet existing or pending regulations. This was accomplished by:

- Selecting solvents with maximum solvent activity for the paint resin(s) system; and/or
- Using VOC-exempt solvents.

Formulating low-VOC high-solids coatings

Further reducing the VOC content of a high-solids coating while maintaining optimal coating performance requires a combination of approaches. It is much more than simply removing additional solvent from the formula.

The most practical reformulating option for lowering the VOC content of a coating is optimizing the solvent blend.* If this approach is not adequate, other steps, often in combination, must be investigated, including:

**Note: The neat viscosity of a given solvent is also a factor in the overall solution viscosity of a coating. However, this solvent property is not as important as its activity or density, particularly when formulating high-solids coatings.*

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- Modifying resin architecture (molecular weight and molecular weight distribution, minimizing amount of functionality and those groups that contribute to hydrogen bonding).
- Adding reactive diluents or plasticizers.
- Choosing pigments with low specific gravities and low oil absorption values.
- Re-evaluating cross-linker choice and levels.
- Selecting solvents with low density and the ability to minimize resin/resin interactions.
- Using VOC-exempt solvents.^{10–18}

As more restrictive VOC guidelines evolve, formulators can no longer add solvents that contribute marginally or not at all (diluents) to the activity of the blend. Each solvent must be as efficient as possible for the resinous binders to achieve maximum viscosity reduction at a given VOC content. As shown earlier, oxygenated solvents having low density and high activity (low solution viscosity at a given VOC content) are the most useful in reducing the VOC level of a coating. Ketones are key components in developing high-solids coatings suitable for meeting the more restrictive VOC limits.

Formulating coatings with VOC-exempt solvents

In 1977, the EPA published a list of “exempt” organic compounds that were deemed to have negligible photochemical reactivity.[†] Unfortunately, these solvents, which were primarily chlorofluorocarbons, offered formulators virtually no relief from the more restrictive VOC guidelines. However, within the past 10 years, the EPA has exempted a few other low reactivity compounds, including acetone, methyl acetate, parachlorobenzotrifluoride (PCBTF), and methylated siloxanes. Paint formulators are making effective use of these newly exempted solvents to reduce the overall VOC content of existing solventborne paints. Status is pending on other solvents such as *t*-butyl acetate and methyl formate.

The use of VOC-exempt solvents provides formulating latitude for satisfying existing and future VOC regulations.^{19–27} Outside of the traditional cost/performance requirements, the use of an exempt solvent and its impact on VOC reduction must be understood in the context of the VOC calculation expression. Permissible VOC limits are usually expressed in terms of g/L or lb/gal; however, this is not true for every industry segment. VOC limits for furniture coatings are expressed as lb VOC/lb of solids, as applied. Since this measurement estimates the emissions for a given amount of coated surface area coated at a specified film thickness, some believe that it is more representative of actual conditions. Figure 6 shows two methods for calculating the VOC content of coatings.

Table 3 provides an illustration of how the lb/gal calculation method yields higher VOC levels because the VOC-exempt solvent must be subtracted from both the numerator and denominator of the expression. The VOC content of the coating is reduced using either method. However, the apparent magnitude of reduction is much less when one uses the more common lb/gal expression.

Figure 6 Calculation methods

Pound/gallon method	
VOC =	$\frac{\text{pounds of solvent-exempt solvent}}{\text{gallon of coating-exempt solvent}}$
	<ul style="list-style-type: none">• Most widely used expression• Limits VOC reduction when using exempt solvents

Pound/pound method	
VOC =	$\frac{\text{pounds of solvent-exempt solvent}}{\text{pounds of solid}}$
	<ul style="list-style-type: none">• Currently used in wood coatings regulations• Better indicator of environmental impact

[†]Note: States may also have their own list of VOC-exempt solvents. Normally the state's list corresponds to that of the EPA; however, since this is not always the case, formulators should verify that the solvent deemed VOC exempt by the EPA is indeed classified the same by their state.

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Table 3 Calculating VOC content of a lacquer with and without a VOC-exempt solvent (acetone)

	Coating containing no VOC-exempt solvent	Coating containing VOC-exempt solvent
Weight of coating, lb	100	100
% Nonvolatile matter	15	19
Total coating volume, gal	13.3	13.2
Total weight of solvent, lb	85	81
Weight of VOC-exempt solvent, lb	0	32
Volume of VOC-exempt solvent, gal	0	4.9
VOC Content calculated as:		
Lb VOC/gal	85 lb VOC/13.3 gal = 6.39	(81-32) lb VOC/(13.2-4.9) gal = 5.90
Lb VOC/lb solids	85 lb VOC/15 lbs solid = 5.70	(81-32) lb VOC/19 lbs solid = 2.58

Reference: ACC Publication "Determining VOC Content"

Table 4 offers an example of the reformulation of a cellulose acetate butyrate wood lacquer from 4.0 lb VOC/lb solids to 1.8 lb VOC/lb solids, as applied (the EPA's VOC limit for wood lacquer topcoats applied in an ozone nonattainment area). In this example, the required VOC limits for furniture topcoats were met by using 34 wt% acetone in the total lacquer composition. Lacquer solids content for satisfactory spray atomization was 23 wt%. Since acetone is very fast evaporating, to achieve smooth films, the solvent balance had to be adjusted to include a higher percentage of retarder solvent such as MAK. The higher level of MAK did not detract from the hardening properties and subsequent print resistance properties of the lacquer.

Acetone is particularly effective in coating applications requiring fast dry such as furniture and automotive refinish. It is important to balance the acetone with slower evaporating solvents to achieve smooth films. Acetone has a very low flash point and is hydrophilic, which might induce blushing or create application problems with urethane systems. Methyl acetate is more hydrophobic and could be used in applications where acetone is not acceptable. Even though lacquers contain high solvent levels, their use is still very common if compliance requirements are met. Lacquers are user-friendly, and easy to apply and repair. The VOC exemptions of acetone, methyl acetate, and PCBTF have extended the life of this traditional technology.

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Based on U.S. air quality regulations and definitions (Continued)

Table 4 Wood lacquer formulations

Components, wt%	CAB control	CAB-A2
Eastman cellulose acetate butyrate CAB-551-0.2	10.0	10.8
Thermoplastic acrylic resin ^a	7.0	9.0
Santicizer™ 160 ^b	3.0	3.2
Methyl ethyl ketone (MEK)	6.0	—
Isopropyl alcohol	12.0	—
Eastman <i>n</i> -butyl alcohol	12.0	—
Eastman MAK (methyl <i>n</i> -amyl ketone)	6.0	15.0
Toluene	29.9	—
Xylene	14.1	12.0
Acetone	—	34.0
Tecsol™ C (95%) ethyl alcohol ^c	—	8.0
Eastman methyl propyl ketone (MPK) ^c	—	8.0
Total	100.0	100.0
Wt% solids	20.0	23.0
VOC (lb/gal) (calculated)	5.88	4.93
VOC (lb/lb solids) (calculated)	4.0	1.8
HAP (lb/lb solids) (calculated)	2.5	0.5
Acetone, wt% of solvent blend	—	44.2
Retarder solvent, wt% of solvent blend ^d	7.5	19.5
Viscosity, cP (mPa·s)	45	40
Dry-to-touch, min ^e	16	16
Spray characteristics ^f	Good	Good
Tukon hardness, Knoop	6.9	7.3
Print resistance ^g	Slight print	Slight print
Solution appearance	Clear	Clear
Film clarity, haze ^h	0.6	0.3
Cold-check resistance ⁱ	Pass	Pass

^aParaloid™ B-66 or equivalent

^bFerro Corporation

^cEastman Chemical Company

^dEastman MAK

^e5 mil wet-drawn on glass, 22°C

^fAtomization, flow and leveling, dry-spray resistance

^g2 lb/in. 2, 50°C for 4 h

^hHazemeter XL-210; values below 1 are not visually detectable

ⁱ18 cycles of 1 h @ 50°C, 1 h room temperature, and 1 h @ -5°C

#Note: Three petitions have been submitted by the ACC (American Chemistry Council) requesting that the EPA delist MEK, MIBK, and EB glycol ether from the HAP list. These petitions were drafted and submitted because it was the belief of the suppliers that the proper use of such materials does not pose a health risk to the public. The EPA has proposed to remove MEK from the Clean Air Act HAP List—Federal Register 40 CFR part 63, pages 32606–32621 (May 30, 2003). On December 19, 2005, EPA issued a final rule removing MEK from the HAPs List. On July 19, 2004, EPA published a notice of completeness on the MIBK delisting petition. The petition is on hold pending the completion of the panel's research and analysis of the NTP study findings. EB glycol ether was removed from the EPA HAPs list on November 18, 2004.

Title III—HAP (hazardous air pollutant) regulations

The original Clean Air Act regulated a few air toxics under National Emission Standards for Hazardous Air Pollutants (NESHAP); however, Title III of the CAAA of 1990 greatly expanded the original list to a total of 189 compounds or classes of compounds. Several solvents commonly used in coating facilities were included:[†] MEK, MIBK, toluene, xylene, and EO glycol ethers [EG 2-ethylhexyl ether (Eastman EEH solvent) was subsequently excluded from the category and is not a HAP].

Pursuant to section 112 of the act, the EPA is establishing Maximum Achievable Control Technology (MACT) Standards that will specify HAP emission limits for various categories of industrial surface coatings. Many MACT standards such as wood furniture finishing are already in place.

Reducing or eliminating HAPs by solvent substitution

Title III does not mandate that a coatings firm eliminate the use of the designated HAP solvents, only that emissions of such be controlled. The options for reducing HAP emissions in an industrial painting facility are similar to those for reducing VOC emissions.

The most practical way to achieve that goal is to replace part or all of the HAP solvents in the formulation with non-HAP solvents. Coating formulators continue to rely on solvent reformulation to reduce HAP emissions, because it remains the lowest cost alternative, requiring minimal equipment changes. In addition, formulators have a familiarity and comfort working with solventborne coatings because of their proven performance.

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Critical to the success of any solvent reformulating effort is matching the evaporation rate and solvent activity of the control blend. This is to ensure that the reformulated coating will have the desired flow characteristics and quality film formation when applied to a surface.

Probably the most challenging HAP reformulation efforts involve replacing the aromatic hydrocarbons (toluene and xylene). These products have been used extensively in many coating systems as either the primary solvent or diluent. Xylene is also used as a synthesis solvent for acrylic resins, and as a reflux/letdown solvent for alkyd and polyester resins.

In most formulas, a combination of a non-HAP oxygenated solvent with an aliphatic hydrocarbon can be used to replace toluene or xylene. The composition of such replacements varies because the exact blend is system dependent. When an aliphatic hydrocarbon is used, the selected grade should have a zero or very low HAP content. In addition, formulating coatings with low or no HAP content requires the formulator to choose resins, pigment pastes, and additives that are supplied in non-HAP solvents. Procurement agents should confirm with their suppliers the levels of HAPs in their purchased raw materials; information that is normally available in supplier Certified Product Data Sheets (CPDS).

Often, when developing coatings with lower HAP content, it is essential that the reformulated coating have equivalent or lower VOC content. Again, the selection of oxygenated solvents that have very low density and high activity, such as non-HAP ketones and esters, is very important in satisfying both HAP and VOC regulatory requirements.

Currently, test method 311 is used for measuring the presence of HAPs in coatings. This method applies only to those volatile HAPs included in the original formula as manufactured, not to those HAPs (methanol and formaldehyde), which may form as the coating cures (cure HAPs). A separate or modified test method can be used for measuring the cure HAP volatiles. Again, some controversy exists over the precision of the test method 311, particularly at very low HAP levels.

Table 5 gives an example of reducing the HAP content of a solventborne coating through solvent substitution. In the example, xylene was replaced with a combination of esters/aliphatic hydrocarbon solvent blend. The total solvent blend composition was optimized to match the physical properties of the control. Similarity in physical properties suggests that the substitute blend represents a good HAP-free alternative to xylene.

The new millennium

What Is MIR?

The decade of the 1990s brought another methodology to formulating coatings to reduce ground-level ozone that appears poised to significantly impact VOC regulations in the new millennium. A concept, known as "incremental reactivity (IR)," was developed to measure relative atmospheric reactivity differences in VOCs.²⁸

These differences have been quantified (recognizing that uncertainties in the measurements and calculations of atmospheric reactivity exist) and are the foundation for a different methodology for controlling ground-level ozone formation. This approach is quite different from the present VOC policy that recognizes only two classes of VOCs: exempt and nonexempt, with ethane being the boundary line between the two classes.

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Table 5 High-solids polyester/melamine coating

Components, wt%	Control	Reformulation 1
Polymac™ HS 57-5776 polyester resin ^{a,b}	35.7	35.7
Kronos™ 2090 TiO ₂ pigment ^c	32.3	32.3
Eastman MAK (methyl <i>n</i> -amyl ketone)	4.4	4.4
Aromatic™ 100 ^d	1.8	1.8
Eastman EEP solvent	2.9	2.9
Cymel™ 303 melamine resin ^e	10.1	10.1
BYK-300 ^f	0.1	0.1
BYK-451 ^f	0.9	0.9
Xylene	9.0	—
Eastman isobutyl isobutyrate (IBIB)	—	5.4
Eastman isobutyl acetate	—	1.8
VM&P Naphtha	—	1.8
Eastman PM acetate	2.8	2.8
Total	100.0	100.0
Wt% solids	80.1	80.1
Solution viscosity, No. 4 Ford cup, 25°C, s	23	23
Electrical resistance, megohms	0.20	0.20
Pencil hardness ^g	4H	4H
Tukon hardness, Knoop ^g	16	16
MEK double rubs ^g	200+	200+
Gloss, 20° ^g	86	87
Gloss, 60° ^g	94	94
Distinctness of image (DOI) ^g	90	90
VOC, lb/gal (calculated)	3.1	3.1
HAP, lb/100 lb formula (calculated)	9.2	0.2

^aThe polyester resin is supplied at 85 wt% solids in PM acetate.

^bEastman Chemical Company

^cKronos

^dExxonMobile Chemical

^eCytec Industries, Inc.

^fBYK-Chemie USA

^gCoatings were spray-applied on 3 x 9 Bonderite™ 100 steel panels at a dry-film thickness of 2.0–2.4 mil, flashed for 5–10 minutes, baked for 30 minutes at 300°F, and aged for 24 hours before testing.

The most common measure of incremental reactivity in the United States is the MIR (Maximum Incremental Reactivity) scale. Using this methodology, each VOC is assigned an individual reactivity value. This MIR value enables the formulator to compare the photochemical reactivity differences of various solvents (including propellants) used in aerosol coatings. Higher values denote more reactive compounds, which have a greater propensity to create ground-level ozone under appropriate conditions (sufficient NO_x, surface temperature, sunlight, etc.).

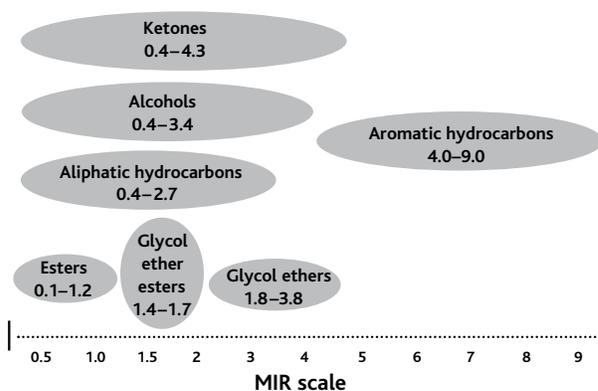
In 2001, the California ARB established the first photochemical reactivity-based limits for regulating ozone formation from aerosol coatings: effective June 1, 2002,²⁹ for general aerosol coatings and January 1, 2003, for specialty aerosol coatings. This regulation replaced the traditional mass-based VOC emission guidelines and was strongly supported by the aerosol coatings industry, which found the new limits much easier to meet than the mass-based limits.

Figure 7 shows the relative range of MIR values for respective families of solvents. As noted, aromatic hydrocarbons such as toluene and xylene have relatively high MIR values. Specific MIR values for some of the more traditional coating solvents (not limited to just aerosol applications) are also shown in Table 6.³⁰

- The maximum change in weight of ozone formed by adding a compound to the “Base ROG (reactive organic gases) Mixture” per weight of compound added, expressed to hundredths of a gram (g O₃/g ROC)[§]

§Reference: “Regulations for Reducing the Ozone Formed From Aerosol Coating Product Emissions”—subchapter 8.5

Figure 7 MIR values—coating solvents



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Table 6 Maximum incremental reactivity

Examples ranked by MIR value	
Mixed xylenes	7.37
Toluene	3.97
MAK	2.80
<i>n</i> -Heptane	1.28
<i>n</i> -Butyl acetate	0.89
Isopropyl alcohol	0.71
Acetone	0.43
Methyl acetate	0.07

Ester solvents, selected ketones, aliphatic hydrocarbons and selected alcohol solvents are particularly useful in reformulating aerosols to meet the newer reactivity limits while maintaining performance properties.

Spreadsheets such as those shown in Tables 7 and 8 can be used to calculate the MIR of an aerosol coating. Table 7 offers an example of an aerosol coating that has a product weighted MIR = 2.543g O₃/g product.³¹ As formulated, this product does not meet the targeted MIR value (<1.50) for clear aerosol coatings. Table 8 shows how, while maintaining similar evaporation rate and solubility parameter property profiles, the solvent blend for the aerosol coating was reformulated to achieve the targeted MIR value.

Table 7 Calculating the ozone (O₃) contribution (product weighted MIR) of an aerosol coating

Ingredient	Weight percent	MIR (g O ₃ /g VOC)	Weighted MIR
Acetone	20	0.43	0.086
Toluene	20	3.97	0.794
Propane	10	0.56	0.056
Xylene	20	7.37	1.474
Butane	10	1.33	0.133
Solids	20	0.00	0.000
Total			2.543

Product weighted MIR = 2.543 g O₃/g product
Reference: Chemical Engineering, December 2000

Table 8 Calculating the ozone (O₃) contribution (product weighted MIR) of an aerosol coating

Ingredient	Weight percent	MIR (g O ₃ /g VOC)	Weighted MIR
Acetone	20	0.43	0.086
Toluene	9.5	3.97	0.377
Propane	10	0.56	0.056
<i>n</i> -Butyl acetate	25.5	0.89	0.227
Xylene	5	7.37	0.369
Butane	10	1.33	0.133
Solids	20	0.00	0.000
Total			1.248

Product weighted MIR = 1.248 g O₃/g product

It is likely that future air quality policies affecting coatings will contain provisions for using the IR concept and will be more efficient than current mass-based regulations for controlling ground-level ozone formation. EPA has announced its intentions to publish an ANPR (advanced notice of proposed rulemaking) on potential modifications to its reactivity policy to include the "incremental reactivity" concept.

The EPA shift from VOC to NO_x

The EPA shifted its ozone-reduction strategy from an emphasis on VOC control to NO_x control. This strategy recognizes that in geographical locations in which the ratio of VOCs to NO_x is high ("NO_x-limited" conditions), additional reductions in VOC levels, regardless of reactivity, will have a minimal impact on air quality. Except for urban centers, which have high NO_x emissions from concentrated vehicular traffic, most parts of the country fall into the NO_x-limited category, because they tend to have high levels of biogenic (green plant synthesized) VOCs and/or low NO_x levels. Thus, in much of the United States, reduction in NO_x emissions should take precedence over reductions in VOC levels. Where states commit to NO_x reductions, it is possible that EPA might not require additional VOC reductions.

As this article is being written, EPA is setting the basic framework and principles for implementing the change from the one-hour standard to the new eight-hour

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standard for measuring the extent of the ozone problem (68 Federal Register 32802 [June 3, 2003]). While it is too early to know all the details of this new regulatory framework, the fundamental principles of effective ozone control strategy remain the same, regardless of the measure used. We would expect the principles set forth in this article to continue into the new system.

Summary

Many issues remain to be resolved as the paint industry and regulatory agencies work together to develop environmentally friendly coatings that meet specific performance standards. Issues such as NO_x reductions, VOC availability (i.e., VOC removal from the atmosphere by rainout, absorption, or deposition), global harmonization of VOC definition, use of IR methodology, etc., all need greater attention at the state and federal levels. The expanding global nature of the paint market magnifies the need for regulatory uniformity.

Solventborne coating technology still represents a major segment of the coating products sold worldwide. Often, they offer the customer performance attributes not available in other finishing technologies. Regulatory agencies should work to ensure that solvent technology is available when needed to allow formulators greater latitude in meeting the required performance/ecology/cost properties requested by their customers.

It is important that the effort to develop lower VOC/ HAP coatings does not compromise performance or involve environmental trade-offs. The use of non-HAP, high-activity solvents and/or VOC-exempt solvents can help formulators develop coatings that satisfy VOC/HAP mass-based regulations. Low-reactivity solvents are very useful in developing coatings designed to meet existing and future photochemical reactivity-based regulations.

Acknowledgments

The author is extremely indebted to Robert J. Avery, Senior Technical Associate, Eastman Chemical Company, for his valuable input in developing this document and Jeannie S. Ramey, Laboratory Technician Associate, Eastman Chemical Company, for assisting in the preparation and editing of the manuscript.

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