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Formulating VOC-Compliant Coatings with Exempt Solvents

A Case Study on Tertiary-Butyl Acetate (TBAc™)

By D.B. Pourreau, G.B. Kelly, L.J. Junker, R.T. Wojcik, S.L. Goldstein
and M.J. Morgan / Lyondell Chemical Co., Newtown Square, PA

Manufacturers of coatings, ink and adhesives have come under increasing pressure to eliminate HAPs and VOCs from formulations. Some of the latest regulations to affect coatings manufacturers include the Architectural and Industrial-Maintenance (AIM) rule,[1] Automotive refinish rule,[2] Wood Furniture CTG and NESHAP,[3] and National Ambient Air Quality Standard (NAAQS).[4]

Since many common solvents are both HAPs and VOCs, these rules have forced many producers to switch to low-solvent technologies such as high-solids, waterborne, powder and low-energy-curable systems. These technologies have their own inherent limitations that can make them more costly and less convenient to use than the traditional lower-solids formulations.

An alternative approach to these technologies is to use non-HAP, VOC-exempt solvents such as acetone and p-chlorobenzotrifluoride (PCBTF). Unfortunately, both have performance features that make them less-than-ideal solvents for coatings. In addition, the EPA is reviewing its VOC policy[5] and, at least in the interim, is proposing to tighten the criteria for exempting VOCs from regulation.[6] Therefore, it is unlikely that many new practical coating solvents will be added to the list of VOC-exempt compounds.

However, the EPA has recently proposed[7] to add Lyondell Chemical's tertiary-butyl acetate (TBAc) to the list of VOC-exempt materials based on its negligible photochemical reactivity. This would make TBAc one of only a handful of HAP- and VOC-compliance tools available to coatings formulators. TBAc is an effective viscosity reducer with an intermediate flash point and evaporation. It has been formulated in a variety of low-VOC coatings, ink, adhesives and cleaners, including the following.

- Nitrocellulose wood coatings
- Urethane automotive refinish coatings
- Air-drying and baking alkyd enamels for metal
- Aerosol coatings
- Flexible packaging ink
- Pressure-sensitive adhesives
- Industrial degreasers
- Paint strippers

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Ultimately, the EPA's VOC policy will probably evolve to a weighted reactivity scale similar to what is being proposed by the California Air Resources Board (CARB) for aerosol coating products.[8] Another possibility is that VOCs would be classified in reactivity "bins," again using some reactivity scale. Regardless of the outcome of this policy reevaluation, TBAc and other low-reactivity solvents will likely continue to be less regulated than the more reactive solvents used today.

Formulating Coatings for Future Compliance

Assuming the EPA will move to a reactivity-based VOC policy, reformulating today with low-reactivity solvents and additives could mean fewer compliance issues in the future. This could impact not only the type of solvents used, but also the choice between waterborne and high-solids technologies. For example, waterborne coatings are generally considered more environmentally friendly than solventborne coatings because of their lower VOC content. That's because the current VOC policy regulates VOCs on a mass (lb/gal) basis and ignores reactivity differences between VOCs. However, the following three factors may become important in the future and should be considered in assessing the environmental impact of coatings.

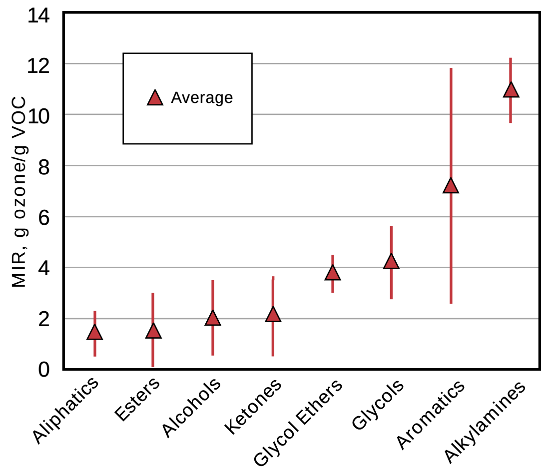
- The photochemical reactivity of the contained VOCs
- The solids content of the coating
- The durability of the coating

Many of the coalescents, additives and amine neutralizers used in waterborne coatings are VOCs, and some are quite photochemically reactive (see Figure 1).

For example, glycol ethers are commonly used to coalesce acrylic latexes and urethane dispersions. They have maximum incremental reactivities (MIRs)[9] in the 3–4.5 g ozone/g VOC range. Glycols, used in architectural paint as freeze-thaw stabilizers, have MIRs in the 3–6 g ozone/g VOC range. Alkylamines are also commonly used to neutralize water-dispersible resins and have MIRs above 10 g ozone/g.

On the other hand, the aliphatic hydrocarbons, esters, alcohols and ketones commonly used to formulate medium- and high-solids coatings have relatively low reactivities. Aromatic solvents, mostly xylene and toluene, are the only solvents used in solventborne coatings that, on average, have higher reactivities than those used in waterborne coatings. By replacing high reactivity solvents with low reactivity ones, it is possible to formulate solventborne coatings with a lower ozone impact than that of their waterborne counterparts. It is

Figure 1 / Maximum Incremental Reactivities of Common Coating Solvents and Additives

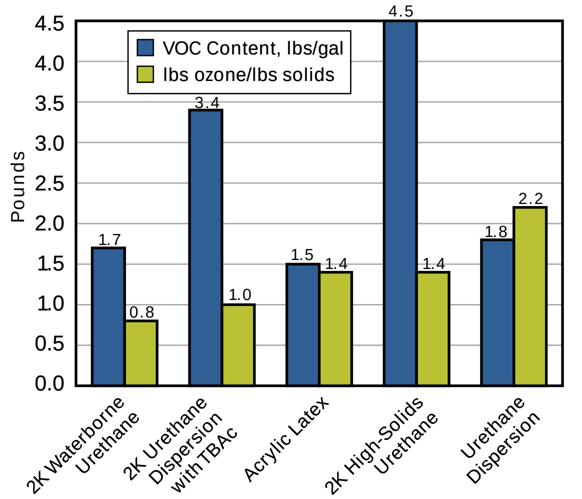


THE Environmental Protection Agency

Last year, the U.S. Environmental Protection Agency (EPA) announced its intent to review its VOC policy in light of new scientific understanding of photochemical reactivity. It also promulgated new rules limiting the VOC content of architectural and industrial-maintenance (AIM), automotive refinish, and wood coatings, and proposed reducing the Nonattainment Air Quality Standard (NAAQS) to 8 parts per billion (ppb). Although the new VOC rules have had an immediate impact on producers and users of the affected coatings, the reduction in the NAAQS and the VOC policy review could have an even greater impact.

For example, under the new NAAQS standard, the number of nonattainment areas in the United States would jump from 245 to 546 in 2002, subjecting many manufacturers to stricter VOC emission limits. On the other hand, a reactivity-based VOC-policy could bring regulatory relief in the form of a greater selection of compliant technologies and more formulation latitude. Although this relief is unlikely to come in time to help achieve compliance with the NAAQS deadline, producers and users of coatings can take steps to prepare for it today.

Figure 2 / VOC Content and Ozone Impact of Representative Industrial-Maintenance Coatings, Assuming Comparable Durability



also possible to formulate waterborne coatings with lower ozone impacts by selecting less reactive coalescents and additives.

The solids content of the coating may also be considered. When comparing coatings, the most appropriate measure of VOC content is pounds VOC per pound of solids applied, not pounds per gallon of paint. Waterborne coatings typically have solids content in the 30–50% range, whereas high-solids coatings have solids content in the 55–100% range. At best, it takes the same amount of waterborne coating to get the same film build as a high-solids coating. However, in most cases, it takes 30–50% more waterborne coating. This affects the actual amount of VOCs emitted during the coating operation.

Finally, the durability of the coating should be considered. The durability of many waterborne coatings, although significantly improved, still lags behind that of solventborne versions. This means that waterborne coatings need to be applied more frequently, which can increase the actual amount of VOCs emitted. Coating durability is the most difficult performance characteristic to quantify, but gloss or hardness retention data from accelerated UV or chemical resistance testing could be appropriate measures, depending on the application.

Table 1 shows how these concepts may be used to calculate the actual ozone impact of different coatings. For the purpose of illustration, the durability of these coatings was assumed to be equal but may need to be quantified for a more accurate comparison.

In this example, the 2K waterborne urethane had the lowest ozone impact of the five systems considered, despite having a slightly higher VOC content than the acrylic latex. The high-solids system had the same ozone impact as the acrylic latex, despite having a VOC content three times higher (4.5 lbs/gal vs. 1.5 lbs/gal). This demonstrates that a high-solids solventborne system can generate less ozone than a lower VOC waterborne coating.

The urethane dispersion selected here had the highest ozone impact despite a VOC content of 1.8 lbs/gal, mainly because triethylamine (MIR ~10 g ozone/g) was used to neutralize the resin. This does not mean that urethane dispersions cannot be formulated to have low ozone impact. In fact, the 2K-urethane dispersion formulated with TBAc had one of the lowest ozone impacts (1.0 lb. ozone/lb. solids) despite containing a glycol ether coalescent and a relatively high VOC content (3.4 lbs/gal).

This discrepancy between the actual ozone impact of a coating and its VOC content is illustrated in Figure 2. It underscores the limitation of using pounds VOC per gallon of paint for regulatory purposes and the need to refine coatings regulations.

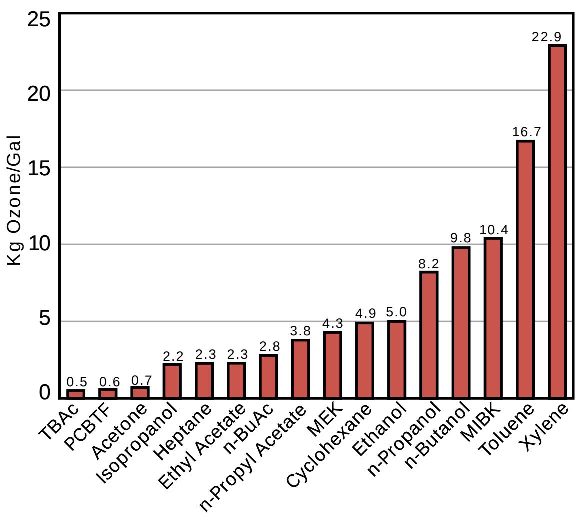
Environmental Considerations

Despite these limitations, the current policy does encourage the use of negligibly reactive exempt solvents. Unfortunately, most of these are either halogenated or extremely volatile. Halogenated solvents are

Table 1 / Relative Ozone Impact of Representative Industrial-Maintenance Coatings

Typical Formulation	2K Waterborne Urethane	2K Urethane Dispersion with TBAc	Acrylic Latex	2K High-Solids Urethane	Urethane Dispersion
Constants					
Weight % solids	42	54	40	57	36
MIR of VOCs	2.0	1.5	3.8	1.6	4.0
lbs/gal	10.0	9.2	10.0	9.2	9.2
lbs ozone/gal	3.4	5.1	5.6	7.4	7.2
VOC content, lbs/gal	1.7	3.4	1.5	4.5	1.8
lbs ozone/lbs solids	0.8	1.0	1.4	1.4	2.2

Figure 3 / Ozone Creation Potential of Common Coating Solvents



seldom used in the coatings industry because of their corrosiveness, poor solvency, toxicity, cost and odor. There are only two nonhalogenated exempt solvents, acetone and methyl acetate. They are so volatile and flammable that they have found only limited use, despite their VOC-exempt status.

TBAc is one of the few nonhalogenated solvents with negligible photochemical reactivity. Based on MIR and other reactivity data, TBAc produces 40–57% less ozone than ethane on a per gram basis, whereas ethane produces 40–57% less ozone than TBAc on a per-mole basis.[10] This makes it one of the least photochemically reactive solvents available to date, including currently exempt solvents (see Figure 3).

Because of its limited atmospheric lifetime and low molecular weight, TBAc also does not contribute significantly to global warming, ozone depletion, acid rain formation or fine particulate (PM2.5) formation. It is also biodegradable, does not bioaccumulate and has low toxicity.[11] Like reactivity, these factors may become more important in future regulations, and will affect the marketability of solvents and the formulations that contain them.

Using TBAc instead of common coating solvents is environmentally sound, especially when considered on a comprehensive basis. Also, because it is a pound-for-pound replacement for these solvents in most applications, substitution for TBAc should not increase overall emissions. In other words, the risk that increased TBAc emissions could outweigh the benefits of these substitutions is essentially nil.

Over the past three years, since we petitioned the EPA to add TBAc to the list of VOC-exempt compounds, it has been tested in a number of coating, ink, adhesive and cleaner formulations. The following paragraphs compare TBAc's key properties to other coating solvents and illustrate how it can be a useful tool for formulating compliant two-component urethane coatings, nitrocellulose lacquers, and alkyds.

Key Solvent Properties

Viscosity Reduction. TBAc has solvency properties similar to other esters. It is an efficient viscosity reducer for a range of commercial resins, including nitrocellulose, alkyds, epoxies, polyesters, acrylics, polyamides, urethanes and

Table 2 / Brookfield Viscosities of Commercial Coating Resins in Common Coating Solvents

Resin	Supplier	Type	% Solids	TBAc cps	MAK cps	n-BuAc cps
Joncryl 587	SC Johnson	Acrylic	50	4,560	826	1,230
Acryloid B-66	Rohm & Haas	Acrylic	40	1,450	374	472
Epon 828	Shell	Epoxy	80	197	89	187
12-035	Reichhold	Alkyd	50	2,240	334	1,020
11-045	Reichhold	Alkyd	50	108	49	69
12-102	Reichhold	Alkyd	50	885	167	433
57-5776	McWhorter	Polyester	73	885	531	531
57-5789	McWhorter	Polyester	75	718	698	796
50-5071	McWhorter	Alkyd	50	79	49	59
RS ½ second	Hercules	Nitrocellulose	12	49	39	39
Cymel 303	Cytec	Amino	90	659	403	403
Versamid 115	Henkel	Polyamide	75	3,380	4,670	1,710
Luxate HB9000	Lyondell	Isocyanate	90	1,970	1,200	1,470
Luxate HT2000	Lyondell	Isocyanate	90	619	403	413

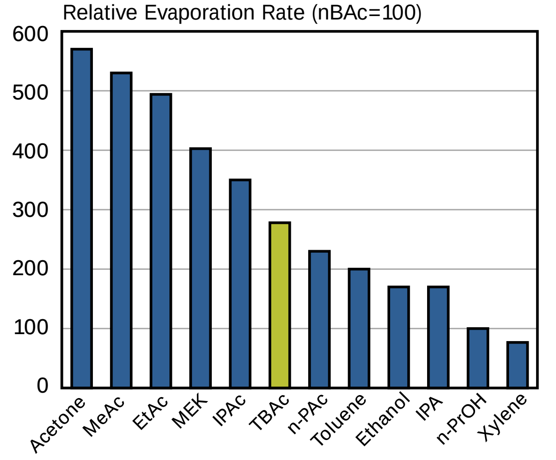
amino resins. Table 2 lists representative resin viscosity data in TBAc and other common coating solvents.

TBAc is miscible in all proportions with common organic solvents but is virtually insoluble in water (~0.3 wt % at 20°C). Its solubility properties are similar to those of other esters, such as n-Butyl acetate and PM Acetate.

Evaporation Rate. After solvency, evaporation rate is probably the most important property for a coating solvent. Unlike methyl acetate or acetone, TBAc evaporates in the same range as toluene and MEK, making it an especially good substitute for these two HAP-listed VOCs (see Figure 4). Unlike the faster-evaporating solvents, TBAc has good blush resistance in humid conditions.

Flash Point. Flammability is another important solvent property, especially as it affects worker safety. Very flammable solvents like acetone are difficult to use safely, especially in pigment-grinding applications. TBAc has

Figure 4 / Evaporation Rate of Common Commercial Resins in Common Coating Solvents



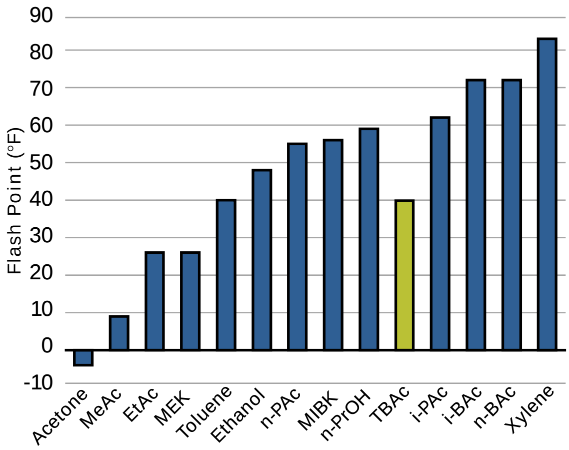
VOC Policy Retrospective

The first step in the EPA's VOC policy review was a Reactivity Workshop, held in March of 1998 in Research Triangle Park, NC. One outcome of this meeting was the creation of a Reactivity Research Work Group whose function is to make recommendations about what additional reactivity research is needed. However, the EPA's goal is much broader: Laying the foundation for a new reactivity-based policy, which may consider not only the ozone-forming potential of VOCs but also their impact on fine particulates, global warming, acid rain, stratospheric ozone depletion, and human health. Many wonder where this will take us, how much it will cost and how long it will take. Others find it difficult to comply today and want to know what, if any, regulatory relief will be available in the interim. Studying the evolution of the EPA's VOC-policy provides some insights into these questions.

In 1977, the EPA published its first policy regulating VOCs in an attempt to control the formation of toxic ozone in polluted urban environments. VOCs were known to react with nitrogen oxides (NO_x) in the presence of sunlight to give ozone. However, it was already clear that all VOCs did not contribute equally to the ozone problem. Some VOCs reacted rapidly to generate ozone while others were relatively inert. Consequently, the first rule stated that VOCs that were less photochemically reactive than ethane would be considered to have negligible impact on ozone formation and therefore could be exempted from VOC regulations and emission controls. The rule also stated that for VOCs with reactivities close to ethane, other environmental benefits could be considered for the purpose of granting VOC exemptions. The rule did not specify how photochemical reactivity would be measured or define the petition process in detail.

In 1990, the Clean Air Act (CAA) amendments were passed, providing a definition of VOC and a list of exempt compounds. These exempt compounds were said to have "negligible photochemical reactivity" because they reacted with atmospheric hydroxyl radicals much more slowly than ethane. These radi-

Figure 5 / Flash Points of Common Coating Solvents



an intermediate flash point, similar to that of many solvents used in coatings today (see Figure 5).

Density. The density, in pounds per gallon, of a solvent can also have an impact on VOC content and the cost of a formulation. For most coatings, VOC content is calculated by subtracting the pounds of exempt solvent from the numerator and the gallons of exempt solvent from the denominator. Theoretically, high-density solvents such as PCBTF (11.2 lbs/gal) should reduce the VOC content more than low-density solvents like acetone (6.6 lbs/gal) or TBAc (7.2 lbs/gal), provided they require the same amount of solvent to reduce viscosity. However, more PCBTF is usually required to achieve the same viscosity reduction per gallon of paint. Also, the formulated cost of the solvent increases with increasing density since solvents are bought by the pound but coatings are sold by the gallon.

cals abstract hydrogens from VOCs to form water and organic radicals. The organic radicals then undergo further decomposition and reactions with NO_x to yield ozone.

The current VOC policy considers only two classes of VOCs — exempt and nonexempt — with ethane as the boundary between the two classes. This policy has the following two limitations.

- VOCs spanning a wide range of reactivities are regulated the same way. Hence, there is no incentive to use less reactive solvents unless they are less reactive than ethane. In reality, formulations with the same amount of VOC can have vastly different ozone impacts. In fact, some low-VOC waterborne formulations actually produce more ozone than high-solids systems formulated with low-reactivity solvents.
- The use of ethane as the boundary severely limits the number of useful solvents that are VOC exempt. If the EPA changes the cutoff from maximum incremental reactivities (MIRs) expressed on a weight basis to a stricter mole-based standard, as it has recently proposed, this limitation will become even more severe.

The end result is that paint companies have little incentive to reformulate to less reactive VOCs. Since the new ethane cutoff virtually eliminates all oxygenates and hydrocarbons from contention as exempt solvents, solvent suppliers also are more limited in their ability to develop better solvents. The only solvents likely to meet the new ethane standard are halogenated solvents, which are typically not used in coatings.

Most parties recognize that there are better ways to reduce ozone formation than by continually reducing VOC content limits. The EPA and scientific community agree that all VOCs do not contribute equally to ozone formation. Most of the current discussion centers around which models best describe the extent to which VOCs' reactivity differs. There are several methods used to estimate the ozone impact of VOCs, each with different implications for a reactivity-based VOC policy. ⊕

Two-Component Urethane Coatings

Two-component (2K) urethane coatings are high-performance systems that are finding increased use in automotive and industrial-maintenance applications because of their durability, chemical resistance, and ease of application. Unlike one-component melamine coatings that must be baked for crosslinking to occur, 2K urethane systems cure under ambient conditions when the acrylic (or polyester) polyol and isocyanate parts are mixed just before application. This is particularly useful for coating large parts that cannot be baked or thermally sensitive substrates such as plastics and wood.

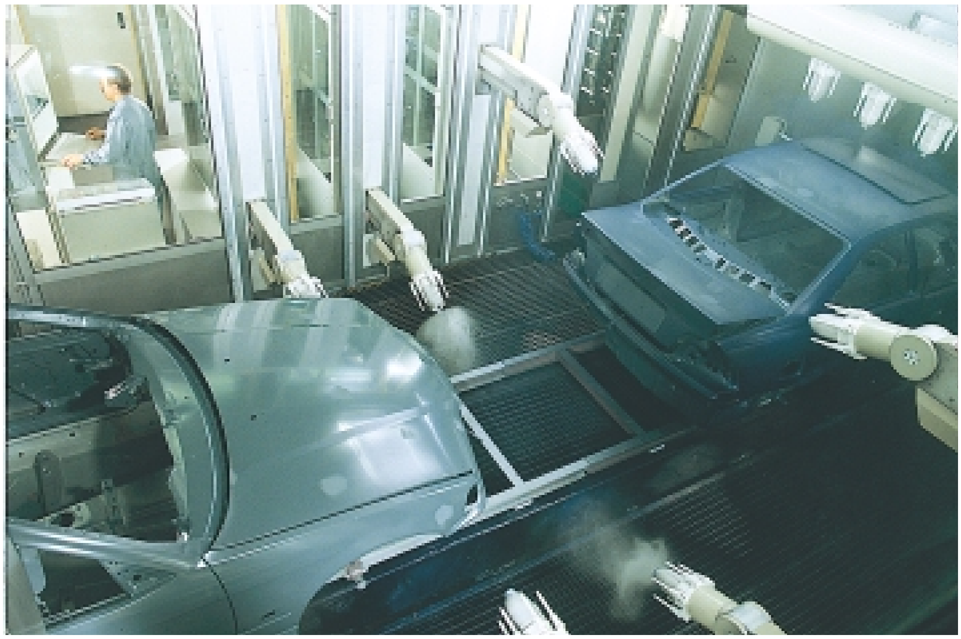


Photo courtesy of ABB Flexible Automation, Paint Automation Group

High-solids acrylic polyols are typically supplied as 80%-solids solutions in solvents such as MAK or n-BuAc. The isocyanate part, typically HDI or IPDI trimers, may also be supplied with up to 25% solvent. After mixing the two components, additional solvent must be added to achieve sprayable viscosity. Typical solids contents at spray viscosity are in the 55–65% range.

Recently, the EPA published a federal rule[2] restricting the VOC content of coating formulations supplied to the automotive refinish industry. The new VOC content limits are listed in Table 3. The compliance date was January 11, 1999.

These new VOC content limits are difficult to achieve without exempt solvents. Waterborne coatings still do not have the dry times and ease of use required by the refinish market. High-solids resins are more difficult to spray and have shorter pot lives than their lower-solids counterparts. Acetone and PCBTF are currently being used to lower the VOC content of some refinish systems, especially for the California market. Their use is limited, however, by their physical properties and cost.

Acetone, for example, evaporates very rapidly and can cause "dry-spray edge" and blushing, a haze caused by moisture condensation in the coating due to excessive evaporative cooling. Its flammability also makes it difficult to use in pigment grinding applications. PCBTF, on the other hand, is relatively expensive and is not as efficient at reducing viscosity as many of the solvents it replaces.

TBAc is an active solvent for acrylic polyols and aliphatic isocyanates, the two main components of thermosetting urethane coatings. It is a slightly less effective viscosity reducer for these polyols than n-BuAc, but still yields low viscosity solutions. These slight viscosity differences in the pure solvents are undetectable in fully formulated systems. For example, TBAc was used to reformulate the automotive refinish clearcoat formulations in Tables 4 and 5.

In both formulations, n-BuAc was replaced with TBAc with no effect on any of the formulation or coating properties. With TBAc being VOC-exempt, the VOC content of these formulations would decrease from 4.4 to 3.3 lbs/gal for the low-solids formulation and from 4.0 to 2.9 lbs/gal for the high-solids formulation. These clearcoats could be applied over conventional 6.6 lb. VOC/gal basecoats and still easily meet the 5.0 lb. VOC/gal limit for 2-stage topcoats based on the standard calculation:

$$\text{Topcoat VOC content (lbs/gal)} = \frac{(6.6 \text{ lbs VOC/gal}) + [2 \times (3.3 \text{ lbs VOC/gal})]}{3}$$

$$= 4.40 \text{ lbs/gal topcoat}$$

Table 3 / VOC Content Standards for Automotive Refinish Coatings

Coating Category	g/L	lbs/gal
Pretreatment wash primer	780	6.5
Primer/Primer surfacer	580	4.8
Primer sealer	550	4.6
Single/2-stage topcoats	600	5.0
Topcoats of 3 or more stages	630	5.2
Multicolored topcoats	680	5.7
Specialty coatings	840	7.0

Table 4 / Formulation Constants

	Conventional	TBAc-Based	High-Solids	TBAc-Based
G-Cure 105 P70	100.0	100.0	50.0	50.0
SCX 920	0.0	0.0	50.0	50.0
T-12 (1% in toluene)	1.9	1.9	0.3	0.3
FC 430 (10% in toluene)	0.3	0.3	0.3	0.3
Luxate HT2090 or XHT2090T	28.3	28.3	33.9	25.4
Luxate XIT1070T	0.0	0.0	0.0	15.6
MAK	25.0	25.0	24.0	24.0
n-Butyl acetate	25.0	0.0	24.0	0.0
TBAc	0.0	25.0	0.0	24.0
Total lbs	205.5	205.5	206.5	213.6
% solids	46	46	51	51
Lbs VOC/gal	4.40	3.28	3.96	2.86
Viscosity, sec #2 Zahn	21.2	21.1	20.9	20.8
Dry Time, hours	3.2	3.5	7	4

Table 5 / Coating Properties

	Conventional	TBAc-Based	High-Solids	TBAc-Based
20° gloss	88	88	90	90
60° gloss	95	95	95	95
DOI	90	90	90	90
Reverse Impact, lbs	160	160	160	160
Direct Impact, lbs	160	160	160	160
Cross hatch adhesion, %	100	100	100	100
10% acid resistance (30 min)	Pass	Pass	Pass	Pass
100 MEK double rubs	Pass	Pass	Pass	Pass
Gloss retention, 2,500hr QUVB	25.42	25.16	——-	——-

Nitrocellulose Lacquers

Nitrocellulose lacquers are still used extensively in the wood coating industry as clearcoats because of their unmatched clarity, depth and ease of use. They are also commonly used as fast-drying primers in the automotive refinish industry. Because of their high solvent content, these coatings have also come under increasing regulatory pressure.

Wood furniture manufacturers are subject to both Control Technique Guidelines (CTG) that limit VOC content and a National Emission Standard for Hazardous Air Pollutants (NESHAP) that limits the HAP content of the products they use.[3] These limits can have a significant economic impact on small to medium-size manufacturers, who either have to install emission control devices or switch to more expensive technologies such as waterborne or UV-curable coatings.

Any switch involves conversion costs and a new set of environmental impacts. For example, switching to waterborne coatings requires that waste products be segregated and can create additional issues in areas such as product application and performance. Even controlling emissions can have a negative environmental impact — incineration of VOC emissions generates NO_x, another precursor to tropospheric ozone. In NO_x-limited areas, incinerating VOCs could actually make the ozone problem worse than emitting them.

TBAc is an active solvent for nitrocellulose. Figure 6 illustrates how it efficiently reduces the viscosity of both RS and SS-type resins for spray application. Low-VOC and low-HAP wood lacquer formulations were also developed. Replacing xylene, MEK, and n-BuAc with TBAc and TBAc/PMAc blends reduced the VOC content from 4.0 lbs/lb. solids to 1.5 lbs/lb. solids and reduced VHAP (volatile hazardous air pollutant) content from 2.3 lbs/lb. solids to 0.23 lbs/lb. solids.

Dry times, gloss, and whiteness were slightly improved over the high-VOC formulation. Propylene gly-

Table 6 / Solution Viscosities

Resin Type	Chain-Stopped Alkyd	Medium-Oil Soya Alkyd	Chain-Stopped Alkyd	
Resin Name	Beckosol 12-054	Beckosol 11-045	Beckosol 12-102	
Solvent or Blend	Solution Viscosity at 50% solids, cps			Relative Evaporation Rate
TBAc	2,240	108	885	2.79
70:30 TBAc:MAK	511	89	295	1.05
n-BuAc	1,020	69	433	1.00
70:20:10 TBAc:PMAc:EEP	668	246	324	0.96
70:20:10 TBAc:MAK:Exxate 600	Gelled	108	344	0.95
70:20:10 TBAc:MAK:EEP	580	89	334	0.90
Xylene	6,400	89	1,690	0.70
70:30 TBAc:Exxate 600	1,170	98	492	0.64
85:15 TBAc:NMP	1,300	118	730	0.49
85:15 TBAc:Exxate 1000	2,530	98	718	0.40
MAK	344	49	167	0.33

col methyl ether acetate (PMAc), a non-HAP glycol ether commercially available from Lyondell, reduced the viscosity of this nitrocellulose-based lacquer formulation better than n-butyl acetate and gave equivalent dry times and coating performance.

Alkyd Coatings

Alkyds are one of the leading coating technologies because of their low cost, ambient curing capability and film properties.[12] They are popular coatings in the architectural, industrial-maintenance and OEM market sectors. However, they also have come under regulatory pressure because of their relatively high VOC content.

Alkyd resins are commonly supplied as 50–60% solids solutions in xylene or mineral spirits and further reduced to 35–50% solids before application. Resin producers and coating formulators have developed high-solids, air-drying alkyds but drying rates and performance are typically inferior to their low-solids counterparts. The wood furniture, aerosol, general metal, light transportation, and machinery and equipment markets would benefit from low-VOC, low-solids alkyd systems that performance as well as conventional formulations.

Figure 6 / Brookfield Viscosity of Nitrocellulose Solutions in TBAc as a Function of Solids Content

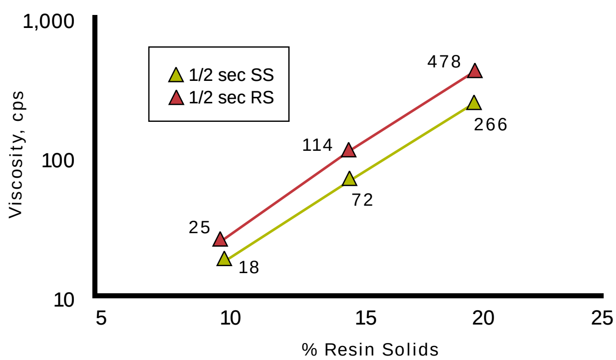


Table 6 lists solution viscosities for three alkyd resins from Reichhold Chemical in a range of solvents and blends. Solvents and blends are listed in order of decreasing evaporation rate. The 70:30 TBAc:MAK blend is a good match for n-BuAc, giving similar solution viscosities for all three resins and a similar evaporation rate. The properties of xylene can be approximated with blends of TBAc and slower solvents such as MAK, PM Acetate, EEP, or Exxates. Low-VOC formulations with these base resins have been developed and new TBAc-based resins are now available from Reichhold. Figure 7 illustrates how using TBAc significantly reduces the VOC content and ozone-forming potential of these formulations.

First, xylene was replaced with a TBAc/MAK/DPM acetate blend in a white enamel formulation based on the commercial chain-stopped alkyd, Beckosol 12-102. This reduced the VOC content of the formulation from 4.8 to 4.0 lbs/gal. More importantly, it reduced its ozone-forming potential from 5.4 to 4.0 lbs ozone per pound of solids applied.

A more significant reduction in both VOC content and ozone impact was achieved when the resin itself was supplied in 95/5 TBAc/xylene. The VOC content was reduced to 1.7 lbs/gal and the ozone yield was 0.8 lbs ozone per pound of solids applied. These numbers are

REACTIVITY: the science behind the policy

Because hydrogen abstraction is a required first step for most VOCs, the rate constant for this step (kOH) was originally considered to be a crude but acceptable measure of a VOC's potential to form ozone. Since then, a few solvents have been added to the original list of VOC-exempt compounds including acetone, p-chlorobenzotrifluoride (PCBTF), and perchloroethylene (PERC). In the case of acetone, Incremental Reactivities (IRs) were used by the EPA to demonstrate that acetone was less reactive than ethane. IR is the amount of excess ozone formed when a VOC is added to a mixture of reactive organic gases in the presence of NO_x and light. Historically, IRs have been expressed as grams ozone formed per gram of VOC added.

IR is a better measure of the ozone-forming potential of VOCs than kOH because some organic radicals, while slow to form, decompose to yield more ozone than more reactive VOCs. IRs also take into account the environment in which the VOC reacts. NO_x, other VOCs, and the amount of light present all affect the amount of ozone formed from the same VOC. Several IR scales have been developed to reflect the varying levels of pollution found in our cities. One of those, the Base Scale, an averaged IR for 39 US cities with different NO_x levels, was the basis for the acetone exemption. Today, the MIR scale is most commonly used to compare VOC reactivities. MIR is the most sensitive scale and represents a high No_x scenario, typical of a polluted urban environment. It describes an environment where VOC contribution to ozone formation is the greatest, ozone yield is high, and the potential impact on human population is highest.

Recently, the accuracy of IR scales in measuring photochemical reactivity has also come into question. Most MIR critics point to the fact that MIR uses a single-day atmospheric box model instead of the more sophisticated multi-day, 3-D airshed models available today. However, these sophisticated models require an accurate inventory of the reactive organic gases present in the atmosphere to correctly predict the reactivity of individual VOCs.

To date, regulatory agencies have been unable to maintain an accurate inventory of the reactive gases present in the atmosphere. It is unlikely that industry can afford to quantify each VOC present in emissions, and biogenic VOC emissions are still not accurately tracked or modeled. Because of these inventory limitations, it is still not clear that airshed models can give a more realistic scale of VOC reactivities than the simpler box models. Until emissions inventories are

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identical to the 2K waterborne urethane system described earlier. In addition, the ozone impact is lower than either the commercial acrylic latex or urethane dispersions shown in Table 6.

This example demonstrates that medium-solids alkyd systems, when properly formulated with exempt solvents, can not only rival the VOC content of water-based and high-solids systems but can also have a lower ozone impact.

Conclusion

The EPA is proposing to exempt TBAc from VOC-regulations because of its negligible potential to form ozone in polluted urban environments. Although TBAc would become the latest VOC-exempt solvent, it also would be one of the first practical solvents for coatings, ink, adhesives and cleaners to be added to the exempt list. In addition, its low reactivity, low toxicity and negligible environmental impact make it likely that TBAc will continue to enjoy a preferred regulatory status even after the EPA completes its VOC policy revision.

Solventborne coatings, when properly formulated with exempt solvents, can be as environmentally friendly as their waterborne versions despite having higher solvent contents. TBAc gives the formulator an additional tool for achieving VOC and HAP compliance without compromising performance, switching to a different technology, negatively impacting the environment, or significantly increasing costs.

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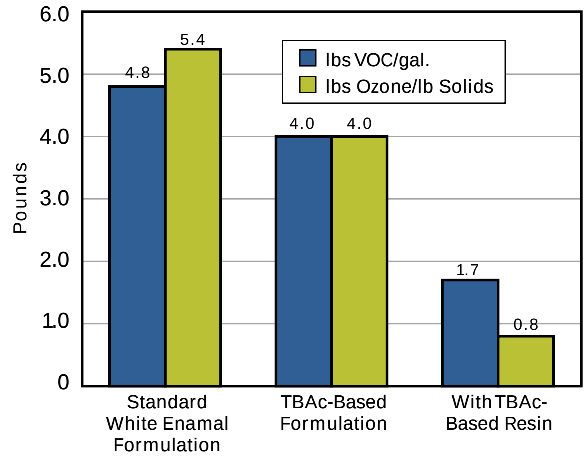
Figure 7 / VOC Content and Ozone-Forming Potential of a Commercial Alkyd Formulation.



refined, MIR is still the best available tool to rank VOCs for the purpose of exemptions or a reactivity-based policy.

Regardless of their differences, both models give similar results for most VOCs. For example, tertiary butyl acetate (TBAc) is 3 times less reactive than ethane using a box model and 2.5 times less reactive using a 3-D, multi-day scenario. Compared to m-xylene, TBAc is 63 times less reactive using a box model and 25 times less reactive using the 3-D model. Although the magnitude of the difference depends on which model is used, the same basic conclusions can be drawn in either case: TBAc is less reactive than ethane, and replacing xylene with TBAc would significantly reduce ozone formation

The challenge is formulating a policy that encourages substitutions such as these without creating other environmental problems or significant economic hardship.

Formulating for Today and Tomorrow

Under the current policy, VOC exemptions are one way for the EPA to encourage the use of low-reactivity solvents. Unfortunately, most exempt solvents are not useful coating solvents and, aside from TBAc, it appears unlikely that many more will be exempted. Ultimately, the EPA's VOC policy will likely evolve to a weighted reactivity scale similar to that proposed by the California Air Resources Board. Another possibility is that VOCs will be classified in reactivity "bins," again using some reactivity scale. Regardless of the outcome of this policy reevaluation, using low-reactivity solvents instead of more reactive solvents is more environmentally sound and should be encouraged.

What does this mean for the formulators and users of coatings? The bad news is that practical, VOC-exempt solvents will continue to be rare. The good news is that a handful are available today and that solvent-based coatings formulated with low-reactivity solvents are likely to be an acceptable compliance option when the new VOC-policy is put in place.

Consequently, reformulating today with non-HAP, low-reactivity solvents can pay both immediate and lasting dividends to those willing to invest. These dividends can come in a variety of forms, including the following.

- Lower compliance costs,
- Lower reformulation costs,
- Universally compliant formulations,
- Improved corporate image and
- Cleaner air. ⊕

For more information on solvents, contact Lyondell Chemical, 3801 West Chester Pike, Newtown Square, PA 19073; phone 888/777.0232; visit www.lyondell.com.

For more information on Apollo Sprayers, write 1030 Joshua Way, Vista, CA 92083; call 760/727.8300 (Parts & Service) or 800/578.7606 (Sales); fax 760/727.9325; e-mail apollo@hvlp.com.

For more information on BetzDearborn, write BetzDearborn, Div. of Hercules Inc., 4636 Somerton Road, Trevose, PA 19053-6783; phone 215/355.3300; visit www.betzdearborn.com.

For more information on ABB Flexible Automation, contact Scott Baldwin, Director of Marketing, ABB Flexible Automation, Paint Automation Group, 1250 Brown Road, Auburn Hills, MI 48326; call 248/391.8492; e-mail scott.e.baldwin@usfla.mail.abb.com.

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5 Proceedings of the First Photochemical Reactivity Workshop, U.S. EPA, May 12-14, 1998.

6 The EPA is proposing to use the reactivity of ethane on a per-mole basis as the criterion for VOC-exemptions. Previous EPA policy documents had stated that the exemption criterion should be the reactivity ethane on a per gram basis.

7 Proposed rule CFR 64-FR-52731.

8 California Air Resources Board Home Page. http://www.arb.ca.gov/consprod/regact/reactsub/reactsub.htm.

9 MIRs for many industrial chemicals and solvents can be downloaded from Dr. William Carter's website at http://cert.ucr.edu/~carter/bycarter.htm

10 The full text of Dr. William Carter's report on TBAc reactivity can be downloaded from his website.[9]

11 A data sheet detailing the environmental properties of TBAc is available from Lyondell Chemical by calling 888/777.0232

12 See, for example, Coatings, VI, A Multiple-Client Study, Skeist Incorporated, Whippany, NJ, October 1998.

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