The Good Solvent: TBAC

Tertiary Butyl Acetate is an exempt solvent in the US and the Canadian paint industry is pushing to have it become an exempt solvent in Canada too.

Environment Canada is in the process of enacting stringent new VOC regulations for a broad range of products and markets, including consumer products and industrial coatings, adhesives, and cleaners. For many Canadians, volatile organic compounds (VOCs) are a relatively new concept, as are their effects on ground-level ozone and particulate emissions. These new regulations are patterned after those enacted by the California Air Resources Board (CARB) and the Ozone Transport Commission, a consortium of thirteen northeastern States.

The impact of these regulations on industry and its products will be profound. Many producers and manufacturers will have to reformulate or switch to entirely new technologies. In some cases, water-based technologies will be used. If water cannot be used, conversion to powder, high solids, energy-curable, and reactive technologies will be used. One option that is often overlooked is the use of VOC-exempt solvents to comply with VOC regulations.

In 1999, when Environment Canada added VOCs to the list of toxic substances in CEPA Schedule 1, it listed 44 exempt compounds identical to the U.S. list of VOC-exempt compounds. This list includes mostly halogenated compounds but also includes acetone and methyl acetate. These 44 compounds were exempted from VOC regulations because it was demonstrated that they have negligible photochemical reactivity, which means they produce essentially no ozone or particular matter when released into the atmosphere.

Since 1999, five more chemicals were added to the U.S. list, including tertiary-butyl acetate (TBAC), a useful solvent for a variety of products and applications. The Canadian list, however, has remained unchanged. TBAC has rapidly become an important compliance tool in the US since its 2004 VOC exemption. In 2005, we petitioned Environment Canada to add TBAC to the list of exempt compounds in CEPA Schedule 1. The Canadian Paint and Coating Association also has requested this addition.

There are several reasons why the VOC exemption of TBAC is needed in Canada. First, the number of practical and cost-effective VOC-exempt solvents is very limited. Second, Canada will be enacting very strict VOC regulations so that all possible compliance options should be made available. Third, the United States has already exempted TBAC and is Canada's main business partner in NAFTA. Thus, not exempting TBAC in Canada would undermine an important goal of NAFTA, which is to promote and harmonize international commerce. TBAC does not contribute to ozone or particulate matter (PM) formation, ozone depletion, or global warming. Last but not least, using it instead of reactive VOCs and toxic chemicals would significantly improve the air Canadians breathe.

WHY ARE SOME SOLVENTS VOC EXEMPT?

Ground-level ozone, a primary lung irritant, is formed by a complex sequence of chemical reactions involving VOCs, nitrogen oxides (NOx), and sunlight. Sunlight is needed to produce OH radicals which kick off the decomposition of VOCs and formation of ozone. However, not all chemicals have the same ozone-forming potential. (See Figure 1.)

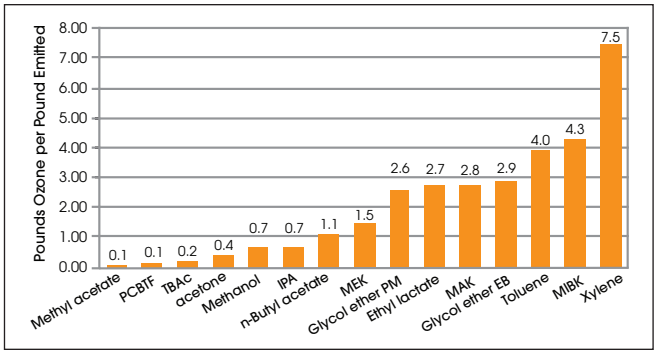

Fig. 1: Ozone Forming potential (MIRs) of Common Coating Solvents.

Maximum Incremental Reactivity, or MIR, is the amount of additional ozone formed when a known quantity of a chemical is injected in a smog chamber under optimal conditions for ozone formation. This concept, developed by Dr. William Carter, has been the scientific basis for several exemptions and California's Reactivity Policy for Aerosol Coatings.

Replacement of reactive solvents like toluene, xylene and MIBK with TBAC in any formulation drastically reduces the ozone formed from these formulations. The US EPA stated that this type of substitution should be encouraged wherever possible, and a VOC policy that includes exemptions for negligibly reactive compounds and a reactivity-based compliance option is an effective way to achieve this goal.

WHERE CAN EXEMPT SOLVENTS BE USED?

Exempt solvents can be used almost anywhere conventional solvents can. However, as with conventional solvents, they must be carefully selected so their properties match the product requirements. For example, there is a limit to the amount of exempt acetone or methyl acetate that can be used in a formulation because their very fast evaporation rates can cause "blushing," a surface haze caused by condensation of moisture into the coating.

PCBTF (para-chlorobenzotrifluoride) is another exempt solvent used in automotive and industrial maintenance coatings. Its principal drawbacks are its high cost and unpleasant odor. PCBTF is also halogenated, making incineration of PCBTF-containing emissions problematic because of the corrosiveness of

TABLE 1: PROPERTIES OF VOC-EXEMPT SOLVENTS

Solvent Properties	Acetone	Methyl Acetate	TBAC	PCBTF
CAS number	67-64-1	79-20-9	540-88-5	98-56-6
Molecular weight	58.08	74.08	116.16	180.5
Boiling point, °C	56	57	98	139
Vapor pressure, Torr at 20°C	185	180	42	5.3
Electrical Resistance, Mohm	<0.01	4.0	23.8	NA
Density, g/mL at 20°C	0.79	0.932	0.867	1.34
(lb/gal) at 20°C	6.59	7.78	7.24	11.2
Evaporation rate, n-BuAc = 1.0	6.3	6.2	2.8	0.9
Surface tension, dyn/cm at 20°C	23.3	25.2	22.4	25.0
Solubility in water, %	100	23	0.3	<0.1
KB value	NA	NA	114	64
Hansen solubility parameters, Total	9.8	9.2	7.7	9.5
Hydrogen bonding	3.4	3.7	2.9	1.9
Dispersion (non-polar)	7.6	7.6	7.0	8.8
Polar	5.1	3.5	1.7	2.9
Flash point, °F	-4	5	40	109
PEL, TWA ppm	750	200	200	NA
MIR, g ozone/g	0.40	0.07	0.20	0.11

the combustion by-products. TBAC also has a strong odor but is less expensive and less dense than PCBTF, resulting in significantly lower formulated costs. Exempt solvent properties are listed in Table 1.

TBAC is a medium-fast evaporating solvent (2.8 times faster than n-BuAc) with low water solubility (0.3 per cent), a flash point of 40°F. [1] Although the odor is not as objectionable as PCBTF or as strong as n-BuAc, it will probably prevent its use in most interior consumer paints. Its low flash point will also keep it out of formulations that have a 100°F flash point requirement. Finally, its low water solubility and fast evaporation rate will prevent its use in most waterborne paints, especially architectural latex paints. Therefore, TBAC will be used predominantly in solvent-based industrial coatings, especially in the following applications.

- Automotive refinish coatings
- Industrial maintenance topcoats
- Air-dry OEM coatings
- Wood lacquers, varnishes and enamels
- Thinners
- Paint gun cleanup and degreasing

WOOD COATINGS

Nitrocellulose (NC) lacquers are among the oldest of paint technologies, and are still used extensively in the wood furniture market because of their low cost, ease of application and repair, and unparalleled clarity and depth-of-image. However, conventional NC lacquers contain 70 per cent to 90 per cent solvents resin at spray viscosity and may no longer comply with the new VOC content limits for lacquers (680 or 550 g/L). Other wood coatings include enamels (250 g/L), wash primers (420 g/L), varnishes (350 g/L), and stains (250 g/L).

Fortunately, TBAC is a good solvent for all these wood coating technologies. This means that manufacturers of wood furniture and cabinetry will continue to be allowed to use low-solids NC

TABLE 2: WOOD LACQUER REFORMULATION FOR HAP & VOC COMPLIANCE

Components	Standard Lacquer	Formulation A	Formulation B
RS 1/2 Nitrocellulose	10.0	10.0	10.0
Beckosol® 12-035	7.0	7.0	7.0
Diisononyl phthalate	3.0	3.0	3.0
Xylene (incl. from 12-035 resin)	35.2	4.7	4.7
MEK	10.7	0.0	0.0
n-Butyl acetate	22.7	13.9	0.0
Isopropanol (from NC)	4.3	4.3	4.3
n-Butanol	7.1	7.1	7.1
TBAC	0.0	41.2	50.0
PM acetate	0.0	0.0	13.9
Total lbs	100.0	100.0	100.0
Formulation Constants			
% solids	20	20	20
lbs Ozone/lb. solids	15.4	4.2	3.9
lbs VOC/lb. solids	4.0	1.9	1.5
Lacquer Properties			
Viscosity, cps	146	185	102
Dry time, min	20	10	10
20 degree gloss	43	50	58
60 degree gloss	86	88	91
Whiteness index	65	66	67
Yellowness index	6.0	5.7	5.4

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lacquers, but without the environmental impact of the old formulations. Table 2 shows the effect of replacing MEK, xylene and n-BuAc with TBAC and PMA in a standard NC wood lacquer.

The lacquer properties were essentially unchanged. However, the VOC content was significantly reduced. In this case, ozone formation was reduced 75 per cent, and the VOC content 63 per cent. This means that the environmental benefit of using TBAC exceeded the compliance benefit provided to the formulator.

TBAC IN TWO-COMPONENT EPOXY[2] AND URETHANE COATINGS

Two-component epoxy and urethane coatings are used extensively in industrial maintenance and automotive applications that require superior corrosion resistance and weatherability. Epoxy resins are crosslinked with amine- or amido-functional curing agents just prior to application to give a tough, flexible, corrosion- and chemically-resistant film. Acrylic and polyester polyols are crosslinked with aliphatic polyisocyanates to give highly weatherable and durable urethane topcoats.

TBAC is a unique ester solvent because it is almost completely unreactive with amines and polyamide crosslinkers. Unlike n-butyl acetate, for example, it can be used to formulate storage stable 2K epoxy coatings. TBAC is also a good solvent for both acrylic polyols and isocyanate crosslinkers. Several suppliers of acrylic polyols are now offering their products in TBAC. Isocyanate suppliers have evaluated the stability of their most common crosslinkers in TBAC and found it to be comparable to toluene. In most formulations, the fast solvents are replaced with TBAC. Slower solvents like MAK or EEP are retained in the formulation to maintain good film appearance and durability. The typical ratio of TBAC to slow solvent in air-dry formulations is 70/30.

TBAC IN ALKYD COATINGS

Alkyd resins suppliers have also begun offering their resins in TBAC or TBAC-containing blend. Unlike acetone, TBAC can be safely used in alkyd resin manufacture. It is a useful compliance tool for industrial baking and air-dry enamels based on short-oil and modified alkyd resins such as phenolic- and silicone-modified alkyds. There are several reasons for this.

First, the industrial market is more tolerant of coatings with flammable or odorous solvents than the architectural market, which relies predominantly on odorless mineral spirits. Second, industrial medium- and short-oil alkyd resins are typically more viscous and require higher solvent levels than their long-oil counterparts for the do-it-yourself or contractor-applied architectural markets.

VOC-exempt solvents are practical and cost-effective tools for VOC compliance. TBAC has an intermediate evaporation rate and broad solvency for coatings resins, making it a more useful formulation tool for VOC-compliant industrial coatings, thinners and cleanup.

Lyondell Chemical Co. and the Canadian Paint and Coatings Association have requested that Environment Canada add TBAC to the list of VOC-exempt compounds in CEPA Schedule 1. Although Environment Canada has not yet granted our request, we anticipate that this will occur before the new VOC regulations come into effect. **CM**

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References: [1]www.tbac.com
[2]http:/www.lyondell.com/html/products/techlit/PC166.pdf