DIMETHYL CARBONATE (DMC) The Newest VOC Exempt Solvent

Kowa American Corp

April 2010

Previous VOC Exempt Coating Solvents

- Realistically there were only a handful of VOC exempt solvents that are not HAPS (or ODS) and under $ 2.00/lb that formulators can use for coating, cleaning & adhesive solvents:
- Acetone
- Methyl acetate (MeAc)
- tert-Butyl Acetate (tBAc)
- p-Chlorobenzotrifluoride (PCBTF)

Dimethyl Carbonate (DMC)

- VOC exemption petition filed July 2004 by Kowa American Corp.
- DMC has perhaps lowest MIR value of any liquid chemical in commercial use based on studies conducted by Dr. William Carter (study funded by Exxon Mobil Chemical)
- Ultra-low MIR is allowing for fast approvals by the various states due to its very favorable ozone reduction potential

DMC & PC recently exempted by the EPA

- Dimethyl Carbonate (DMC) & Propylene Carbonate exempted by EPA on Jan 13, 2009
- Each state must also exempt DMC & PC for stationary source VOC rules.
- Almost all states beside California will have exempted DMC by the end of 2010 (33 states have now exempted DMC (April 2010)).
- California must have each of their Air Districts separately exempt DMC for coatings, Inks and adhesives, which is proceeding forward.

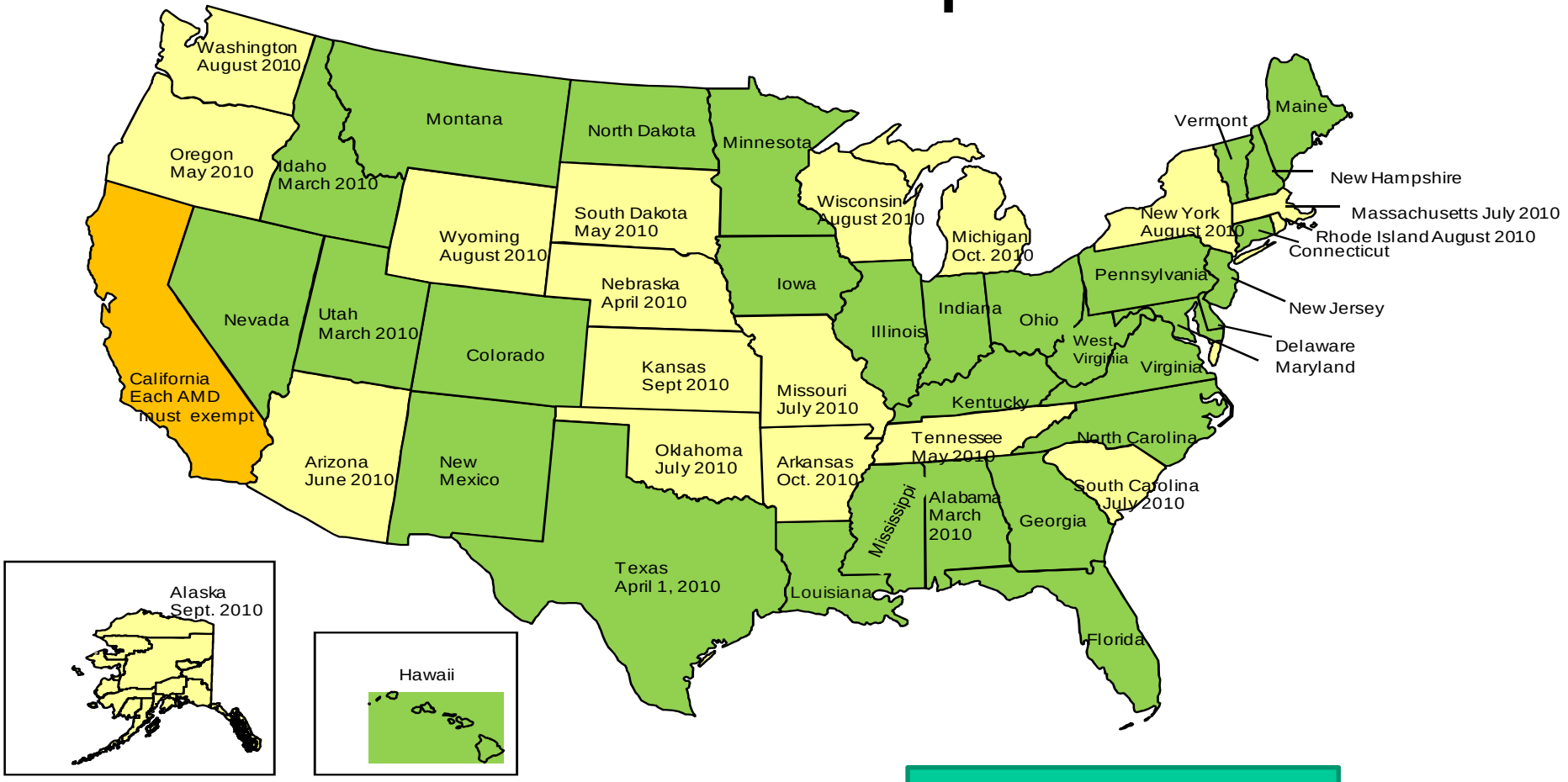
DMC for Architectural, Aerosol & Automotive Refinish Coatings

- DMC is VOC exempt in all states except CA, NY, RI, MA for:

  Architectural Coatings (subpart D), Automotive Refinish Coatings (Subpart B) and Consumer Items (subpart C) based on Federal VOC rules (40 CFR part 59)

- DMC (with its ultra low MIR value) can soon be used nationwide in aerosol coatings (already approved for use in all of Calif.).

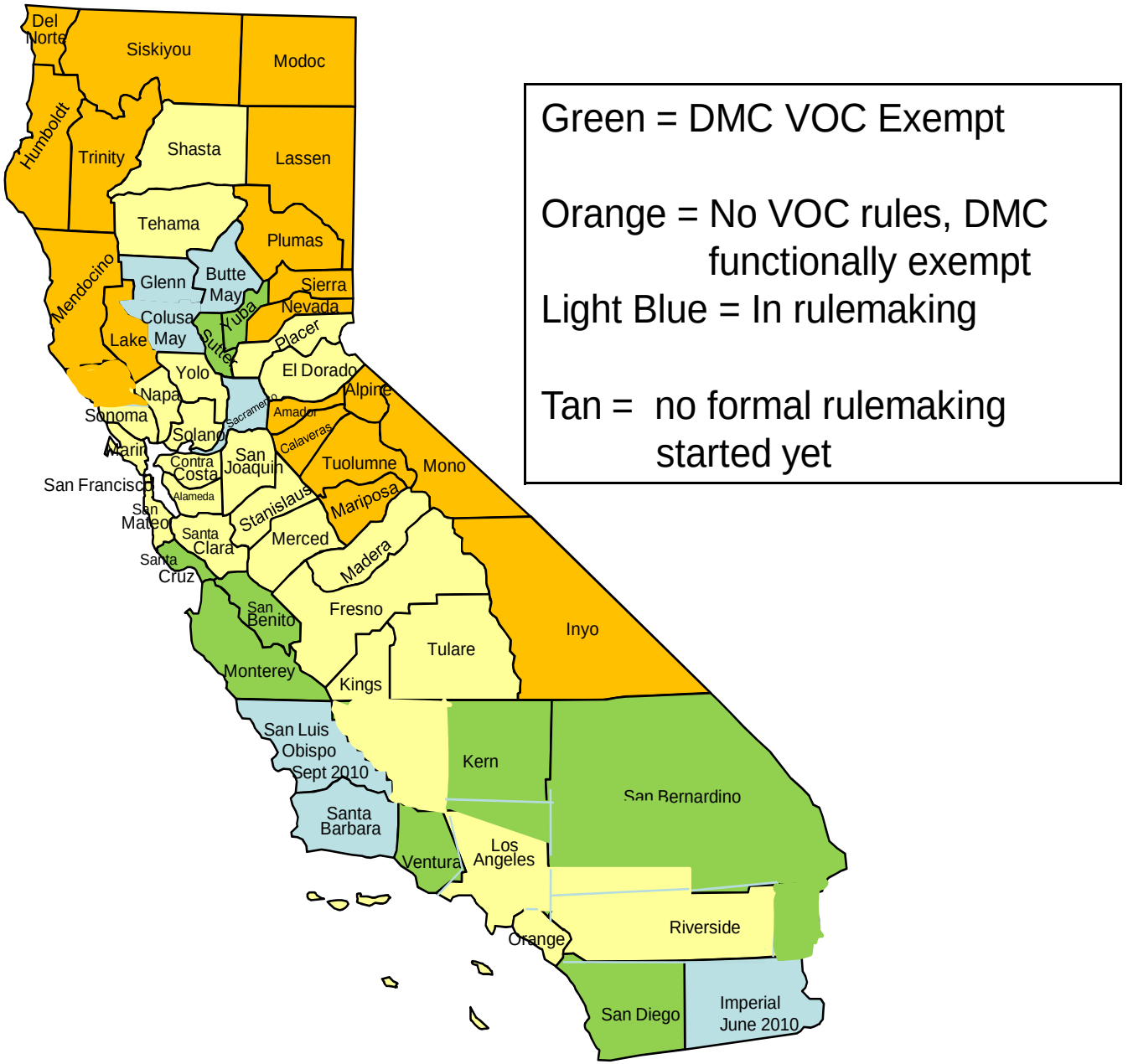
DMC VOC Exempt States



DMC VOC exempt states in green

DMC Exemption Status in Calif.

- San Diego, Monterey, Mohave, Ventura & Feather River AMD's have exempted DMC
- Most county districts plan to exempt or have no VOC rules (DMC functionally exempt)
- 3 main regional AMD's delaying process, we need help in showing them DMC's appeal
- SCAQMD (L.A.)Naveen Berry 909-396-2363
- Bay Area QMD Dan Belick 415-749-4786
- San Joaquin George Heinen 559-230-6100



Green = DMC VOC Exempt

Orange = No VOC rules, DMC functionally exempt

Light Blue = In rulemaking

Tan = no formal rulemaking started yet

MIR Reactivity Values (2009)

	MIR gram basis	MIR mole basis
DMC	0.055	4.95
Ethane	0.26	7.8
Acetone	0.35	20.3
Methyl Acetate	0.067	5.2
Prop Carbonate	0.27	27.56
Benzotrifluoride	0.28	40.91

DMC General Properties

- DMC is a colorless, fast evaporating solvent
- Has substantial polar nature, and moderate h-bonding strength effective in replacing esters, glycol ethers and ketones in formulations
- Has low toxicity, an unobjectionable methanol type odor and low skin irritation
- Freezes at 2 – 4 ºC (36 –38 ºF)
- Flammable Liquid, Flash point 17 ºC (63 ºF)

DMC Evaporation Rate

Fast to moderate evaporation rate (3.22 – 3.4, BuAC = 1.0), similar to tBAC (2.8), toluene (2.0) and isopropyl acetate (3.0)

Can be used to as slightly slower evaporating replacement for MEK (3.8), Ethyl Acetate (4.1- 4.2), or as faster evaporating replacement for IPA (1.7), MPK (2.3), Ethanol (1.8) and MIBK (1.6)

DMC - Flammability

- DMC has a flashpoint of 63ºF (17ºC)
- Flammability will limit use in consumer coatings, cleaning or indoor applications
- Flammability risk still much lower than acetone (-4º F), ethyl acetate (26ºF) or MEK (26ºF), which DMC can readily replace
- Partially water soluble (up to 13 % in water), which allows water to be more effective in fighting DMC based fires.

Flashpoint, E. rate, Boiling point

	Evaporation Rate BuAc =1.0	Flashpoint ºF	Boiling point ºC
DMC	3.22	63	90
PCBTF	.9	109*	139
Acetone	5.6	-4	56.5
Prop Carb	<.005	269.6	240
tBAc	2.8	40	98
BTF	2.8	54	102

DMC Solubility Properties

- Hildebrand solubility parameter 20.3 Mpa
- Hansen solubility parameters: Dispersion 15.5 polar 3.9 h-bond 9.7 molar vol. 84.2
- Similar solubility parameters to some common glycol ethers: cellosolve acetate, ethylene glycol butyl ether acetate, propylene glycol monobutyl ether and propylene glycol monoethyl ether acetate

DMC Solubility Properties

- DMC has been described as useful in acrylics, urethane and alkyd systems as a co-solvent
- DMC is miscible with almost all organic solvents
- DMC would easily replace oxygenated solvents like esters and glycol ethers
- DMC should replace alcohols and ketones with appropriate co-solvents

DMC’s Odor Profile

- One of DMC’s most favorable properties is a mild and non-offensive odor.
- PCBTF and Tert-Butyl Acetate odors are much more pronounced and pungent
- Noxious solvent odors are perhaps the most important concern of neighbors to body shops, factories, print shops and other industrial settings
- Mild odor is well received by workers handling DMC or used in their work areas

DMC – Toxicity

- Dimethyl carbonate (like all methyl esters) rapidly de-esterifies in the body to methanol & CO_2
- DMC has low acute oral toxicity (LD50 rat 12,900 mg/Kg, LD50 mouse 6,000 mg/Kg)
- DMC was found to be negative in mutagenic tests (*in vitro* Ames & comet assay)
- Readily biodegradable and has low potential to bio-accumulate, possibly toxic to algae
- Not expected to be toxic to fish or bacteria

DMC & Methanol toxicities

- Federal EPA confirms that there is no evidence Methanol is carcinogenic from all studies done
- EPA feels teratogenicity is major endpoint health concern of environmental exposure for Methanol (and therefore DMC)
- Well run study by Exxon/Mobil on DMC's teratogenic potential confirms it is virtually identical to Methanol's (NOEL 1,000 ppm)
- Kowa recommends an 8 hour industrial PEL of 100 ppm based on DMC's toxicity profile

California OEHHA Assessment

- Califonia's Office of Environmental Health Hazard Assessment issued a toxicity assessment of DMC in Dec.2009 that used used the toxicity of its primary metobolite methanol and existing DMC studies to issue a toxicologicol assessment of DMC
- Reported there were **no** concerns that DMC like methanol would be carcinogenic

Calif. OEHHA Conclusion

- OEHHA report concluded that doses levels of DMC likely to be achieved by environmental exposures to the general public by inhalation appears to have "**relatively minor"** environmental health concerns
- Established interim REL consistent with Methanol it's primary metabolite

DMC - Azeotropes/Binary systems

- There have been a few cryptic references in literature to DMC forming azeotropes with alcohols and ketones without further data
- Azeotropes using DMC could be the “wild card” in developing coating or cleaning formulations, substantially changing the evaporation rate, solubility and perhaps flammability profiles
- Using DMC & PC together can replace PCBTF, Xylene, butyl acetate, aromatic 100

Propylene Carbonate

- Propylene Carbonate is a very slow evaporating solvent (evaporation rate <.005, BuAc =1). This will restrict its solvent use.
- Low viscosity 2.4 cps, high flashpoint 253º F
- Practically non-toxic by oral, dermal or Inhalation, slight skin irritant, eye irritant
- Available from Kowa from same Chinese source as our Dimethyl Carbonate.

Propylene Carbonate

- Propylene Carbonate's very low toxicity profile allows it's use in cosmetic products, therefore PC safe for all consumer items
- Readily biodegradable
- Useful as a co solvent, wetting agent or tailing solvent (last solvent to evaporate).
- Literature suggest can be used in binary & tertiary solvent systems to replace common solvents like trichlorethane and toluene

BENZOTRIFLUORIDE - BTF

- Proposed VOC exempt solvent, EPA recently tabled petition due to recently revised MIR values in 2009
- Low MIR of 0.28 (2009) should shortly be allowed for aerosol coatings on federal level, now allowed in Aerosol coatings in Calif. with a MIR value of .26 (2004 table)
- Almost a direct replacement for toluene, similar solvency and evaporation rate (2.8)