VIII.

Reformulation Options to Meet the Proposed Reactivity Limits

In this Chapter, Air Resources Board (ARB) staff provides information on methods a manufacturer may employ to reduce the overall reactivity of an aerosol coating to comply with the proposed limits. However, no specific "formulas" are suggested as to how a currently non-complying product would reformulate to comply with the proposed reactivity limits. ARB staff recognizes that an aerosol coating is a "package" and simply suggesting a lower reactive solvent for a currently used higher reactive solvent is inappropriate. Properly formulated aerosol coatings must provide for adequate solvency of the particular resin system and pigments. In addition, a combination of slower and faster evaporating solvents is required to allow for proper film formation once the product is applied. The propellant system must also maintain constant pressure such that the entire product can be expelled uniformly.

Rather than suggesting specific "formulas," or solvent substitutions, ARB staff provides information on the wide range of reactivities of propellants, as well as, slower and faster evaporating solvents that could be used to reduce the reactivity of aerosol coating products. An abbreviated list is provided here, but manufacturers have the option of choosing from several hundred reactive organic compounds (ROC) in the Tables of Maximum Incremental Reactivity (MIR) Values contained in proposed new Subchapter 8.6, sections 94700-94701, and also included as part of Appendix A of this Technical Support Document.

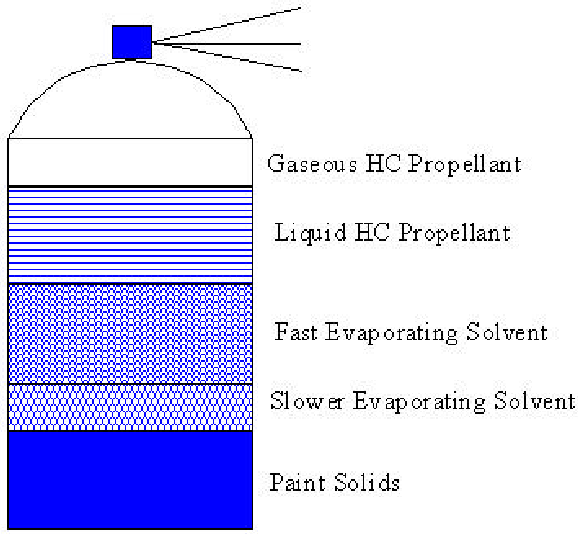
The proposed reactivity limits may not necessarily require reductions in total ROC content, but likely will require lower reactive ROCs to be used to reduce the ozone formed from products. Of course, reductions in product reactivity can also be achieved by increasing the coatings "solids," which in turn leads to reductions in the total amount of ROC contained in a product. By requiring products to reduce their overall reactivity, rather than total mass of VOCs, the proposed reactivity limits provide an equivalent air quality benefit as would be associated with the mass-based VOC limits, and provide more reformulation options at potentially less cost.

Before discussing the variety of solvents and propellants available, basic information on aerosol coating product design is provided.

A. Product Formulation of Solvent-based Aerosol Coatings

Shown below is a schematic diagram of an aerosol coating and the types of ingredients contained.

FIGURE VIII-1 SOLVENT-BASED AEROSOL COATING PRODUCT



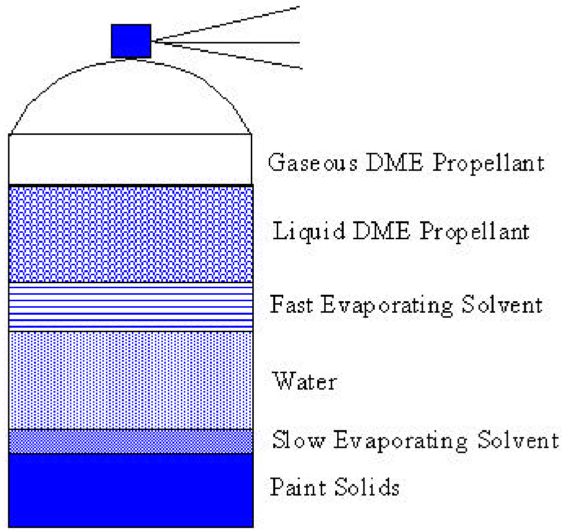
As shown in Figure VIII-1, solvent-based aerosol coatings consist primarily of propellants (which exist in an equilibrium state between the gaseous and liquid forms), fast and slower evaporating solvents, and coating solids. All of the ingredients, except the gas phase propellant, are in a single homogeneous phase after the product is shaken to evenly distribute the coating solids. The hydrocarbon propellants and solvents are the ROCs, while the solids account for the non-ROC ingredients. The propellants are almost without exception hydrocarbon blends including propane, n-butane, or isobutane. A wide variety of solvents are used including ketones (primarily acetone), esters, alcohols, aliphatic and aromatic hydrocarbons. Generally, a balance of fast and slower evaporating solvents is used, with a larger proportion of fast evaporating solvent.

B. Product Formulation of Water-based Aerosol Coatings

Water-based aerosol coatings account for about five percent of the aerosol coatings market. These products are formulated differently than solvent-based products, and generally are lower in reactivity than solvent-based products.

As shown in Figure VIII-2, water-based aerosol coatings consist primarily of propellant (which exists in an equilibrium state between the gaseous and liquid forms), water, fast and slower evaporating water-miscible solvents, and coating solids. Figure VIII-2 does not show ingredients used in small amounts such as surfactants, solvents used as carriers for resins, drying agents, wetting agents, and thickeners. The propellant in water-based products is almost always dimethyl ether (DME) because it is water-soluble, unlike the hydrocarbon propellants. DME also serves as a cosolvent in water-based coatings. The faster evaporating solvents are typically alcohols such as ethyl or propyl alcohol, while the slower evaporating (coalescing) solvents are generally glycols or glycol ethers.

FIGURE VIII-2 WATER-BASED AEROSOL COATING PRODUCT



In “water-reducible” water-based aerosol coatings, all the ingredients except the gas phase propellant are in a single homogeneous phase (after the product is shaken to evenly distribute the coating solids). In most “emulsion” or “dispersion” water-based systems, the resin and carrier solvent are dispersed in tiny “droplets” within the “continuous” phase of water, water soluble solvents, and liquid DME propellant. The original aerosol coatings staff report provides a detailed discussion of the different types of water-based aerosol coatings (ARB, 1995).

C. Reactivity-based Reformulation Strategies

The most likely path non-complying products would take to reformulate to meet the proposed reactivity limits is to substitute lower reactive ROC solvents for the higher reactive solvents currently used in their products. Other options include use of lower reactive propellants and increasing coating solids (which likely leads to reduced ROC content). It should be noted, that reducing total ROC content may also be a path to reduce product reactivity and ozone formation potential. The path that manufacturers choose to reformulate their products will be based on maintaining the proper balance of slower and faster evaporating solvents. Staff believes that by requiring “substitution,” rather than “reductions,” efficacious products will continue to be available.

Provided in Table VIII-1, is an abbreviated listing of ROCs and their respective MIR values. For our purposes here ROCs are divided into propellants, fast evaporating and slow evaporating solvents. Commonly evaporation rate is compared relative to that of n-butyl acetate, which has a value of 1.0. Slower and faster evaporating ROCs are categorized by having evaporation rates of < 0.8 to 3.0; and > 3.0, respectively. In addition to considering evaporation rate we suggest that manufacturers consider any potential toxics impacts.

TABLE VIII-1
CLASSES OF ROCS AND THEIR MIRS

	ROC	MIR
Propellants	HFC-152a	0.00
	Dimethyl Ether	0.93
	Propane	0.56
	n-Butane	1.33
	Isobutane	1.35
Faster-evaporating Solvents	Acetone	0.43
	Methyl Acetate	0.07
	Ethyl Acetate	0.64
	Isopropanol	0.71
	Ethanol	1.69
	2-Butanol	1.60
Slower-evaporating Solvents	Para-Xylene	4.25
	Xylene Isomers Mixture	7.37
	Meta-Xylene	10.61
	Toluene	3.97
	Ethylbenzene	2.79
	PCBTF	0.11
	t-Butyl Acetate	0.22
	Isobutyl Isobutyrate	0.64
	Isobutyl Acetate	0.67
	n-Propyl Acetate	0.87
	n-Butyl Acetate	0.89
	n-Butyl Propionate	0.89
	1-Methoxy-2-Propyl Acetate (PGME Acetate)	1.71
	Ethyl 3-Ethoxy Propionate	3.61
	Isobutyl Isobutyrate	0.64
	VM & P Naphtha	2.03
	Odorless Mineral Spirits	0.91
	Methyl Ethyl Ketone	1.49
	Methyl Propyl Ketone	3.07
	Methyl Isobutyl Ketone	4.31
	Methyl Amyl Ketone	2.80
	Methyl Isoamyl Ketone	2.80
	1-Methoxy-2-Propanol	2.62
	3-Methoxy-1-Butanol	0.97
	Diacetone Alcohol	0.68

1. Solvent-based Products

a. Propellants

Regarding propellants, the current hydrocarbon propellants used are moderately reactive. However, propane (MIR = 0.56) is considerably less reactive than butane (MIR = 1.33) or isobutane (MIR = 1.35). Using a propellant blend with more propane, such as an A-70 blend (51 percent propane, 49 percent isobutane) or an A-108 blend (100 percent propane), may be an effective means to reduce product reactivity. Another option would be to replace all or part of the hydrocarbon propellant with hydrofluorocarbon-152a (HFC-152a) (MIR= 0).

b. Faster-Evaporating ROCs

For the current mass-based VOC limits, increased use of acetone was suggested as a likely reformulation option (ARB, 1998a). The same could very well be true for reformulating to meet the proposed reactivity limits. As the faster evaporating solvent constituent, acetone is currently the solvent of choice in aerosol coatings. Acetone is also low reactive (MIR = 0.43). To the extent that acetone content could be increased to replace a higher reactive solvent, the product's reactivity would be lowered. Another solvent with similar properties to acetone, with even lower reactivity, is methyl acetate (MIR = 0.07). However, there are limitations to these options, because a balance must be maintained between fast evaporating solvents and slower evaporating solvents. Too much of a fast evaporating solvent such as acetone can produce defects such as bubbles, pinholes, or "blushing" (Hydrosol; Plasti-kote; Raabe; Seymour of Sycamore).

c. Slower-Evaporating ROCs

However, to efficiently reduce the product's overall reactivity, it is likely that lower reactive substitutes would need to be found for the slower-evaporating solvents. Slower-evaporating aromatic solvents, such as xylene and toluene are currently used. These aromatic ROCs are also among the most reactive ingredients used in aerosol coatings. Depending on the resin system used, other reformation options include consideration of n-butyl acetate, isobutyl acetate, ethyl acetate, isobutyl isobutyrate, methyl isobutyl ketone, methyl ethyl ketone, 1-methoxy-2-propyl acetate (propylene glycol monomethyl ether acetate), or ethyl-3-ethoxy propionate (EEP).

N-butyl acetate can be used as solvent for acrylics, nitrocellulose, and most modified alkyds (Eastman, 2000). Although the evaporation rate for n-butyl acetate is higher than that for xylenes, solvents like 1-methoxy-2-propyl acetate, methyl amyl ketone, n-butyl propionate, methyl isoamyl ketone, or isobutyl isobutyrate can be blended with the n-butyl acetate to slow its evaporation rate (Eastman, 2000). Although these solvents may or may not be used in a one-to-one by-weight mass substitution for the relatively higher reactive solvents, a combination of one or more of the lower reactive ones may be considered.

2. Water-based Products

For this discussion, we define "water-based" aerosol coatings as products formulated with a blend of water and DME. Water-based aerosol coatings, as stated above, are all formulated very similarly with the primary ROC being DME, which serves as both propellant and co-solvent. The DME serves as the faster-evaporating solvent. Dimethyl ether is moderately reactive with an MIR value of 1.02, significantly lower than the weighted reactivity of the ROCs used in solvent-based products. The other ROCs used in water-based products include smaller amounts of alcohol and other oxygenated solvents such as glycol ethers or glycols. Alcohols are typically faster while the glycol ethers are the coalescing slower-evaporating solvents.

In a typical water-based aerosol coating, the amount of DME is equivalent to the amount of water, which is approximately 35 percent-by-weight. There is generally 5 percent-by-weight of a secondary alcohol, such as 2-butanol, and 5 percent-by-weight of a glycol ether, such as 2-butoxy-ethanol. The remaining percentage is composed of solids. Thus, the overall reactivity profile of the water-based ROC emissions yields a lower ozone-formation potential.

There are water-based products in four of the general coating categories of aerosol coatings. One hundred percent of these current water-based products would comply with the proposed reactivity limits.

D. Conclusion

This proposal presents a new approach of regulating the emissions from aerosol coating products. Under a mass-based VOC reduction, all VOCs are treated equally in terms of ozone formation potential, or in some cases (exemptions), form so low an amount of ozone that they are not regulated. Therefore, a reactivity-based control strategy could be viewed as a “refinement” of mass-based control approaches. The reactivity-based approach proposed here relies primarily on ROC substitution rather than ROC reduction, yet still preserves the ozone reduction benefits of the previously adopted mass-based VOC limits. A reduction in the total VOC content may not be necessary. By requiring “substitution” rather than “reduction” of ROCs, staff believes that reformulation to meet the reactivity limits, as explained in Chapter XI, Economic Impacts, will be more cost-effective.

Given the wide variety of ROCs available that can serve as propellants and slower or faster evaporating solvents and their wide range in reactivities, staff believes that the proposed reactivity limits are feasible for both solvent-based and water-based aerosol coatings. As was shown in Chapter VII, in almost all categories a significant complying marketshare exists for both solvent-based and water-based aerosol coatings. In fact, for water-based coatings we note that all reported products currently comply with the proposed limits.

REFERENCES

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