

Selecting effective xylene replacements for protective coatings

Abstract

This publication is designed to assist formulators in replacing xylene in traditional solventborne coatings. An aromatic hydrocarbon such as xylene is more active than an aliphatic hydrocarbon and is a very important component in formulating protective coatings. Xylene is used extensively in many coatings systems as either the primary solvent or as a diluent. It is also commonly used in aerosols and as a synthesis solvent for acrylic resins and a reflux/letdown solvent for alkyd and saturated polyester resins.

Evaluations were conducted on a series of paint formulations to determine whether combinations of an oxygenated solvent and aliphatic hydrocarbon could successfully be used to replace xylene. Three solvents (methyl amyl ketone [MAK], *n*-butyl propionate, and isobutyl isobutyrate [IBIB]) were shown to be effective in replacing xylene in traditional solventborne coatings. In the study, the three oxygenated solvents provided coatings with very low HAP content while maintaining coatings performance. At the same time, it was demonstrated that the oxygenated solvent could be blended with an aliphatic hydrocarbon to reduce cost without loss of coatings appearance or performance.

Background

Title III of the Clean Air Act (CAA) of 1990 established a list of chemicals and chemical categories that are designated as hazardous air pollutants (HAPs). Included on that list were several solvents that are commonly used in coatings facilities, e.g., MEK, MIBK, toluene, and xylene. The Environmental Protection Agency (EPA) has developed Maximum Achievable Control Technology (MACT) standards that establish HAP emission limits for 12 categories of industrial surface coatings pursuant to Section 112 of the Act.

Several options exist for reducing HAP emissions in surface-coatings operations. The three primary choices include (1) continue with existing coatings and invest in emission control equipment and technology; (2) select a different coatings technology such as water-based, powder, or UV-cure; or (3) reformulate present coatings using non-HAP solvents.

Many coatings users believe that solvent reformulation (option 3) is the lowest cost alternative. This choice is also based on other factors such as familiarity with current coatings, minimal equipment changes, and proven coatings performance. When this option is chosen, coatings suppliers must reformulate their coatings using non-HAP solvents.

Table 1 shows three oxygenated solvents (MAK, IBIB, and *n*-butyl propionate) that are useful in formulating xylene replacements. Each solvent is supplied by Eastman and can be used to develop surface coatings with lower HAP content or essentially no HAPs. Each solvent is urethane grade (<500 ppm H₂O) and is suitable for use in lacquers and thermoset and ambient-cured enamels.

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Table 1 Physical properties for suggested xylene replacements

Physical properties	Xylene	<i>n</i> -BuOPr	MAK	IBIB
Evaporation rate (<i>n</i> -BuOAc = 1)	0.7	0.5	0.4	0.4
Specific gravity @ 20°/20°C	0.865 ^a	0.876	0.818	0.855
TLV, ppm	100	—	50	—
Max. incremental reactivity (MIR) value ^b	7.37	0.89	2.80	0.61
HAP	Yes	No	No	No
Electrical resistance, megohms	>20	>20	0.4	>20
Solubility, water in, wt%	<0.5	0.7	1.3	<0.2
Solubility, in water, wt%	<0.5	0.4	0.5	<0.1
Boiling range, °C	135–146	145–149	147–153	145–152
Flash point TCC, °F	83	97 ^c	102	104

Hansen solubility parameters				
Total	8.7	8.5	8.6	8.1
Nonpolar	8.6	7.7	7.9	7.4
Polar	0.5	1.5	2.8	1.4
Hydrogen bonding	1.5	2.9	2.0	2.9

Solvent activity, cP				
R ¹ / ₂ -sec NC (8 wt%)	Insoluble	34	25	42
CAB-381-0.5 (8 wt%)	Insoluble	116	20	Insoluble
Paraloid™ B-66 (40 wt%)	520	878	580	2,450
Epon™ 1001F (50 wt%)	Insoluble	117	82	Insoluble
Acrylamac™ HS 232-2980 (70%)	548	538	498	668
Duramac™ HS 57-5720 (65%)	778	671	581	868
Polymac™ HS 57-5776 (65%)	157	155	123	212

^a60°/60°F

^bReference—“Regulation for reducing the ozone formed from aerosol coating product emissions” (subchapter 8.6)

^cSetaflash

Acrylamac™ acrylic resin supplied at 80 wt% solids in MAK and reduced to 70 wt% solids with the given solvent.

Duramac™ alkyd resin supplied at 75 wt% solids in 90/10 wt% MPK/*n*-butyl acetate blend and reduced to 65 wt% solids with the given solvent.

Polymac™ polyester resin supplied at 85 wt% solids in PM acetate and reduced to 65 wt% solids with the given solvent.

Developing xylene replacement blends using non-HAP solvents

The choice of an alternative solvent or solvent blend can be greatly simplified by using computer software that allows the user to match or exceed the designated performance requirements. Particularly useful to the formulator is the ability to select solvents such that the solvent blend will dissolve the resin(s) used in the coatings formulation. This capability, which is predicting the miscibility characteristics of polymers and solvents, is possible through the use of solubility parameters. Once the solubility parameters have been established for a control blend containing xylene, the software will provide a non-HAP solvent blend with similar values that will dissolve the resin(s) of choice for the selected coating.

Also critical to the success of the replacement blend is its evaporation rate characteristics. The solvent blend of choice must provide the desired application and film formation properties. Again, computer software allows the user to match the evaporation rate profile of a control blend with that of a reformulated blend. This tool provides two very useful evaporation rate values. First, the "R.E.R." value denotes the "relative evaporation rate" compared to *n*-butyl acetate = 1. Second, the program will provide information containing "weight % solvent composition versus weight % of the blend evaporated." The composition of the solvent blend is shown at 10%, 30%, 50%, 70%, and 90% weight loss. In addition, the solubility parameters for the blend are shown at each composition interval. The data allow the user to design a solvent replacement blend for a selected coating, which when applied to a surface ensures adequate flow and quality film formation.

For a majority of coatings applications, the use of oxygenated solvents is required to satisfy the needs for a suitable non-HAP xylene replacement blend. If the xylene content is relatively low in the coating (<10% of the volatiles), a direct substitution with one of the solvents in Table 1 might be the most cost-effective substitution. However, for blends containing higher levels of xylene, it may be desirable to examine combinations of oxygenated solvents with an aliphatic hydrocarbon to lower total formulating costs.

Although not shown in this study, alcohols such as *n*-butanol can also be used to develop alternatives to xylene. The ratio of oxygenated solvent(s) to aliphatic hydrocarbon should be determined for each coating because resins vary in aliphatic hydrocarbon tolerance. Also, other solvents present in the blend can increase or decrease this effect. Again, the use of the solubility parameter concept is very valuable in estimating an appropriate range of aliphatic hydrocarbon level for a specific coatings system.

If an aliphatic hydrocarbon is used in the selected blend reformulation, one should choose a product with a very low HAP content. In addition, the aliphatic hydrocarbon should not be the last solvent to evaporate from the film to avoid potential resin blush.

Formulating low HAP or HAP-free coatings also requires the formulator to choose resins, pigment pastes, and additives that are supplied in solvents that are not regulated as HAPs. Buyers should confirm with their suppliers the level of HAPs in their purchased products, if any.

Often when developing coatings with lower HAP content, it is essential that the reformulated coating have equivalent or lower VOC content. This is necessary when regulatory guidelines for VOC emissions are applicable for the specific coatings category. This additional restriction on formulating latitude makes the choice of a suitable alternative blend even more crucial. The selection of oxygenated solvents that have very low density and good solvent activity, such as ketones and esters, is very important in satisfying VOC regulatory requirements.

Table 2 shows some suggested replacement blends for xylene that were used to formulate a series of coatings for comparative evaluations. The table highlights some of the physical properties of xylene and the replacement blends. Similarity in physical properties suggests that the given blends represent good replacement candidates for developing HAP-free alternatives to xylene.

Table 2 Suggested solvent blend replacements for xylene

Composition, wt%	Control	MAK/Aliph. hydrocarbon	<i>n</i> -BuOPr/Aliph. hydrocarbon	IBIB/Aliph. hydrocarbon
Xylene	100.0	—	—	—
MAK	—	57.1	—	—
<i>n</i> -Butyl propionate	—	—	63.2	—
IBIB	—	—	—	56.4
VM&P Naphtha 66 ^a	—	42.9	36.8	43.6
Total	100.0	100.0	100.0	100.0

Solvent blend properties				
Evaporation rate (<i>n</i> -BuOAc = 1)	0.7	0.7	0.7	0.7

Hansen solubility parameters				
Total	8.74	7.91	7.83	7.60
Dispersion	8.60	7.68	7.58	7.40
Polar	0.50	1.55	0.96	0.75
Hydrogen bonding	1.50	1.11	1.73	1.55
Wt/gal	7.17	6.59	6.91	6.75

^aThe aliphatic hydrocarbon of choice should have a very low HAP content and an evaporation rate similar to or higher than xylene.

Reformulating coatings using non-HAP solvents

The following section provides coatings reformulation and physical property information for three systems: a high-solids phenolic-modified alkyd air-dry primer, a conventional acrylic/urethane 2K enamel, and a polyester/melamine high-solids coating. In each reformulation, the objective was to replace xylene while maintaining the solubility/application/performance characteristics of the control. The total solvent composition for each formula was optimized to match the properties of the control blend containing xylene.

Tables 3, 4, and 5 contain the respective formulations used for this study coupled with the solution and physical property evaluations. When each coating was applied at similar film thickness and cured, the control and the replacement formulas had essentially equivalent properties. These screening studies revealed that various combinations of an oxygenated solvent with an aliphatic hydrocarbon can effectively be used as xylene replacements in protective coatings.

Selecting effective xylene replacements for protective coatings (Continued)

Table 3 Hydroxyl functional acrylic 2K white enamel

Component A		Replacements		
Grind:	Control wt%	#1 wt%	#2 wt%	#3 wt%
Acrylamac™ 232-1375 (70% NV)	9.83	9.83	9.83	9.83
Eastman™ PM acetate	5.02	5.02	5.02	5.02
Xylene	5.15	—	—	—
Eastman™ MAK	—	2.85	—	—
Eastman™ <i>n</i> -butyl propionate	—	—	3.09	—
Eastman™ IBIB	—	—	—	2.83
VM&P Naphtha 66	—	2.30	2.06	2.32
Bentone™ SD-2	1.34	1.34	1.34	1.34
Ti-Pure™ R-900 TiO ₂	22.34	22.34	22.34	22.34
Grind to 7 Hegman Letdown:				
Acrylamac™ 232-1375 (70% NV)	22.72	22.72	22.72	22.72
Eastman™ <i>n</i> -butyl acetate	3.50	3.50	3.50	3.50
Eastman™ MPK	5.24	5.24	5.24	5.24
Xylene	4.77	—	—	—
Eastman™ MAK	—	2.64	—	—
Eastman™ <i>n</i> -butyl propionate	—	—	2.86	—
Eastman IBIB	—	—	—	2.62
VM&P naphtha 66	—	2.13	1.91	2.15
BYK™-300	0.19	0.19	0.19	0.19
Premix—then add component B				
Tolonate™ HDB-75BX (75% NV)	13.11	13.11	13.11	13.11
Eastman™ <i>n</i> -butyl acetate	6.79	6.79	6.79	6.79
Total	100.00	100.00	100.00	100.00
Formula constants				
% NV (weight)	56.39	56.39	56.39	56.39
% NV (volume)	39.70	39.43	39.58	39.50
Wt/gal (lb)	9.95	9.88	9.92	9.90
Pigment:binder	40:60	40:60	40:60	40:60
Theoretical VOC (lb/gal)	4.34	4.31	4.33	4.32
Viscosity, #4 Ford cup, s	40	39	42	45
NCO/OH ratio	1.1:1	1.1:1	1.1:1	1.1:1
HAP content, wt% on volatiles	27.86	5.11 ^a	5.11 ^a	5.11 ^a
Typical cured film properties (10 days air dry)				
Dry film thickness (mils)	1.1–1.5	1.1–1.5	1.1–1.5	1.1–1.5
Pencil hardness	2H	2H	2H	2H
Impact—direct/reverse (in./lb)	45/<5	41/<5	43/<5	32/<5
MEK rubs (100 double rubs)	Pass	Pass	Pass	Pass
Gloss (60/20)	92/82	92/82	93/83	92/82
Crosshatch adhesion, % removed	<5	<5	<5	<5

^aHAP content can be reduced to 1.35 wt% by replacing Tolonate™ HDB-75 BX with Tolonate™ HDB-75 B.

Selecting effective xylene replacements for protective coatings (Continued)

Table 4 High-solids phenolic-modified alkyd primer

Components Grind:	Control wt%	Replacements		
		#1 wt %	#2 wt%	#3 wt%
Duramac™ HS 57-5754 (75% NV)	15.89	15.89	15.89	15.89
Imsil™ A-10	2.62	2.62	2.62	2.62
Aerosil™ R-972	0.44	0.44	0.44	0.44
Mapico™ red #347 offset	5.17	5.17	5.17	5.17
Sparmite™	26.06	26.06	26.06	26.06
Calcium carbonate	17.32	17.32	17.32	17.32
Eastman™ MAK	10.65	10.65	10.65	10.65
Disperse to 7 Hegman Letdown:				
Duramac™ HS 57-5754	11.63	11.63	11.63	11.63
Cobalt (12%)	0.07	0.07	0.07	0.07
Zirconium (18%)	0.23	0.23	0.23	0.23
Activ™-8	0.08	0.08	0.08	0.08
Exkin™ #2	0.05	0.05	0.05	0.05
Xylene	9.79	—	—	—
Eastman™ MAK	—	5.59	—	—
Eastman™ <i>n</i> -butyl propionate	—	—	6.19	—
Eastman™ IBIB	—	—	—	5.52
VM&P Naphtha 66	—	4.20	3.60	4.27
Total	100.00	100.00	100.00	100.00
Formula constants				
% NV (weight)	72.63	72.63	72.63	72.63
% NV (volume)	51.35	50.42	50.98	50.79
Wt/gal (lb)	12.32	12.09	12.22	12.18
Pigment:binder	71:29	71:29	71:29	71:29
Theoretical VOC (lb/gal)	3.37	3.31	3.35	3.33
Viscosity, #4 Ford Cup, s	40	32	33	34
HAP content, wt% on volatiles	40.66	4.90	4.90	4.90
Typical cured film properties (7 days air dry)				
Dry film thickness (mils)	1.4–1.5	1.4–1.5	1.4–1.5	1.4–1.5
Pencil hardness	F	F	F	F
Impact—direct/reverse (in./lb)	16/<5	16/<5	16/<5	16/<5
Gloss (60/20)	11/<2	13/<2	11/<2	11/<2
Crosshatch adhesion, % removed	<5	<5	<5	<5

Selecting effective xylene replacements for protective coatings *(Continued)*

Table 5 High-solids polyester/melamine enamel

Components Grind:	Control wt%	Replacements		
		#1 wt%	#2 wt%	#3 wt%
Polymac™ HS 220-2882 (97% NV)	34.53	34.53	34.53	34.53
Ti-Pure™ R-960 TiO ₂	31.93	31.93	31.93	31.93
Disperse to 7.5 Hegman Letdown:				
Cymel™ 303	14.35	14.35	14.35	14.35
Eastman™ <i>n</i> -butyl alcohol	1.79	1.79	1.79	1.79
Eastman™ EEP solvent	1.60	1.60	1.60	1.60
Eastman™ MAK	10.00	11.99	10.00	10.00
Xylene	4.96	—	—	—
Eastman™ <i>n</i> -butyl propionate	—	—	2.29	—
Eastman™ IBIB	—	—	—	2.03
VM&P Naphtha 66	—	2.97	2.67	2.93
Fluorad™ FC-430 (20% NV)	0.48	0.48	0.48	0.48
<i>p</i> -TSA catalyst (40% NV)	0.36	0.36	0.36	0.36
Total	100.00	100.00	100.00	100.00
Formula constants				
% NV (weight)	80.01	80.01	80.01	80.01
% NV (volume)	68.58	68.10	68.20	68.13
Polyester:melamine	70:30	70:30	70:30	70:30
Wt/gal (lb)	11.03	10.94	10.96	10.95
Pigment:binder	40:60	40:60	40:60	40:60
Theoretical VOC (lb/gal)	2.20	2.19	2.19	2.19
Viscosity, #4 Ford cup, s	38	41	37	42
HAP content, wt% on volatiles	24.81	<0.1	<0.1	<0.1
Typical cured film properties—bake 350°F/20 min				
Dry film thickness (mils)	1.6–1.7	1.4–1.5	1.5–1.6	1.5–1.6
Pencil hardness	2H	2H	2H	2H
Impact—direct/reverse (in./lb)	128/8	126/7	114/7	116/8
MEK rubs (200 double rubs)	Pass	Pass	Pass	Pass
Gloss (60/20)	93/74	92/70	89/64	93/71

Replacing xylene in aerosol coatings

Aerosol coatings products contain solvents and propellants that contribute to VOC emissions released into the atmosphere. The California Air Resources Board (CARB) has established photochemical reactivity-based limits for regulating emissions from aerosol coatings.

It is well known that VOCs differ in their ability to form ozone at ground level. A concept known as “incremental reactivity” has been developed to assess these relative atmospheric reactivity differences in VOCs. These differences have been quantified (although recognizing uncertainties in the measurements and calculations of atmospheric reactivity exist) and are the foundation for a different methodology for controlling emissions of VOCs. CARB is already using incremental reactivity in their aerosol coatings rule.

The most common measure of incremental reactivity used in the United States—and the one used by CARB in their aerosol rule—is the Maximum Incremental Reactivity (MIR) scale, in which each VOC is assigned an individual reactivity value. This value enables the formulator to compare reactivity differences for various solvents used in aerosol preparations. Higher values denote more reactive compounds. As shown in Table 2, the MIR value of xylene (7.37) is considerably higher than most other alternatives, except for other aromatic hydrocarbons. Particularly useful in reformulating aerosols to meet the newer reactivity limits while maintaining performance properties are ester solvents and selected ketones.

Choosing a polymerization or reflux solvent for resin processing

Resin design and processing is critical in optimizing paint performance while satisfying regulatory requirements. Traditionally, xylene has been used as a polymerization solvent for acrylic resins and as a reflux/letdown solvent in manufacturing alkyd and polyester resins. In the latter, the reflux solvent helps azeotrope the water of condensation from the reactor to allow successful processing of the resin.

MAK is very useful as a polymerization solvent for high-solids acrylic resins. Its high-boiling range (147°–150°C) aids in the production of low molecular weight acrylic resins with low molecular weight distribution. The low polydispersity (M_w/M_n) of the resin coupled with MAK's excellent solvent activity allows the development of high-performance coatings with very low VOC content. MAK is also used in processing HAPs-free alkyd and polyester resins. More information on the processing of resins in MAK solvent is available in Eastman publication M-285C.

Likewise, higher-boiling ester solvents are also useful in preparing low molecular weight acrylic resins for use in high-solids coatings. Their use in acrylic polymerization is well documented in the public domain. However, in processing alkyd and polyester resins, the use of ester solvents is not suggested because of transesterification reactions that will impair resin molecular weight development.

Conclusion

Each of the oxygenated solvents has characteristics that make them suitable for reformulating coatings where xylene must be reduced or eliminated. None are listed as HAP compounds, and all have an evaporation rate in the range that can provide comparable application and dry characteristics to that of xylene.

Of the three, MAK has the best solution viscosity reduction efficacy. This is extremely valuable when trying to maintain or lower the VOC content of a coating. It also has the lowest density which makes its choice for high-solids coatings even more attractive since VOC regulations limit the weight of solvent per volume of coating. MAK is a linear ketone with excellent solvent release from an applied coating.

In applications where MAK is not acceptable, *n*-butyl propionate can effectively be used to replace xylene. It has good viscosity reduction efficacy, low odor, and the proper volatility for use in high-solids coatings. Its high electrical resistance is especially suited for electrostatically sprayed coatings. Like MAK, this ester solvent has a linear structure that aids its diffusion through paint films.

IBIB is the most cost-effective xylene replacement for NC lacquers, purge solvents, and lacquer thinners. It is not as active as the other two oxygenated solvents; therefore, its use should be limited to those coatings in which acceptable solution viscosity/VOC content can be maintained.



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