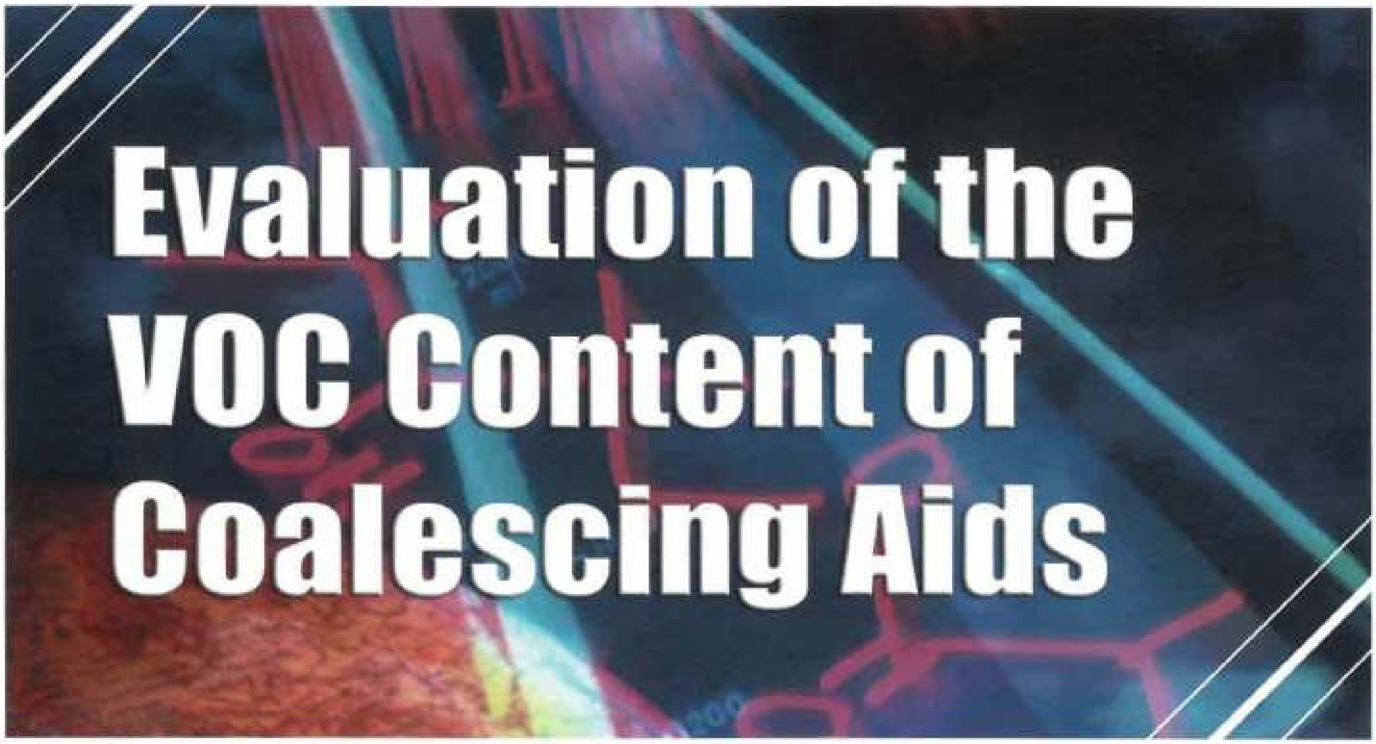

Evaluation of the VOC Content of Coalescing Aids

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The current standard for determination of volatile organic compounds (VOCs) in paint and coating systems in the United States is EPA Method 24 (ASTM D 3960-02). It has been reported that VOC measurements carried out using this method have errors which increase nearly exponentially at VOC levels less than 250 g/L.[1] Due to the uncertainties inherent in this test method, certain classes of coatings additives have traditionally been evaluated as neat products rather than in fully formulated paints. This article outlines experimentation that was carried out to quantify the actual VOC levels of two representative coalescing aids in formulated paints using both EPA Method 24 and a proposed alternative test method that utilizes an automated thermal desorber (ATD) with flame ionization detection (FID). Results indicate that in formulated paints, the measured VOCs of coatings additives are in some cases less than the VOCs observed when these additives are tested as neat materials.

INTRODUCTION

EPA Federal Reference Method 24[2] is the current standard utilized for determination of volatile organic compound (VOC) content in coatings. This method is nearly analogous to the procedure outlined in ASTM D 3960-02.[3] It has been noted that these methods tend to be prone to exponentially increasing amounts of error at VOC levels below 250 g/L.[1] Coatings additives such as coalescing aids are generally minor components of paint formulations, and, as such, their VOCs are difficult to assess due to the large uncertainties inherent in this test method at low VOC. As a result, these additives have traditionally been evaluated as neat products rather than in formulated paints.

Both the EPA and ASTM test methods require determination of (a) total volatile content at a specified time and temperature, (b) water content,

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(c) coating density, and (d) exempt solvent content. Total volatile content is calculated by determining the percent of weight lost at 110 + 5°C for one hour in a forced air oven (according to ASTM D 2369). Water content may be determined by a Karl Fischer method (ASTM D 4017) or by gas chromatography (ASTM D 3792). The density of the coating is obtained using a pycnometer or a weight per gallon cup (according to ASTM D 1475). Exempt solvent content may be determined by a direct injection gas chromatography technique outlined in ASTM D 4457. Based on work carried out at the Paint Research Association, the water and nonvolatile measurements were shown to be the largest contributors to error in the current VOC test methodology.[1] One of the difficulties in utilizing this test method stems from the fact that organic volatiles are determined indirectly by measuring total volatiles and subtracting water and exempt solvent contents. At low VOC, water becomes the primary volatile, and the *difference* between the total volatiles and the water content (the organic solvent content) becomes small, and any error in the water measurement leads to large variation in the calculated VOC level.

Within the last five years, an alternative test method using an automated thermal desorber (ATD) with flame ionization detection (FID) was developed by Battelle as a potential alternative to EPA Federal Reference Method 24.[3] In contrast to EPA Method 24, in which VOCs are determined indirectly, the ATD/FID method provides a means to directly analyze the volatile compounds. A number of literature references outline information related to the use of this ATD/FID method.[2-6] In this method, a paint sample is introduced to an ATD and held for 30 minutes at 110°C while it is purged with helium. Volatiles are collected on a trap held at -30°C, and are then desorbed at 325°C and detected using an FID. This process is then repeated on the initial sample such that the total time at 110°C is one hour, which matches the conditions outlined in EPA Method 24. Quantification of volatiles content is achieved by using calculated response factors relative to ethylene glycol monobutyl ether (EB).[7]

As mentioned previously, it is difficult to quantify the VOC content of additives such as coalescing aids in formulated paints by EPA Reference Method 24. The purpose of this work was to determine analytically the VOC content of select additives in formulated paints (rather than as neat materials) using the standard EPA Method 24, the ATD/FID technique developed at Battelle, and a related ATD/FID technique in which an analytical column is placed between the ATD and the FID in order to enable speciation and quantification of the volatiles in each formulation.

Testing was performed on a total of six paints with very low VOC levels to which solvents were added in known quantities. The VOC levels of each solvent were then analyzed by one or more of the aforementioned analytical methods for comparison with the results observed when each solvent was tested as a neat material according to EPA Method 24.

EXPERIMENTAL

EPA Federal Reference Method 24

Evaluation of the VOC content of formulated paints according to EPA Method 24 was carried out on a contract basis with the Paint Research Association Laboratories (PRA Labs) in Ypsilanti, Michigan. Testing on neat additives by EPA Method 24 was completed in-house.

ATD/FID (Battelle Method)

Determination of volatiles using the ATD/FID method was carried out in accordance with the experimental procedures outlined in previous work completed at Eastman Chemical Company.[5] A general description of the equipment and the conditions is provided below.

This method utilized a Perkin-Elmer Model ATD-400 fitted with a 3 mm ID sorbent trap containing a 10 mm long section of Tenax GR and a 10 mm long section of Carbopack B. The ATD-400 was connected to the FID of an HP-5890 GC (without any column) using a deactivated fused silica transfer line. *Figure* 1 provides a simple illustration of the experimental setup which is utilized by this test method.

Sample analysis chambers consisted of 8.9 cm long stainless steel tubes with 6.4 mm OD and 5 mm ID that were fitted with end caps. Polytetrafluoroethylene (PTFE) liners that were 5.1 cm in length with a single

Figure 1—Illustration of the ATD/VOC test protocol.

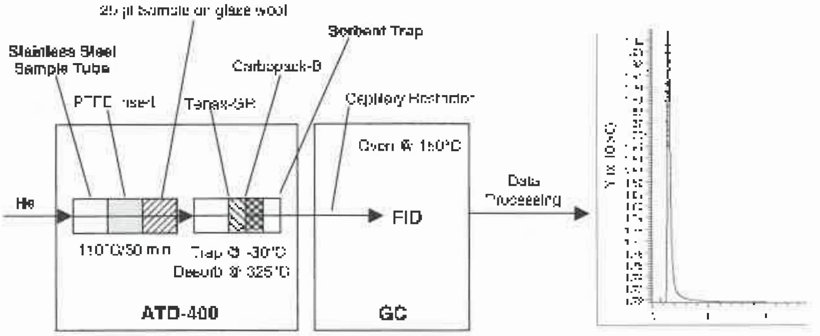


Table 1—VOC Recovery by ATD-FID of Various Solvents from an IM Formulation

Organic Compound	BP (°C)	RS	% VOC
Ethylene glycol monobutyl ether	171	1.000	116
Propylene glycol	187	0.583	146
Dipropylene glycol monobutyl ether	225	1.058	76
Diethylene glycol monobutyl ether	231	0.922	67
Texanol ester-alcohol	255	1.204	70
Optifilm Enhancer 300	281	1.213	43

beveled end were inserted into the stainless steel tubes. A plug of silanized glass wool approximately 2 cm in length was packed into the beveled end of the PTFE insert. Paint samples were diluted 1:1 with water, and 25 µL of the resulting mixture was introduced to the PTFE liner. The liner was then placed in the sample tube, which was loaded into the ATD-400.

The ATD-400 was set to a tube desorption temperature of 110°C with a desorption time of 30 min. Two desorptions and injections were used per tube (for a total of one hr at 110°C). The switching valve temperature and the transfer line temperature were both 175°C, while the tube desorption flow rate was 5 cm^3/min. The trap low temperature was –30°C, the trap high temperature was 325°C, the trap hold time was 5 min, the trap heating rate was 5°C/sec, the trap inlet split flow rate was 100 cm^3/min, and the trap outlet split flow rate was 50 cm^3/min. The flow rate of the helium to the FID was 2 cm^3/min with a helium pressure of 20 psig. The HP 5890 was configured to an oven temperature of 150°C with an FID temperature of 250°C. Various mixtures of EB and water were used to calibrate the FID response. HP Chemserver was used as the chromatographic data system.

Modified ATD/FID Method (Incorporating a Column Between the ATD and FID)

In order to obtain speciated VOC results, the ATD/FID experimental setup described in the previous section was modified by the addition of a column between the desorber and the detector. Sample size and sample preparation were unaffected by this change. Separation was achieved using an RTX-200 column 30 meters in length with a 0.32 mm ID and a 1.0 µm film thickness with a column flow rate of 1.1 cm^3/min. The oven temperature profile consisted of 5 min at 40°C followed by a 10°C/min ramp up to 250°C.

Paints Analyzed

Six different paints were analyzed as a part of this work—four of which were formulated internally, and two which were purchased commercially. The commercial coatings were a zero-VOC interior flat and a zero-VOC interior semigloss. Paints that were formulated in-house were initially prepared without any glycol or coalescent. These paints were then "spiked" with one or more solvents in known amount such that the VOC contribution of individual solvents could be determined. An interior flat based on a vinyl-acrylic resin was formulated to an initial VOC level of about 10 g/L. An all-acrylic resin was incorporated into an interior/exterior semigloss formulation with an initial VOC level of approximately 10 g/L. A styrene-acrylic latex was formulated into a high gloss formulation with an initial VOC level of about 15 g/L. Finally, an industrial maintenance (IM) formulation based on an all-acrylic resin was prepared with an initial VOC level of about 15 g/L. Solvents were slowly introduced into these paints utilizing a low shear mixer. Following solvent addition, the paints were placed on rollers for at least 24 hr prior to testing in order to allow sufficient time for equilibration. The main solvents that were examined as a part of this work were 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (Eastman Texanol ester-alcohol) and 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (Eastman Optifilm Enhancer 300), propylene glycol, and ethylene glycol. The levels of solvent incorporation will be discussed in detail in the Results and Discussion section.

RESULTS AND DISCUSSION

Background

Previous work carried out at Eastman Chemical Company using the ATD/FID method illustrated the tendency for an inverse relationship between the boil-

Table 2—Composition of Paints for EPA Method 24 and ATD/FID VOC Testing

Solvent	Base Paint (g)	Solvent (g)	Water (g)	% of Solvent
Texanol ester-alcohol	150.00	17.00	0.00	10.18
	150.00	11.33	5.67	6.78
	150.00	5.72	11.33	3.42
Optifilm Enhancer 300	150.00	17.00	0.00	10.18
	150.00	11.33	5.69	6.78
	150.00	5.67	11.37	3.39

Table 3—VOC Levels by EPA Method 24 of a Basic Paint Spiked with a Single Solvent

Solvent	Wt % Solvent	% Nonvolatile	% Water	ρ (#/gal)	VOC g/L Theory	VOC g/L Method 24	% VOC Recovered
Texanol ester-alcohol	10.18	50.22	41.15	9.93	255	202	79
	6.78	49.46	42.61	9.95	190	193	102
	3.42	48.81	47.96	9.97	112	91	81
Optifilm Enhancer 300	10.18	51.43	40.63	9.89	255	182	71
	6.78	51.46	44.36	9.96	190	106	56
	3.39	49.84	46.74	9.97	112	93	83

ing point of a given solvent and its measured VOC content when tested in a simplified IM formulation.[5] This ATD/FID technique initially provides a quantification of volatiles *as EB*, so a relative sensitivity (RS) correction must be applied to compensate for differences in FID response between a target compound and the EB standard.[7] *Table* 1 provides a summary of the boiling point, relative sensitivity correction, and the % VOC recovery determined when six solvents were utilized as the sole volatiles in an IM formulation.[5] From this data, it appears that the amount of propylene glycol is significantly overestimated. The course of the overestimation is still under investigation. These results indicate that the measured VOCs of high boiling solvents are in some cases less than the VOCs observed when these additives are tested as neat materials.

Comparison of EPA Method 24 and ATD/FID Results

In order to utilize EPA Method 24 to analyze the VOC content of a specific additive in a paint formulation, another IM paint was prepared without glycol, coalescent, thickener, or preservatives. Two different solvents were then post-added to the simplified paint formulation at three different levels (which yielded a total of six paints for analysis). *Table* 2 provides a summary of the solvents added, the levels of incorporation, and the weight percent of each volatile as a percentage of the overall formulation.

The six paints described in *Table* 2 were tested according to EPA Method 24 at PRA Labs in Ypsilanti, MI, and according to the ATD/FID method (without speciation) that was outlined in the Experimental section. Since the VOC level of the base paint (prior to the addition of either of the two solvents) was relatively close to zero, a percent VOC recovery for each individual solvent was calculated according to the ratio of the measured VOC level to the theoretical VOC level. The theoretical VOC level was calculated assuming that each individual solvent would have been 100% volatilized under the specified test conditions of 110°C for one hour. In a typical paint formulation with multiple volatile organic components, the VOC contribution of an individual solvent cannot be identified according to EPA Method 24. The ATD/FID determination of VOC was repeated four times for each of the six samples in order to evaluate the reproducibility of this method (with particular emphasis on the paints with VOC levels close to 100 g/L). *Table* 3 provides a summary of the EPA Method 24 results on these six paints, including the total volatiles, nonvolatiles, water content, density, and VOC level as compared to the theoretical VOC. The percent VOC recovered was calculated by the ratio of the EPA method 24 VOC as compared to the theoretical VOC. The average percent Texanol ester-alcohol recovered by this method was 87%, while the average recovery of Optifilm Enhancer 300 was 70%. A large degree of fluctuation was noted in the percent recovery results, in accordance with expectations due to the large errors anticipated when using EPA Method 24 at reduced VOC levels. This data is supportive of the premise that high boiling solvents may not be completely volatilized from a typical paint formulation under the conditions of EPA Method 24.

Each of the six paint samples was tested four times by the ATD/FID method (two times initially, and two more times about one month later). The paints were desorbed twice for 30 min at 110°C, and the sum of the areas under the FID curves was quantified in terms of EB (this is referred to as *ATD/FID uncorrected*). As outlined in the Background section, a relative sensitivity (RS) correction must be applied to compensate for differences in FID response between a target compound and the EB standard. The corrected ATD/FID weight percent is calculated by dividing the ATD/FID uncorrected value by the RS number that was presented previously for several common solvents in *Table* 1. *Table* 4 provides a summary of the actual volatile content, uncorrected volatile content, and corrected volatile content, as well as the corresponding VOC levels and the percent VOC recovery (calculated as illustrated for *Table* 3) as measured using ATD/FID. For each solvent at each weight percent, the top two rows are from the initial testing, and the lower two rows are from the subsequent testing. Although there is a slight downward trend in the VOC recovered as a function of weight per-

Table 4—VOC Levels by ATD/FID of a Basic Paint Spiked with a Single Solvent

Solvent	Wt % Solvent	ADT/FID Wt% Volatile Uncorrected	ATD/FID Wt% Volatile Corrected	VOC (g/L) Theory	VOC (g/L) ATD/FID	% VOC Recovered
Texanol ester-alcohol	10.18	10.65	8.85	255	222	87
		10.37	8.62	255	216	85
		10.41	8.64	255	217	85
		10.74	8.93	255	224	88
	Average	***10.54***	***8.76***	***255***	***219***	***86***
Texanol ester-alcohol	6.78	6.21	5.16	190	145	76
		6.98	5.80	190	163	86
		6.74	5.60	190	157	83
		6.72	5.59	190	157	82
	Average	***6.66***	***5.54***	***190***	***155***	***82***
Texanol ester-alcohol	3.42	3.12	2.59	112	85	76
		3.51	2.92	112	96	85
		3.35	2.78	112	91	81
		3.16	2.63	112	86	77
	Average	***3.28***	***2.73***	***112***	***89***	***80***
Optifilm Enhancer 300	10.18	7.46	6.15	255	154	60
		6.95	5.73	255	144	56
		6.18	5.09	255	128	50
		5.88	4.85	255	121	48
	Average	***6.62***	***5.46***	***255***	***137***	***54***
Optifilm Enhancer 300	6.78	4.35	3.59	190	101	53
		3.79	3.13	190	88	46
		4.05	3.34	190	94	49
		4.13	3.41	190	86	50
	Average	***4.08***	***3.37***	***190***	***94***	***50***
Optifilm Enhancer 300	3.39	1.77	1.46	112	48	43
		1.49	1.23	112	41	36
		2.17	1.79	112	59	53
		1.73	1.43	112	47	42
		1.80	1.49	112	49	44
	Average	***1.79***	***1.48***	***112***	***49***	***44***

cent of solvents in the paint, at a given weight percent of solvent the ATD/FID method provides excellent reproducibility relative to EPA Method 24. The average percent Texanol ester-alcohol recovered by ATD/FID testing on this simplified paint was 83%, while the average recovery of the less volatile Optifilm Enhancer 300 was 49%.

When tested under the conditions of EPA Method 24 as a neat solvent, Texanol ester-alcohol was completely volatilized. Optifilm Enhancer 300 was tested under analogous conditions, and was shown to be 97 to 98% volatile. With the test paint illustrated previously, Texanol ester-alcohol was only 87% volatile by EPA Method 24 and 83% volatile by the ATD/FID method. Similarly, Optifilm Enhancer 300 was 70% volatile by EPA Method 24 and 49% volatile by the ATD/FID method. This information suggests that neither Texanol ester-alcohol nor Optifilm Enhancer 300 is completely volatilized out of a formulated paint after one hour at 110°C. Two questions that still remained as a result of this work were: (1) would the results change if these solvents were tested in a fully formulated (not simplified) paint and (2) would the concurrent incorporation of multiple solvents influence the VOC measurement relative to a paint formulated with one primary volatile solvent. It was concluded that EPA Method 24 did not possess the requisite sensitivity to judge the relative VOC of paints containing multiple solvents. As a result, the remainder of this work was carried out with either the basic ATD/FID technique or the modified ATD/FID

Table 5—Percent VOC of Solvents Post-Added to Two Commercial Zero-VOC Paints

Sample Description	Wt % Solvent Added	ATD/FID Wt % Volatile Uncorrected	ATD/FID Wt % Volatile Uncorrected-Background	ATD/FID Wt % Volatile Corrected	% VOC Recovered
Interior flat (IF) control	0	0.04	—	—	—
IF+1% Texanol ester-alcohol	0.994	0.90	0.86	0.72	71.6
IF+2% Texanol ester-alcohol	1.957	1.81	1.77	1.47	75.2
IF+1% Optifilm Enhancer 300	0.995	0.67	0.62	0.52	51.6
IF+2% Optifilm Enhancer 300	1.979	1.36	1.31	1.08	54.7
Semigloss (SG) Control	0	0.05	—	—	—
SG+1% Texanol ester-alcohol	0.988	0.92	0.87	0.72	73.3
SG+2% Texanol ester-alcohol	1.986	1.92	1.87	1.56	78.4
SG+1% Optifilm Enhancer 300	0.991	0.70	0.65	0.54	54.5
SG+2% Optifilm Enhancer 300	1.953	1.36	1.31	1.08	55.4

method (with a column) that was outlined in the Experimental section.

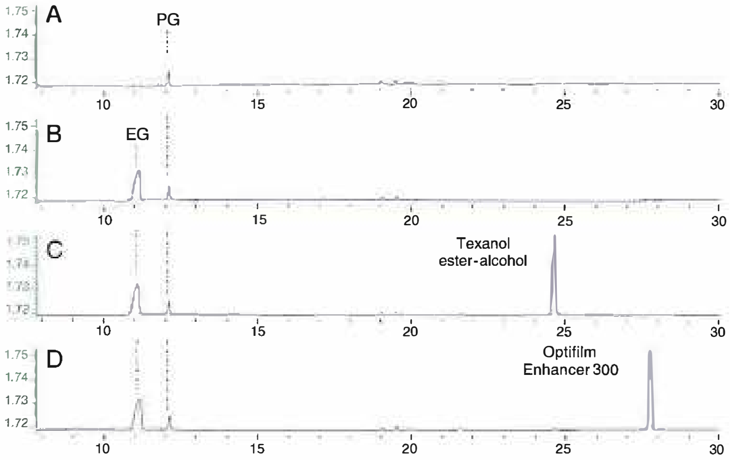
ATD/FID Results with Solvents Spiked into Commercial Zero-VOC Paints

In order to address the question of the VOC content of solvents in fully formulated paints, a zero-VOC interior flat (IF) and a zero-VOC interior semigloss (SG) paint were purchased such that Texanol ester-alcohol and Optifilm Enhancer 300 could be post-added at two levels (1% and 2% by weight) and tested for VOC by ATD/FID. The paints were also tested as purchased in order to use these results as a baseline to which the modified paints could be compared. *Table* 5 summarizes the percent VOC determined when Texanol ester-alcohol and Optifilm Enhancer 300 were post-added to two zero-VOC paints at two levels. From the data, it was evident that these two control paints were very low in VOC as purchased, and there was minimal variation in the percentage of VOC recovered either as a function of paint type or level of incorporation. In this testing, the average percent Texanol ester-alcohol recovered was 75%, while the average recovery of Optifilm Enhancer 300 was 54%. These values are similar to the results outlined in the previous testing by EPA Method 24 and ATD/FID.

RESULTS OF MODIFIED ATD/FID TESTING ON FOUR FORMULATED PAINTS

The experimentation outlined in the previous section demonstrated once again that some portion of high boiling solvent is not volatilized under the conditions of EPA Method 24. The final section of work was designed to determine if the incorporation of multiple solvents into a formulated paint influences the experimentally measured VOC relative to a paint formulated with one primary volatile solvent. Four paints were analyzed, including one commercial zero-VOC interior flat and three paints formulated in-house. The three paints included an interior flat based on a vinyl-acrylic latex, an interior/exterior semigloss based on an all-acrylic latex, and an interior high gloss based on a styrene-acrylic latex. These paints were prepared in order to examine the impact of latex composition on the volatiles released under the conditions of EPA Method 24. Paints were tested as prepared (with no glycol or coalescent), as well as with single solvents (propylene glycol (PG)), Texanol ester-alcohol, and Optifilm Enhancer 300), and with multiple solvents (PG + Texanol ester-alcohol and PG + Optifilm Enhancer 300). All solvents were in-

Figure 2—GC traces used in the quantification of volatiles in an interior high gloss paint.



corporated at 2.5% by weight. The formulation for the interior high gloss paint utilized a dispersant that contained PG. As a result, this paint was spiked with the solvents outlined previously, but was also tested with the addition of ethylene glycol (EG), EG + Texanol ester-alcohol, and EG + Optifilm Enhancer 300. Post-adding EG instead of PG eliminated potential uncertainty that could have resulted from having two sources of PG in the paint.

In order to quantify the amount of each solvent released from the paints under investigation, a modified ATD/FID setup was utilized in which a column was added between the ATD and the FID to speciate the volatiles. Each of the peaks observed by the FID was quantified in terms of EB and then corrected with the appropriate RS factor, as illustrated previously for the original ATD/FID method. *Figure* 2 provides an illustration of some typical results. Trace A was from the control interior high gloss formulation. The single peak was from the PG in the dispersant, while the other peaks in the 19 to 20 min range (observed in all traces) were due to slight levels of volatiles from other additives. Trace B was from the same paint with the addition of 2.5% EG. Trace C was from the base paint plus 2.5% each of EG and Texanol ester-alcohol (note the shoulder in the peak stemming from the two isomers of Texanol ester-alcohol), while Trace D was from the base paint plus 2.5% each of EG and Optifilm Enhancer 300. This technique allows for relatively simple separation and quantification of a series of volatiles in formulated paints.

Table 6 provides a summary of the VOC results obtained from the four paints outlined previously. The paints were analyzed both unmodified (as a control) and also with solvents added as described, at 2.5% by weight. Several of these samples were tested six times, and the average relative standard deviation was approximately 2%, which is indicative of the outstanding re-

Table 6—VOC Levels of Four Paints with 2.5% Post-Added Solvents by Modified ATD/FID

	Propylene Glycol		Ethylene Glycol		Texanol EA		Optifilm Enhancer	
Sample Description	Wt % Corrected	% VOC Recovered	Wt % Corrected	% VOC Recovered	Wt % Corrected	% VOC Recovered	Wt % Corrected	% VOC Recovered
0 VOC Flat (ZVF) Ctrl								
ZVF + PG	3.70	147						
ZVF + Texanol EA					1.84	73.9		
ZVF + Optifilm Enhancer							1.32	52.6
ZVF + PG + Texanol EA	3.01	120			1.67	66.9		
ZVF + PG + Optifilm Enhancer	3.17	127					1.30	52.0
Interior Flat (IF) Ctrl								
IF + PG	3.56	143						
IF + Texanol EA					1.86	74.5		
IF + Optifilm Enhancer							1.32	52.9
IF + PG + Texanol EA	3.66	142			1.79	71.6		
IF + PG + Optifilm Enhancer	3.56	142					1.31	52.4
Semigloss (SG) Ctrl								
SG + PG	3.62	145						
SG + Texanol EA					1.82	72.9		
SG + Optifilm Enhancer							1.37	54.7
SG + PG + Texanol EA	3.44	137			1.71	68.4		
SG + PG + Optifilm Enhancer	3.20	128					1.25	49.6
Interior High Gloss (HG) Ctrl	0.33	additive						
HG + PG	4.15	153[a]						
HG + Texanol EA	0.24	additive			1.82	72.6		
HG + Optifilm Enhancer	0.24	additive					1.30	51.7
HG + PG + Texanol EA	3.93	144[a]			1.82	73.0		
HG + PG + Optifilm Enhancer	3.89	143[a]					1.24	48.6
HG + EG	0.34	additive	3.79	151				
HG + EG + Texanol EA	0.31	additive	3.67	146	1.68	66.9		
HG + EG + Optifilm Enhancer	0.30	additive	4.29	171			1.30	52.0

(a) For these samples, the weight % PG from the dispersant (0. 33%) was subtracted prior to calculation of % VOC.

Table 7—Summary of Measured VOC Contents

Measurement Technique	Form of Solvent (Neat vs. in Paint)	Texanol Ester-Alcohol (% VOC)	Optifilm Enhancer 300 (% VOC)
(A) EPA Method 24	Neat solvent	100	98
(B) EPA Method 24	Post-added to basic IM paint (no additives)	87	70
(B) ATD/FID	Post-added to basic IM paint (no additives)	83	49
(C) ATD/FID	Post-added to commercial zero-VOC interior flat	73	53
(C) ATD/FID	Post-added to commercial zero-VOC semigloss	76	55
(D) Modified ATD/FID (with column)	Post-added to commercial zero-VOC interior flat	70	52
	Post-added to vinyl-acrylic interior flat	73	53
	Post-added to all-acrylic int./ext. semigloss	71	52
	Post-added to styrene-acrylic int. high gloss	71	51

producibility inherent to this technique. Comparison of the results obtained from testing of the four paints indicated that neither the variation in latex type nor the differences in pigment volume concentration (PVC) significantly impacted the percentage of each VOC that was recovered. No differences were observed in the VOC recovery in samples formulated with a single solvent versus those formulated with multiple solvents. Using the modified ATD/VOC method with the paints, the average percent Texanol ester-alcohol recovered was 71%, while the average recovery of Optifilm Enhancer 300 was 52%. As seen previously (in *Table* 1), the percentages of VOC recovered from small glycol molecules such as PG and EG were significantly overestimated. This observation will be the subject of further evaluation as outlined in the Future Work section of this article.

Summary of Measured VOCs of Solvents By EPA Method 24 and ATD/FID

This work provided an overview of the results of various VOC test methods with a focus on determination of the VOC levels of two coalescing aids in formulated paints. *Table* 7 summarizes the measured VOC of Texanol ester-alcohol and Optifilm Enhancer 300 as characterized by the experimentation outlined previously.

Table 7 illustrates that in neat form, both Texanol ester-alcohol and Optifilm Enhancer 300 are nearly 100% volatile by EPA Method 24 (*A* in table). Analysis of a simplified paint formulated with minimal additives demonstrated that both EPA Method 24 and the ATD/FID test proposed to EPA by Battelle as a potential alternative to Method 24 quantify Texanol ester-alcohol and Optifilm Enhancer 300 as substantially less than 100% volatile (*B* in table). Although the actual measured VOC levels between the techniques were not in complete agreement, this may be due in part to the fact that EPA Method 24 may have significant error when used to analyze paints formulated at reduced VOC. ATD/FID testing of two commercial zero-VOC paints to which Texanol ester-alcohol and Optifilm Enhancer 300 were added revealed minimal variation in the percentage of VOC recovered either as a function of paint type or level of incorporation (*C* in table). Finally, four different types of fully formulated paints were speciated and quantified by a modified ATD/FID method in which a column was placed between the desorber and the detector. This test method exhibited excellent reproducibility, with an average relative standard deviation of 2%. Results indicated that the four different latexes that were used in the paint formulations did not lead to differences in the percent recovery of any of the solvents under investigation (*D* in table). Since the modified ATD/FID allows for speciation, it was also shown that the VOC recovery in samples formulated with a single solvent matched the recovery when that same solvent was incorporated in a paint containing multiple volatiles. Using the modified ATD/VOC method with the paints, the average percent Texanol ester-alcohol recovered was 71%, while the average recovery of Optifilm Enhancer 300 was 52%. Both Texanol ester-alcohol and Optifilm Enhancer 300 appear to be substantially lower in VOC when tested in formulated paints rather than as neat materials.

CONCLUSIONS

Coalescing aids are often evaluated in neat form according to EPA Federal Reference Method 24. This is due in part to uncertainty in the measurement which becomes more pronounced at low VOC, but is also due to the difficulty in quantifying the behavior of a single solvent in a formulated paint containing several solvents. In neat form, both Texanol ester-alcohol and Optifilm Enhancer 300 are nearly 100% volatile by EPA Method 24. Analysis of a simplified paint formulated with minimal additives demonstrated that both EPA Method 24 and the ATD/FID test method quantify Texanol ester-alcohol and Optifilm Enhancer 300 as substantially less than 100% volatile. A quantitative, speciating ATD/FID method was used to test four different types of formulated paints. Results illustrated that the average percent Texanol ester-alcohol recovered was 71%, while the average recovery of Optifilm Enhancer 300 was 52%. Neither the variation in latex type nor the differences in pigment volume concentration significantly impacted the percent recovery of any of the solvents under investigation. The results of this investigation strongly suggest that both Texanol ester alcohol and Optifilm Enhancer 300 are substantially lower in VOC when tested in a formulated paint rather than as neat materials.

FUTURE WORK

Extensive testing utilizing the ATD/FID test method for VOC determination has illustrated that this technique provides a direct measure of volatiles with very good reproducibility. Due to the complexity of this methodology, other test methods (including a headspace/FID method) are still being evaluated and refined in order to achieve a balance between precise and accurate VOC results with ease of testing. Future work will include examination of the issues that may lead to overestimation of small molecule glycols by this test method. Other efforts will entail extraction of paint residue after EPA Method 24 testing in an attempt to achieve a mass balance on the whereabouts of solvents following VOC testing, and in order to confirm the volatility of various solvent additives. These topics will be the subject of a future publication.

References

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