

ESTIMATING EMISSIONS FROM THIN RADIATION-CURABLE COATINGS

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Introduction

There is little argument about the environmental friendliness of radiation-cured coatings when compared to solvent-based coatings. Despite the slowdown in the U.S. economy over the past few years, the usage of UV&EB resins grew at an annual rate of more than 7% in 2006, providing strong evidence of the widespread acceptance of this green technology. The major market continues to be the graphic arts where radiation-curable inks and overprint varnishes (OPV) account for close to 50% of the total volume of materials consumed.³

The U.S. Environmental Protection Agency defines a VOC as any compound containing at least one atom of carbon. This includes any such compound having a vapor pressure of 0.1 mm Hg at 20° C or greater, or, if the vapor pressure is unknown, consists of twelve carbon atoms or less.⁴ Certain non-reactive organic compounds are exempted.

Measurement of volatile emissions from coatings is an important requirement for demonstrating compliance with air emission standards as set by the EPA. Despite the volume of resin consumed, there is no established ASTM test method for measuring these emissions from thin radiation-curable coatings. In an effort to address this gap, a joint RadTech and ASTM task force worked for more than 10 years to develop a test method that would be appropriate for measuring emissions from these coatings but the initiative was abandoned in 2007 without resolution. The lack of an acceptable test method has placed an undue burden on print shops using radiation-curable formulations in Southern California where the South Coast Air Quality Management District (SCAQMD) is no longer willing to accept supplier and industry claims that emissions from these coatings are negligible and has begun asking end-users in the District to provide data supporting their continued classification as low VOC coatings.

In the absence of an industry-proposed method to quantify emissions, in 2007 SCAQMD funded a research project with Cal Poly San Luis Obispo to develop a test protocol based on a GC-MS headspace analysis.⁵ While the general applicability of this method remains to be demonstrated for thin radiation-curable coatings, it would be inordinately expensive for end-users as well as ink manufacturers to generate the emission data, keeping in mind that the test would need to be run on each different ink formulation. Some companies have portfolios consisting of several thousand radiation-curable inks and OPVs.

As an alternative to a direct method for measuring the VOCs from a coating, the District has publicly stated that calculated emissions for a coating based on the weighted contributions of the emissions from the individual coating components are acceptable as long as the emissions data used is based on an accepted test protocol.⁶ This paper details a test method that we have developed for measuring emissions from reactive monomers, oligomers and blends of monomers and oligomers that is based on ASTM Method D-5403. It is particularly well suited to measure emissions from an acrylate monomer, oligomer or blend. The proposed method would allow raw material suppliers to provide

an emissions number which could subsequently be used to calculate an estimate of the emissions for a fully formulated ink or OPV. This approach takes the responsibility for measuring emissions out of the hands of end-users and moves it up the supply chain to coating formulators and raw material suppliers.

Experimental

All monomers, oligomers, blends and photoinitiators were used as received without further purification. One-quarter ounce metal cans (PN 5562-01) were obtained from SKS Bottle & Packaging, Inc. (Watervliet, NY).⁷ Only the lids are used. The metal lids were heated at 110°C for a minimum of 60 minutes and stored in a desiccator prior to use. Lids were handled with crucible tongs or forceps to avoid contamination.

The experimental setup for irradiating a sample is shown schematically in Fig. 1. Exposures were made using a Hamamatsu Lightningcure 200 UV Source Model L-7212-01 (Bridgewater, NJ) equipped with a 200W mercury-xenon lamp and a liquid light guide positioned normal to the sample plane. The height of the fiber tip from the sample plane was adjusted to give a UVA irradiance of $150 \pm 5 \text{ mW/cm}^2$ at the sample plane as measured using an EIT PowerPuck® II (Sterling, VA). All samples were cured in air.

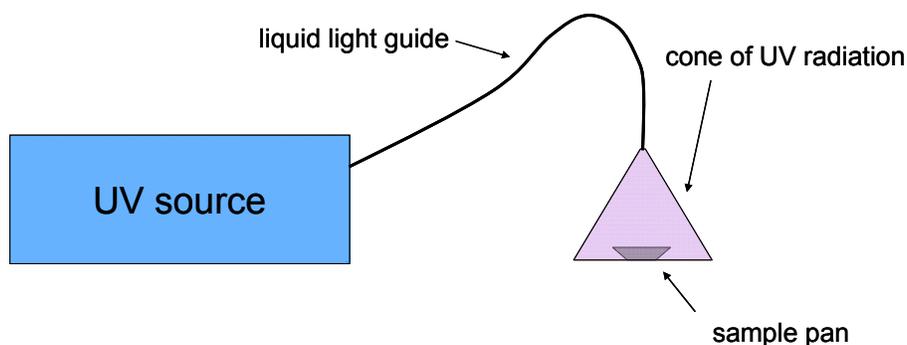


Figure 1. Experimental setup for irradiating samples.

Two percent by weight of ethyl-2,4,6-trimethylbenzoylphenylphosphinate, commercially available as Lucirin® TPO-L from BASF (Ludwigshafen, Germany), was added to each sample prior to testing. A description of the procedure is given below.

1. Remove a lid from the desiccator;
2. Weigh the inverted lid on an analytical balance to the nearest 0.01 mg (W_{t1});
3. Uniformly spread approximately 200 mg of a sample to be tested over the recessed area of the inverted lid using a wooden applicator or equivalent – discard the lid and sample if the sample contacts the area beyond the recessed area of the inverted lid;
4. Weigh the lid plus the sample to the nearest 0.01 mg (W_{t2});

5. Center the lid on the base under the fiber tip;
6. Expose the sample for 60.0 sec;
7. Weigh the lid with the exposed sample to the nearest 0.01 mg (Wt_3);
8. Heat the lid with the exposed sample for 60 minutes at 110°C;
9. Allow the lid with the exposed sample to cool then weigh the lid with the sample to the nearest 0.01 mg within 5 minutes of removing it from the oven (Wt_4).

Careful spreading of the resin to give a fairly uniform coating thickness is a key to getting good repeatability. More viscous materials, including most oligomers and many oligomer blends, tend to be difficult to spread. However, because of their higher molecular weights and lower volatilities, this was found to be much less critical than it is for more volatile low molecular species.

Results and Discussion

The majority of the radiation-curable chemistries used in inks and OPVs are based on free-radically polymerizable monomers or oligomers containing one or more acrylate moieties. For this reason, the test method was developed primarily for acrylate chemistries and the results reported are for acrylate monomers, oligomers and their blends.

ASTM D-5403 specifies applying a minimum of 200 mg of a radiation-curable formulation onto a metal or metal foil substrate of a size sufficient to allow the material to be applied at the supplier's recommended film thickness followed by a cure step and a thermal bake cycle to determine process, potential and total VOCs. Radiation-curable inks and OPVs are typically applied at a thickness of 10 micrometers or less. When coated thicker, the coatings will not cure properly and use of D-5403 gives erroneous results.

The ASTM/RadTech committee chartered to tackle this issue was unsuccessful because the committee focused on a direct test method in which a fully formulated coating with pigments, stabilizers and surfactants was applied at the recommended thickness. In order to get the mass necessary to minimize weighing errors, however, large areas were required which made handling, curing and weighing significantly more difficult. As an example, 200 mg of a coating designed to be applied 5 micrometers thick would need to be coated onto a substrate having a surface area of about 60 square inches.

The procedure proposed here does not test a fully formulated coating but rather is an indirect method in which emissions from the individual reactive components or blends of reactive components are tested in the absence of any non-reactive additives. As such, the thickness restriction is removed. Under these conditions, we have found that emission measurements can be made that are both repeatable and reproducible.

Substrate

Use of an aluminum panel or a piece of foil as a substrate is specified in D-5403 test Method A. However, for the procedure proposed here, these substrates are not suitable because the low viscosity of many monomers requires some form of containment. A variety of sample containers were tried but of those, only the lids from the one-quarter ounce metal cans were found to give repeatable results. When inverted, an SKS can lid provides a 2.54 cm-diameter recessed well that results in a coating thickness of about 625 microns (25 mils) if wet out with 200 mg of a sample resin. This also effectively controls the total surface area so any air inhibition effects are comparable.

Photoinitiator

TPO-L was chosen as the standard photoinitiator because 1) it is a liquid and quickly dissolves into both monomers and oligomers, 2) it has a long wavelength UVA absorption band, away from any aromatic interferences and 3) it has low odor, low volatility and photobleaches. A 2% level was selected as a default based on a series of screening experiments looking at measured emissions from low emission acrylate monomers as a function of photoinitiator concentration at a fixed exposure. As shown in Fig. 2, as the amount of TPO-L increases, the VOC_{total} for propoxylated (3) glyceryl triacrylate decreases. In addition, the low VOC_{total} values even with 8% TPO-L suggest that any volatiles resulting from the TPO-L photolysis and their contribution to the VOC_{total} are negligible.

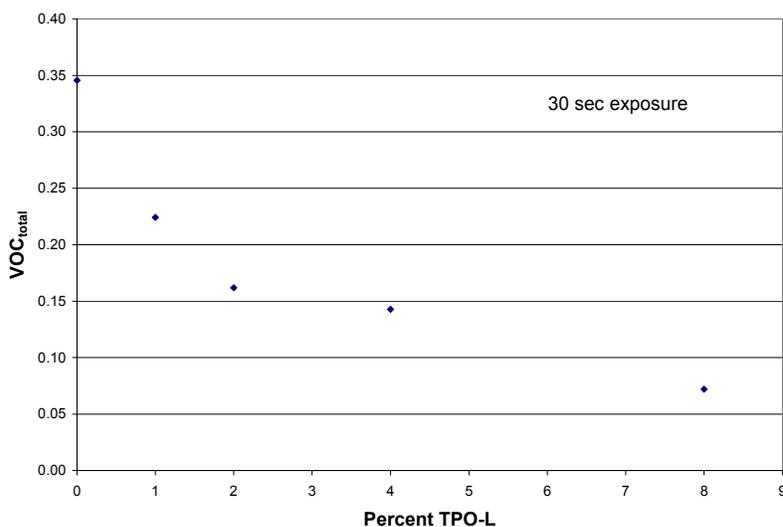


Figure 2. VOC_{total} for TPO-L in propoxylated (3) glyceryl triacrylate

UV Source

Another source of error that hampered the ASTM/RadTech committee involved defining the conditions used to cure a sample. ASTM D-5403 requires that a sample be cured in the manner prescribed by the supplier. However, cure conditions are often vague and subject to interpretation. As an example, use of a medium-pressure mercury lamp is often the only information provided. The number of commercial medium-pressure mercury lamps coupled with the different power levels, reflector types, geometries, bulb types, lamp configurations, etc. is large. As a result, ambiguous cure conditions became another source of error.

Our early attempts to develop a test method looked at both static and dynamic exposures. Exposures using a high-radiance medium-pressure mercury lamp mounted on a conveyor were found to give very erratic results, even using the preferred can lids. Therefore, we evaluated a number of alternative light sources and found the most consistent results using static exposures from a spot cure unit coupled with a liquid light guide. The spectral energy distribution of the source through the Hamamatsu light guide is shown in Fig. 3. While the bulb is broadband, the amount of UVC radiation transmitted through the light guide is relatively low. We are in the process of repeating the original measurements using a quartz fiber guide to provide a spectrum more typical of a medium-pressure mercury source. The impact with TPO-L as photoinitiator should be low. However, in blends containing other photoinitiators, sensitizers and synergists, the affect may be more pronounced.

The distance of the light guide tip to the sample was set to provide a circle of illumination having a diameter approximately equal to three times the diameter of the sample pan. At this height, the UVA irradiance at the center of the illuminated area was found to be 150 mW/cm^2 .

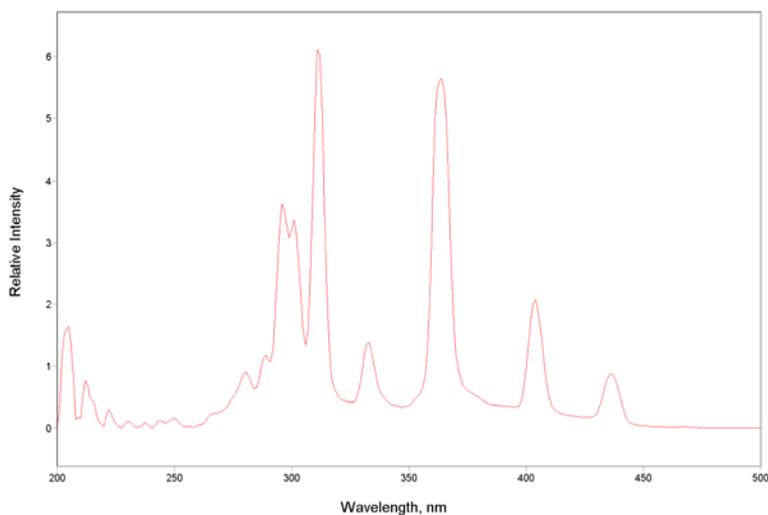


Figure 3. Spectral output of a 200W mercury-xenon lamp.

Test Results

D-5403 classifies VOCs as process VOCs, potential VOCs and total VOCs. The three types are easily calculated from the detailed procedure using the following equations:

$$VOC_{process} = \frac{Wt_2 - Wt_3}{Wt_2 - Wt_1} \times 100 \quad \text{Eq. 1}$$

$$VOC_{potential} = \frac{Wt_3 - Wt_4}{Wt_2 - Wt_1} \times 100 \quad \text{Eq. 2}$$

$$VOC_{total} = VOC_{process} + VOC_{potential} = \frac{Wt_2 - Wt_4}{Wt_2 - Wt_1} \times 100 \quad \text{Eq. 3}$$

VOC_{total} data for a number of acrylate monomers and oligomers are shown in Table I ranked from highest to lowest. Each sample represents the average of three tests. From the table, it is seen that, in general, the monomers follow the expected trend monofunctional > difunctional > trifunctional. Note that in some cases, the same monomer from different suppliers was found to be statistically different, suggesting that the method can also provide a facile means to compare monomer purities.

Table I

VOC_{total} Data for Representative Acrylate Monomers and Oligomers

Identification	Functionality	Total	Std. Dev.
octyl/decyl acrylate	1	4.54	0.08
decyl acrylate	1	4.39	0.10
2-ethylhexyl acrylate	1	4.23	0.04
isooctyl acrylate	1	3.08	1.03
benzyl acrylate	1	2.40	0.08
2-(2-ethoxyethoxy)ethyl acrylate	1	2.32	0.08
2-phenoxyethyl acrylate	1	2.13	0.07
cyclic trimethylolpropane formal acrylate	1	2.05	0.16
tetrahydrofurfuryl acrylate	1	2.00	0.02
alkoxylated phenol acrylate	1	1.59	0.02
cyclohexyl acrylate	1	1.58	0.06
isobornyl acrylate	1	1.49	0.05
tripropylene glycol diacrylate	2	1.20	0.27
neopentyl glycol diacrylate	2	1.15	0.16
ethoxylated (4) nonyl phenol acrylate	1	0.69	0.01
1,6-hexanediol diacrylate	2	0.69	0.05
diethyleneglycol diacrylate	2	0.59	0.02
acryloyl morpholine	1	0.52	0.08
trimethylolpropane triacrylate	3	0.34	0.15
polyethylene glycol (200) diacrylate	2	0.27	0.06
pentaerythritol triacrylate	3	0.10	0.02

VOC_{total} data for representative oligomers and oligomer blends were also measured with the results shown in Table II. Note that the VOCs for three of the oligomers (identified with an *) were done in the absence of any photoinitiator and curing step using EPA Method 24 which involves only the heating step. Not surprisingly, the measured VOCs for oligomers, including cured oligomer blends with reactive diluents, tended to be low.

Table II
VOC_{total} Data for Representative Oligomers and Oligomer Blends

Identification	Total	Std. Dev.
75:25 urethane acrylate:isobornyl acrylate	0.44	0.08
80:20 epoxy acrylate:tripropylene glycol diacrylate	0.13	0.05
88:12 urethane acrylate:1,6-hexanediol diacrylate	0.13	0.08
amine modified acrylate oligomer	0.35	0.05
polyester acrylate oligomer	0.61	0.07
bisphenol A epoxy diacrylate	0.02	0.05
aromatic monoacrylate oligomer	1.32	0.09
* bisphenol A epoxy diacrylate oligomer	0.54	0.09
* polybutadiene diacrylate	0.28	0.02
*aliphatic urethane acrylate	0.42	0.01

The test method is presently limited to acrylates in scope because non-acrylate monomers having significantly lower reaction rates such as methacrylates and vinyl lactams such as N-vinylpyrrolidinone are unfairly listed by this method as being high VOC_{total} because of their slow rates of homopolymerization. In reality, many of those same monomers are readily incorporated into copolymers with acrylates to give very low VOC coatings. The ability to run the emission tests on blends of reactive components as well as neat monomers allows reasonable data to be obtained when such monomers are used.

Because of this dependence on homopolymerization rates, we looked at the monomer reactivity of individual monomers as defined by the Q-e scheme⁸ and found that there was indeed some correlation. While Q-values for many of the acrylate monomers shown in Table I could not be found, we were able to compile the data for the acrylates shown in Table III which show that, while not perfect, the VOC_{total} does show an inverse relationship to the corresponding Q value. N-vinyl pyrrolidinone was added to the Table because it has a very low Q value but copolymerizes with acrylates and is used as a reactive diluent in acrylate formulations. It should be noted that correlation of emissions with Q-values is a very simplistic view, however, and does not take into account a number of factors that affect the measured VOC_{total} including monomer molecular weight, vapor pressure, hydrogen bonding and reaction exotherm.

Table III

Correlation of Monomer Reactivity Q with VOC_{total}

Monomer	Q ⁹	VOC _{total}
N-vinyl pyrrolidinone	0.18	16.9
n-octyl acrylate	0.35	3.082
2-ethylhexyl acrylate	0.41	4.23
tetrahydrofurfuryl acrylate	0.54	2.00
benzyl acrylate	0.68	2.40
2-hydroxyethyl acrylate	4.08	1.38

As a test of the proposed method, a round robin was conducted on a series of five commercial acrylate monomers. Study participants included several resin suppliers with data collected over the course of two months. A Gage Repeatability and Reproducibility (Gage R&R) analysis was done using Minitab 14.20. The results for total volatiles from the five test monomers are shown graphically in Figure 4. Similar results were seen on both process and potential VOCs.

A key indication of the validity of a test method is the Percent Study Variability (%SV). An acceptable test method of this type should have a %SV of about 30%. For the round robin, the process, potential and total VOC %SV values obtained were 41.29, 30.58 and 34.83%, respectively. These were slightly higher than desired. Part of the variability is likely explained by subtle differences between test locations. For example, not every test site had an analytical balance able to read to the nearest 0.01 mg.

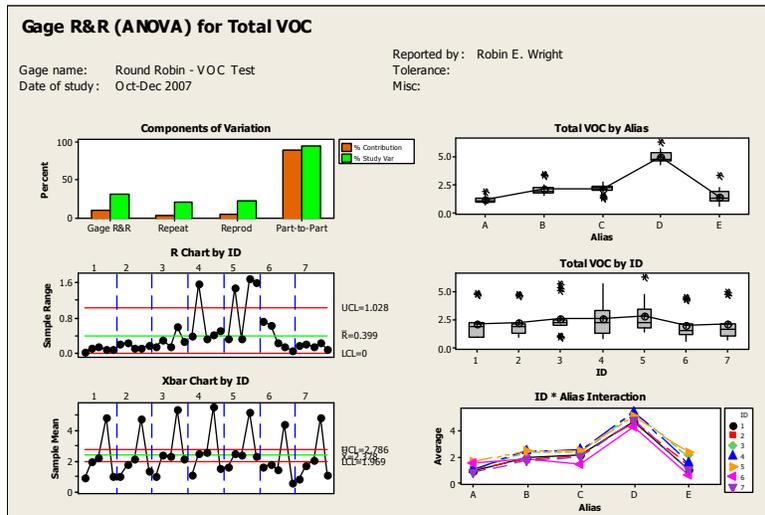


Figure 4. Summary of round robin Gage R&R results.

In an effort to establish entitlement for the testing protocol, the VOC data collected in our lab on the five test solutions were analyzed as an independent set of observations. Since June 2007, we have run hundreds of these tests and have optimized our procedures to minimize the test variability. The VOC tests were run twice on all five stock solutions prior to sending samples to the outside test locations and then repeated a third time when the samples were returned to 3M at the conclusion of the round robin testing. This allowed us to verify that the stock solutions had not changed during the round robin. The Gage R&R analysis using only our data is presented in Fig. 5.

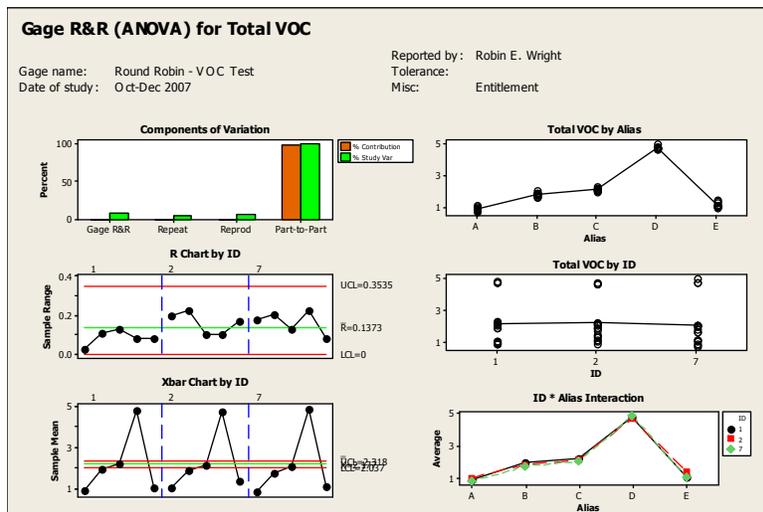


Figure 5. Estimate of the Gage R&R entitlement for the proposed test method.

The ANOVA (analysis of variance) entitlement results showed that the operator identity is a statistically insignificant term. Using the three sets of data gave a %SV for

process, potential and total VOCs of 17.99, 11.20 and 10.08%, respectively. The %SV values are all very acceptable and indicative of a good test method. Another important piece of statistical information coming out of the Gage R&R analysis was the number of distinct categories. In essence, the number of distinct categories indicates how many statistically discrete levels span the data - the greater the number of levels, the better the resolution of the test method. The Gage R&R using all operator data indicated that there were only three statistically distinct categories for the 5 different samples whereas the entitlement data showed 13 discrete levels.

The proposed test specifically requires 2% TPO-L as the photoinitiator. Real-life inks and OPVs typically contain a mixture of photoinitiators designed to achieve both surface and bulk cure. In many cases, the total photoinitiator level may be in excess of 10%. In addition, other common additives that might make up a total photoinitiator package used in an ink or OPV include amine synergists and sensitizers. Thus, it was desirable to test our method on a generic ink blend. Two formulations having the compositions shown in Table IV were evaluated. Formula 2 contained only the reactive acrylate ingredients while Formula 1 represented the entire formulated ink less any pigments.

Table IV
Percent Composition of Generic Ink Formulations (less pigments)¹⁰

	Formula 1	Formula 2
2-hydroxy-2-methyl-1-phenylpropan-1-one	1.50	
optical brightener	0.10	
trimethylolpropane triacrylate	37.10	45.2
flow additive	0.50	
triethanolamine	6.50	
benzophenone	8.30	
1,6-hexanediol diacrylate	14.40	17.5
bisphenol A epoxy diacrylate	30.60	37.3
benzyl dimethyl ketal	1.00	

The results of our analysis are shown in Table V. Using the measured VOC_{total} for the individual reactive components and applying the compositional percentages of Formula 2 above, a calculated VOC_{total} of 0.28% was predicted. This compares well with the measured value of 0.36%. Even with the additional components included in Formula 1, an increase of only 0.04% was measured in the VOC_{total} .

Table V
 VOC_{total} from Reactive Components of Generic Ink

	VOC _{total}	Std. Dev.
trimethylolpropane triacrylate	0.34	0.15
1,2-hexanediol diacrylate	0.68	0.07
bisphenol A epoxy diacrylate	0.02	0.05
Formula 2	0.36	0.05
Formula 1	0.40	0.07

Summary

A method for estimating VOCs from thin radiation-curable coatings is proposed. The method allows estimated VOC_{total} values to be calculated based on the weighted contributions from individual reactive components or allows the VOC_{total} value for a blend of reactive components to be measured. The current procedure is endorsed by RadTech International North America and has been submitted for review to a number of printing organizations, including the Specialty Graphics Imaging Association (SGIA), Printing Industry Association of Southern California (PIASC) and the National Association of Printing Ink Manufacturers (NAPIM). Acceptance by raw material suppliers as well as ink formulators is a first step in this process. The VOC_{total} data are consistent with a number of intuitive trends:

higher functionality equates to lower VOC_{total}

oligomers have inherently lower VOC_{total}

high VOC_{total} monomers tend to be those that are slow to homopolymerize

high molecular weight monomers have decreased VOC_{total}

The proposed method is easy to run and does not require significant investment. It is amenable to both raw material suppliers and formulators, both large and small. If approved by the AQMD and USEPA, the data obtained by the material suppliers will allow end-users and formulators to estimate VOCs for formulated inks and OPVs by a simple calculation based on composition. As an alternative, a fully formulated blend less pigment and other non-reactive additives can also be tested using this method.

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² current address University of Michigan, Ann Arbor, MI.

³ Gary Cohen, "Status of UV&EB in North America 2006", www.radtech.org.

⁴ CFR Title 40, 51.100S

⁵ SCAQMD Board Meeting minutes, June 1, 2007.

⁶ see for example, minutes from AQMD Board Meeting May 4, 2007 (Agenda Item No. 29) and June 1, 2007 (Agenda Item No. 38).

⁷ www.sks-bottle.com/340c/fin7.html

⁸ Alfrey and Price, *J. Polym. Sci.* **2**, 101 (1947).

⁹ Lewis Young, *Polymer Handbook*, 2nd Ed. 1975 (II-341-362).

¹⁰ blends provided by H. Ragin, Craig Adhesives and Coatings, Newark, NJ.