Transmittal
of
ARB Staff Rule Review Comments

To: Mr. Kevin Williams, PhD
Associate Air Quality Engineer
Sacramento Metropolitan Air Quality Management District
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From: Alex Krichevsky, (916) 324-6222
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The following draft rules, which are scheduled for a public workshop to be held by your
District staff on April 28, 2008, were received by us on April 1, 2008, for our review:

Rule 450  Graphic Arts Operations
Rule 454  Degreasing Operations
Rule 463  Wood Products Coating
Rule 464  Organic Chemical Manufacturing Operations
Rule 465  Polyester Resin Operations
Rule 466  Solvent Cleaning

We have reviewed the rules and have the comments on the following pages. We
believe that our comments are important to the effectiveness and enforceability of the
rules.

Ms. Stephanie Lee of the Strategy Evaluation Section, Measures Assessment Branch,
Stationary Source Division, discussed our comments with you on April 22, 2008. You
agreed that you would consider making the recommended changes.

We received the rules after the ARB/CAPCOA protocol date. When we receive draft
rules at least 30 days before a workshop, our staff is afforded sufficient time to conduct
a thorough, comprehensive review and you will likely receive our comments well before
the workshop.
If you have any questions about our comments on Rules 450, 454, 463, and 466, please contact Mr. James Nyarady, Manager of the Strategy Evaluation Section, at (916) 322-8273.

If you have any questions about our comment on Rule 465, please contact Ms. Peggy Tarrico, Manager of the Technical Analysis Section, Emissions Assessment Branch, Stationary Source Division at (916) 323-4882.

Rule review comments are on the following pages
Air Resources Board Staff Comments on
Sacramento Metropolitan Air Quality Management District
Draft Rules 450, 454, 463, 464, 465, and 466

Rule 450 Graphic Arts Operations

1. **Section 110.1:** This section exempts any graphic arts operation which emits less than 60 pounds of VOC per calendar month, including emissions from solvent cleaning. Ventura County Air Pollution Control District (VCAPCD) Rule 74.19 contains a current exemption limit of 200 pounds per rolling 12-month period. We recommend that the District lower the exemption level to 200 pounds per rolling 12-month period. By lowering the exemption level, more sources will be subject to the rule.

2. **Section 300:** The VOC limit for “Extreme Performance Ink/Coating” for screen printing is currently 800 g/l. San Joaquin Valley Unified Air Pollution Control District (SJUUAPCD) Rule 4607 Section (5.3) and Bay Area Air Quality Management District (BAAQMD) Rule 8-20 Section (307) both limit the VOC content for this category to 400 g/l. We recommend incorporating this lower limit. The VOC limit for “Sign Ink/Coating” for screen printing is currently 500 g/l. SJUUAPCD Rule 4607 Section (5.3) limits the VOC content for this category to 400 g/l. We recommend incorporating this lower limit.

3. **Section 302.1:** The proposed VOC content limit for Ultraviolet Inks is a technology forcing limit. South Coast Air Quality Management District (SCAQMD) recently extended the effective date of this limit from January 1, 2008 to January 1, 2009. Sacramento Metropolitan Air Quality Management District’s limit for Ultraviolet Inks is effective January 1, 2010. ARB recommends that the district revisit this limit when South Coast’s limit takes effect.

4. **Section 303.2:** This section allows the use of an emission control system, in lieu of complying with VOC content limits. The collection and control efficiency combined yields an overall efficiency of 67%. San Diego County Air Pollution Control District (SDAPCD) Rule 67-16 Section (e)(ii) has an overall collection and control efficiency of 85%. We recommend increasing the efficiency requirements to be as stringent as San Diego rule.

5. **Section 502.3:** This section references ASTM Test Method D 4457-02. This test method has been replaced by ASTM Test Method D 4457-02(2008). We recommend changing this reference to reflect the most current version of the ASTM Test Method.
6. **Section 502.7:** This section references ASTM Test Method D 2879-97(2002)e1. This test method has been replaced by ASTM Test Method D 2879-97(2007). We suggest changing this reference to reflect the most current version of the ASTM Test Method.

7. **Rule 454 Degreasing Operations**

7. **Section 310:** This section stipulates emission control equipment standards that can be used in lieu of complying with the applicable requirements of Sections 302, 304, or 307. The proposed changes to this section would have this section expire one year and one day after the date of adoption of the revised rule. This change would leave a loophole in Section 309. Section 309 states that a lip exhaust system "shall not be used on any degreaser, unless it is vented to an emission control system, pursuant to Section 310." Since the proposed changes to Section 310 would have it expire one year and one day after adoption of the revised rule, a lip exhaust system could then be used on any degreaser without having to be vented to an emission control system. We recommend revising the rule language to address this loophole.

8. **Rule 463 Wood Products Coatings**

8. **Section 110:** Sources using less than 55 gallons per year are exempt from the requirements of this rule. Bay Area Air Quality Management District (BAAQMD) Rule 8-32 Section (111), El Dorado County Air Quality Management District (EDAQMD) Rule 237 Section (C), San Joaquin Valley Unified Air Pollution Control District (SJVUAPCD) Rule 4606 Section (4.1.2), and Santa Barbara County Air Pollution Control District (SBAPCD) Rule 351 Section (B)(5) limit this exemption to 20 gallons per year. We recommend lowering the exemption from 55 gallons per year to 20 gallons per year.

9. **Section 300:** The VOC limit for "High-Solid Stain" is 350 g/l. EDAQMD Rule 237 Section (237.3)(A)(1), SJVUAPCD Rule 4606 Section (5.1), SBAPCD Rule 351 Section (D)(1), and Ventura County Air Pollution Control District (VAPCD) Rule 74-30 (B)(1) all have a limit of 240 g/l for High-Solid Stain. We recommend that the District include this lower limit in the rule. The VOC limit for "Sealer" is 275 g/l. VAPCD Rule 74-30 Section (B)(1) has a limit of 240 g/l for this category. We recommend that the District include this lower limit in the rule.

10. **Section 303:** The VOC limit for strippers is 350 g/l. San Diego County Air Pollution Control District (SDAPCD) Rule 67-11 Section (d)(5)(i) has a limit of 200 g/l for strippers. We recommend that the District include this lower limit in the rule.

11. **Section 503.3:** This section references ASTM Test Method D 4457-02. This test method has been replaced by ASTM Test Method D 4457-02(2008). We recommend changing this reference to reflect the most current version of the ASTM Test Method.
12. **Section 503.7:** This section references ASTM Test Method D 5403-93(2002). This test method has been replaced by ASTM Test Method D 5403-93(2007). We recommend changing this reference to reflect the most current version of the ASTM Test Method.

**Rule 464 Organic Chemical Manufacturing Operations**

We have no comments on this rule.

**Rule 465 Polyester Resin Operations**

13. **General:** The Sacramento Metropolitan Air Quality Management District (District) staff is proposing amendments to Rule 465 Polyester Resin Operations (Rule) to satisfy the requirements for All Feasible Control Measures (AFCM).

Based on Air Resources Board (ARB) staff review, we have determined the current overall control efficiency of the control system required by the Rule does not meet the AFCM criteria for the District. The staff of ARB considered South Coast Air Quality Management District (SCAQMD) Rule 1162 as the basis in our BARCT and AFCM determinations pertaining to emission control system requirements for polyester resin operations.

Section 301.2 of this rule states “the VOC emission control system shall provide an overall system, as determined by Section 404, of not less than 85 percent by weight.” While an overall 85 percent collection and control efficiency may be acceptable for solvent cleaning operations, it is less stringent than SCAQMD Rule 1162 requires for polyester resin operations. The overall capture and control efficiency of SCAQMD Rule 1162 is 90 percent or more on a mass basis. We recommend the District amend the proposed Rule to be consistent with the overall capture and control efficiency of SCAQMD Rule 1162, which is an overall capture and control efficiency of 90 percent or more on a mass basis.

**Rule 466 Solvent Cleaning**

14. **Section 502.2:** This section references ASTM Test Method D 4457-02. This test method has been replaced by ASTM Test Method D 4457-02(2008). We recommend changing this reference to reflect the most current version of the ASTM Test Method.
COMMENTS

Proposed Amendment to SMAQMD Rule-450
Graphic Arts Operations XX-XX-08

The following comments reflect the opinions of the Office of State Publishing (OSP) relevant to proposed changes to Sacramento Metropolitan Air Quality Management District (SMAQMD) Rule-450, Graphic Arts Operations.

1. **Section 302.1:** "Lithographic and Letter Press Printing" is subdivided by substrates..."Newsprint" and "Other than Newsprint". Solvent VOC compliance dates are one-year from rule implementation for "Newsprint" and 1/1/2010 for other substrates.

   **Comment:** Compliance dates by substrate are not appropriate for printers who use both newsprint and non-newsprint in their products from the same presses. At OSP, the same cleanup solvents are used on these presses regardless of substrate. Printers who use the same materials regardless of substrate should be allowed the maximum compliance period which is until 1/1/2010.

2. **Section 302.1:** Effective one-year from rule implementation, the VOC limit for solvents used to clean "Removable Press Components" will be lowered from 100 grams/liter to 25 grams/liter.

   **Comment:** This is unreasonable because in most cases, the contamination is the same material removed from ink rollers and blankets. Therefore, blanket and roller washes are often used to clean parts removed from the press. VOC limits for "Removable Press Components" should match those of "Blanket and Roller Washes".

3. **Section 501.3b1:** The last sentence states "Effective (one year after date of adoption) and expiring on January 1, 2010, usage records shall differentiate between materials used for printing on newsprint and materials used for printing on other substrates".

   **Comment:** Printers such as OSP use the same fountain solutions, same solvents, same adhesives, and essentially the same inks on presses that run both newsprint and other substrates. Therefore, the list of materials used for newsprint would be identical to the list of materials for other substrates. This requirement serves no practical purpose in this case, and should be dropped.
JIMMY CHENG

From: Ted Huff [THuff@smud.org]
Sent: Monday, May 05, 2008 3:56 PM
To: KEVIN LEONARD; ALETA KENNARD; JIMMY CHENG
Subject: SMAQMD Rule 466, Solvent Cleaning

Lady and gentlemen,

SMUD appreciates this opportunity to comment on the proposed revisions to the SMAQMD Rule 466, Solvent Cleaning. We request that an exemption be added to the rule in Section 110.2c., that would include high voltage gloves, hot sticks, rubber blankets, line hoses, mechanical jumpers, insulator covers and high voltage test equipment leads. This equipment is used by personnel on energized circuits to perform testing, switching, equipment repairs, protection of personnel and other related functions to equipment and apparatus that cannot be practically de-energized. This high voltage equipment (hot sticks, gloves, rubber blankets, line hoses, mechanical jumpers, insulator covers and high voltage test equipment leads) represents in some cases, the individual’s only protection from injury or death from electrocution while working on energized circuits or equipment. The products currently used for cleaning of this high voltage equipment provides the necessary level of cleaning to ensure that the equipment remains safe for use on live or energized circuits. The concern is that lower VOC-content products may not clean the surface as thoroughly and leave a residue allowing tracking and flashover of the device.
May 5, 2008

Jimmy Cheng
Sacramento Metropolitan AQMD
777 12th Street, 3rd Floor,
Sacramento, CA 95814


Dear Mr. Cheng,

As the developer and producer of tertiary-butyl acetate (TBAC), Lyondell Chemical appreciates the opportunity to comment on the proposed amendments to the solvent cleaning requirements of several District rules.

The draft rules impose stringent VOC limits on a number of cleaning operations but fail to provide businesses with an important compliance tool, VOC-exempt tertiary butyl acetate (TBAC). Several studies have shown that TBAC offers numerous advantages over acetone for cleaning operations. We therefore request that the draft rules be revised to include a VOC exemption for TBAC.

TBAC produces 50% less ozone than acetone. TBAC was exempted from the federal VOC definition in November 2004 because of its negligible photochemical reactivity. The federal exemption is now recognized in 49 States and several California district and county rules. It’s MIR (Maximum Incremental Reactivity) is 0.17 g ozone/gram, which is half the MIR of acetone (0.35 grams ozone/gram). Exempting TBAC would provide additional ozone reduction benefits compared to not exempting it.

TBAC is a much better degreaser than acetone.¹ Acetone is an aggressive, polar solvent. It is a poor solvent for greases and other non-polar soils such as machining oil. TBAC, on the other hand, is an excellent solvent for a variety of greases, oils and non-polar soils. By recognizing the VOC exempt status of TBAC, the SMAQMD would also reduce the amount of solvent used in cleaning operations because less TBAC is required.

TBAC can be used on sensitive plastics such as acrylics, carbonates, PVC and ABS which are used extensively in the automotive and electronic sectors. Acetone dissolves

these plastics. Exempting TBAC will provide businesses with a practical cleaning solvent for these substrates. Acetone also swells printer rollers and blankets. TBAC does not and is a suitable solvent for lithographic and flexographic ink cleanup.\textsuperscript{2}

TBAC is 2.75 times less volatile than acetone. This means TBAC is easier to contain and evaporative losses from containers and in operations will be reduced compared to acetone. TBAC’s lower evaporation rate also improves its cleaning performance vs. acetone. Less TBAC is needed as less evaporates from the substrate being cleaned.

TBAC is significantly less flammable than acetone, with a flash point of 40°F compared to 0°F. Exempting TBAC would reduce the risk of fire in cleaning operations.

TBAC has low acute and subchronic toxicity. There has been speculation that TBAC could potentially pose a cancer risk to humans because its metabolite TBA caused a slight increase in naturally-occurring tumors in laboratory animals at high doses. However there is considerable evidence that these tumors are rodent-specific and not relevant to human carcinogenicity or typical occupational exposures. TBAC is also not mutagenic, genotoxic or a reproductive toxin.

TBAC is also not a TAC, HAP, TRI chemical, ozone depleter, PM precursor, or greenhouse gas. It is an excellent solvent with a superior environmental profile that can be safely used by trained technicians and operators in a variety of industrial operations. By exempting TBAC from the VOC definition in your District rules, the AQMD will reduce workplace hazards, reduce overall solvent usage, reduce ozone and PM formed from cleaning emissions, and reduce the financial impact of these new rules on District businesses. Thank you for considering these comments. Please feel free to call me if you have questions.

Sincerely,

\[\text{Daniel B. Pourreau, Ph.D.}\]
\text{Technical Advisor}\n
\textsuperscript{2} P1A-GATF Swells tests of TBAC and acetone on blanket and rollers, 2005 attached.
Degree of Swell Report
Lyondell Chemical Company

Dan Pourreau
August 2005
Lindsay Ferrari
TLS 5402

Executive Summary

Lyondell Chemical Company has requested that PIA/GATF determine the degree of blanket swell using t-butyl acetate and six other cleaning materials.

Test performed:

- PIA/GATF Degree of Swell test

Results of the test are as follows:

- LV10, Autowash 6000, and Naphtha had less swell than the t-butyl acetate
- Anchor A240 performed similarly to t-butyl acetate
- T-butyl acetate experienced less swelling than Xylene and Acetone

Recommendations:

- T-butyl acetate appears to have an acceptable interaction with blanket rubber
- Lyondell should consider moving forward with on-press roller washing tests.

NOTICE: The conclusions drawn in this report are based on the facts and conditions that were observed by or reported to us. They include PIA/GATF test results and/or information believed to be reliable. Since there are so many variables in the process, these conclusions might not remain valid if the information given to us was incorrect and of incomplete. We do not assume any responsibility for the use of this report. It is confidential and is not to be quoted or published.
Degree of Swell Test

Background
The degree of swell is a very important test for blankets and blanket washes. The blanket is soft and porous and washed frequently. The degree of swell is more difficult to perform with rollers. According to best practices, an adverse swelling of a blanket suggests swelling of rollers on the press. Industry guidelines suggest that percent swell should be less than 5%. The objective of this test is to determine under laboratory conditions the degree of swell of a blanket.

Methodology
A three inch square piece of blanket was cut from a larger blanket, then measured with a Cady gauge for initial caliper. Twenty-six milliliters of cleaning solution were placed in a glass crystallization dish. The blanket was placed over the top of the dish, blanket printing face pointing toward the liquid cleaner. The dish and blanket were placed in a clamping device and inverted such that the liquid was in contact with the blanket face. After one hour, the blanket was removed from the cell, the solvent was wiped from the surface, and the caliper of the blanket was measured. The blanket was returned to contact with the liquid for an additional four hours. Again, the caliper was measured. Percent swell was calculated according to the following equation:

\[
\text{Percent Swell} = \frac{\text{Final Caliper} - \text{Initial Caliper}}{\text{Initial Caliper}} \times 100
\]

Results and Conclusion
After one hour and after four hours the naphtha showed a small degree of swell. The LV10 and Autowash 6000 also had a minimal degree of swell. The Anchor A240 and the t-butyl acetate had an acceptable degree of swell after one hour. However after four hours the degree of swell was greater than five percent. Xylene and Acetone had the most swell. The extreme degree of swell makes them unacceptable.

The important observation here is that t-butyl acetate had similar swelling to Anchor A240, which is a commercial product used in large quantities.
Table 1 shows the percent swell after one hour and after four hours.

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Table 1 Percent Swell

NOTICE: The conclusions drawn in this report are based on the facts and conditions that were observed by or reported to us. They include PIA/GATF test results and/or information believed to be reliable. Since there are so many variables in the process, these conclusions might not remain valid if the information given to us was incorrect and/or incomplete. We do not assume any responsibility for the use of this report. It is confidential and is not to be quoted or published.
Tertiary-Butyl Acetate (TBAC): A Technical Overview and Regulatory Update on the Latest VOC-Exempt Solvent

Daniel B. Pourreau

By the end of 2007, most states and possibly Canada are expected to have exempted TBAC from VOC regulations. This will allow manufacturers to formulate compliant solvent-borne cleaners for precision cleaning applications for which current low-VOC technologies cannot be used or do not meet basic performance standards.

Tertiary-butyl acetate (TBAC™ solvent or, generically, TBAC), is an oxygenated ester solvent. Until recently, it had found limited use as a pharmaceutical intermediate. However, in December 2004, the U.S. EPA granted Lyondell Chemical Company’s 1997 petition to add TBAC to the list of VOC-exempt compounds. This action ended an eight-year process during which the company was asked to demonstrate that TBAC not only had negligible photochemical reactivity, the official requirement for exemption, but that it also had low toxicity and was not likely to have other adverse environmental effects.

This exemption also spurred considerable interest in TBAC as a compliance tool in a variety of applications, including coatings, adhesives, inks and cleaners. TBAC is not only VOC-exempt, but it is also non-HAP, not a TRI or Prop 65 chemical, and SNAP-approved as a replacement for ozone-depleting substances. TBAC’s two main drawbacks are its odor, which is strong and camphor-like, and its flash point at approximately 40°F. However, Lyondell and other companies have identified several maskants and odor attenuators, as well as co-solvents that increase or eliminate the flash point of TBAC.

The federal exemption marked the beginning of a similar and, fortunately, more expeditious process at the state level. This article attempts to bring the reader up-to-date on the current status of the TBAC exemption and provides a brief overview of the cleaning technologies for which TBAC will likely become an important HAP- and VOC-compliance tool.

**TBAC VOC Exemption Status**

As of the date this article was submitted, TBAC was already fully exempt in 37 states and partially exempt in 49 states. The status of the TBAC exemption, as of June 2006, is shown in Figure 1. The states in green either exempted TBAC automatically or have already completed their VOC definition update. States in yellow grant some form of interim relief during the rulemaking period or have limited exemptions. How this relief is granted varies from state to state, with some states simply requiring that TBAC users report their emissions, as required by the federal rule, while others will allow TBAC to be used as an exempt compound only via permits.

By early 2007, TBAC is expected to be fully exempt in all 50 states. Wyoming, Alaska and New Jersey will allow the use of TBAC as an exempt solvent during their rulemaking process. California does not grant interim relief during their rulemaking process.

California has none-the-less begun the process to exempt TBAC. In a recent draft Environmental Impact Assessment, the California Air Resources Board (CARB) indicated that it plans to exempt TBAC in certain consumer and commercial product...
Raytheon Systems has evaluated TBAC in hand-wipe and cold cleaning applications. It reported its cleaning efficiency versus MEK and MPK in removing common oils from aluminum and composite substrates. The soils evaluated included liquid oil, machine oil, silicone, and mineral lubricants. The authors concluded that all three solvents had comparable cleaning efficiency.

An internal evaluation was also conducted on five different industrial greases and resin flux. The greases were applied to steel coupons and immersed for three minutes in solvent. The numbers shown in Figure 1 represent the average grease or flux removed from three coupons. The greases tested were silicone grease, axle grease, Vaseline™ petroleum jelly, lithium grease, and Cosmuline™ grease.

TBAC removed an average of 76 percent of these contaminants from the coupons (Figure 1). It performed poorly only on Cosmuline grease (31 percent removal). It performed almost as well as common halogenated solvents such as trichlorethylene (TCE; 98 percent), n-propyl bromide (nPB; 97 percent), and perfluorohexane (PFH; 86 percent). It also performed better than Naphtha (70 percent) and MEK (36 percent) and markedly better than the low- or zero-VOC degreasers recommended by the SAOGMD by the Institute of Research and Technical Assistance (IRTA).

Several of these low-VOC “cleaners” produced an increase in contaminant on the coupons or were essentially ineffective. Acetone and IPA, the two main solvents recommended for non-aqueous cleaning, removed an average of 22 percent and 10 percent of these six soils, respectively. Clearly, TBAC is a much more effective degreaser than these low-VOC alternatives and would result in lower solvent costs and fewer solvent emissions if it were exempt and used instead of acetone and IPA.

TBAC is also much less aggressive than acetone on common plastics such as ABS, acrylic, polycarbonate, and polyethylene. It is also less flammable, less volatile, and less hygroscopic than acetone. However, TBAC’s strong odor and flammability could be a nuisance and a safety hazard if not properly managed. For this reason, Lyndell and others have been evaluating blends of TBAC with non-flammable solvents and odor masks.

n-Propyl bromide (nPB) is a VOC, but it is also an excellent non-flammable degreaser. Based on information provided by NAVAIR, the degreasing efficiency and measuring the flash point of various blends of TBAC and nPB are being evaluated. Preliminary results suggest that adding as little as 15 percent nPB to TBAC significantly increases its degreasing efficiency on certain greases and also suppresses the flash point. This could provide an improved margin of safety in hand-wipe, cold cleaning and, especially, vapor degreasing applications.

Microcare® is also evaluating TBAC as a cold cleaning solvent prior to vapor degreasing with Vetro™ solvents and achieving promising results. Hydrofluorocarbon solvents are VOC exempt but have relatively low K-value but are often blended with polar solvents to improve their cleaning efficiency on polar oils and greases. These polar solvents include methanol and trans-1,2-dichloroethane, which are VOCs. TBAC, with its K-value of 114 and VOC exempt status, is a potential substitute for these polar solvents in blends with hydrofluorocarbons.

Notes:
2. Vaseline™ is a registered trademark of Unilever Corp.
3. Cosmuline™ is a registered trademark of Houghton International.
5. Dr. El-Sayed Anlat, personal communication.
6. TBAC is being evaluated as a replacement for MEK and other VOC solvents for precision cleaning, thinning, and paint cleanup as part of the DOD ESTCP project.
7. The author wishes to thank Karl Leopke and John Dingess of Enviro Tech International for samples of EnSol™ and EnSol-LO cleaners and technical information on the flash point of these products. EnSol is a registered trademark of Enviro Tech International.
8. A flame is sometimes observed at the ignition source with closed cup testing but does not propagate, suggesting efficient quenching of the flame by the nPB.
<table>
<thead>
<tr>
<th>Rule</th>
<th>Point Source</th>
<th>Production or operation</th>
<th>VOC content limit, g/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1122</td>
<td>Solvent degreasers</td>
<td>Cold cleaners</td>
<td>25</td>
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<tr>
<td>1122</td>
<td>Solvent degreasers</td>
<td>Vapor degreasers</td>
<td>50</td>
</tr>
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<td>1124</td>
<td>Aerospace assembly</td>
<td>Cleaning Solvents</td>
<td>200</td>
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<tr>
<td>1124</td>
<td>Aerospace assembly</td>
<td>Strippers</td>
<td>300</td>
</tr>
<tr>
<td>1136</td>
<td>Wood products coatings</td>
<td>Strippers</td>
<td>360</td>
</tr>
<tr>
<td>1171</td>
<td>Solvent cleaning operations</td>
<td>Surface preparation, general</td>
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<tr>
<td>1171</td>
<td>Solvent cleaning operations</td>
<td>Surface preparation, electrical components</td>
<td>100</td>
</tr>
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<td>1171</td>
<td>Solvent cleaning operations</td>
<td>Surface preparation, medical devices</td>
<td>800</td>
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<td>1171</td>
<td>Solvent cleaning operations</td>
<td>Repair &amp; Maintenance, general</td>
<td>25</td>
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<td>Solvent cleaning operations</td>
<td>Repair &amp; Maintenance, electrical components</td>
<td>100</td>
</tr>
<tr>
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<td>Solvent cleaning operations</td>
<td>Repair &amp; Maintenance, medical devices</td>
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<td>Solvent cleaning operations</td>
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</tr>
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<td>1171</td>
<td>Solvent cleaning operations</td>
<td>Coating and adhesive application equipment</td>
<td>25</td>
</tr>
<tr>
<td>1171</td>
<td>Solvent cleaning operations</td>
<td>Ink application equipment, flexographic</td>
<td>25</td>
</tr>
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<td>1171</td>
<td>Solvent cleaning operations</td>
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<td>Solvent cleaning operations</td>
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<tr>
<td>1171</td>
<td>Solvent cleaning operations</td>
<td>Ink application equipment, Litho roller washes</td>
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</tr>
<tr>
<td>1171</td>
<td>Solvent cleaning operations</td>
<td>Ink application equipment, Litho press components</td>
<td>25</td>
</tr>
<tr>
<td>1171</td>
<td>Solvent cleaning operations</td>
<td>Ink application equipment, screen printing</td>
<td>500</td>
</tr>
<tr>
<td>1171</td>
<td>Solvent cleaning operations</td>
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</tr>
<tr>
<td>1171</td>
<td>Solvent cleaning operations</td>
<td>Ink application equipment, Specialty flexographic</td>
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</tr>
<tr>
<td>1171</td>
<td>Solvent cleaning operations</td>
<td>Cleaning of polyester resin application equipment</td>
<td>25</td>
</tr>
</tbody>
</table>

Table 1: VOC content limit of cleaners and strippers in the South Coast Air Quality Management District.

categories. CARB has tied the exemp-tion to its CONS-2 rule-making process, which will probably not be completed until 2007. So, TBAC will probably not be available as a compliance tool for consumer cleaner categories for another year or two.

The districts and counties regulate VOC emissions from point sources such as printing shops and solvent-cleaning operations. The South Coast Air Quality Management District (SCAQMD) has proposed to amend rule 1171 for solvent cleaning operations, but has not yet proposed to exempt TBAC in that rule or in any of the other rules that regulate the VOC content limit of products used in industrial cleaning operations, such as 1122, 1124 and 1136 (see Table 1). Lyondell is submitting comments requesting that the SCAQMD exempt TBAC in rule 1171. The proposed rule is scheduled to go before the board for approval in June 2006.

The SCAQMD did, however, exempt TBAC in some automotive coatings (rule 1151) and has also proposed to exempt it in industrial maintenance coatings, in response to a request by the Southern California Alliance of Publicly Owned Treatment Works. Clearly, interested parties in Southern California and elsewhere can influence whether TBAC is exempted in certain operations. Other districts and counties are expected to follow the lead of SCAQMD and CARB in the coming months.

Canada has also recently proposed strict new VOC regulations for surface cleaners used in automotive refinishing. The new rule limits the VOC content in surface cleaners for plastic substrates to 780g/L, and all other substrates to 200g/L and will be effective in 2007. The proposed Canadian rule contains the same list of VOC-exempt compounds that will need to be updated to exempt TBAC. Lyondell has formally requested that Environment Canada do so. Environment Canada is considering the request, but has not yet committed to exempting TBAC.

**Where Can TBAC Be Used?**

The stringent VOC content limits imposed on products used in cleaning operations has led many in California to switch to water- or acetone-based cleaners or exempt halogenated solvents. Likewise, stringent HAP content and emission limits have led formulators in other parts of the country to move away from MEK, toluene, xylene and other HAPs in their cleaners.

TBAC is a fast-evaporating solvent (2.8 times faster than n-BuAc) with very low water solubility (0.3 percent), a KB value of 114, a flash point of 40°F, and a strong camphor-like odor. It can be used in most applications where acetone, MEK and toluene are used. Its low flash point will also keep it out of formulations that have a 100°F flash point requirement unless it is blended with a co-solvent that can increase or suppress its flash point.

TBAC will be used predominantly in solvent-based industrial cleaners, es-picially in the following applications:

- **Hand-wipe cleaning**
- **Cold cleaning**
- **Aerosol degreasers**
- **Brake cleaners**
- **Vapor degreasers (in blends with non-flammable halogenated solvents)**
- **Paint strippers**
- **Paint gun and adhesive gun cleanup**
- **Ink cleaners**

The Degreasing Efficiency sidebar illustrates TBAC’s broad
affinity for greases, making it a potentially useful component in compliant cleaners and degreasers. TBAC is also a good solvent for a variety of resins used in coatings, inks and adhesives.

**Conclusions**

VOC-exempt TBAC provides cleaner formulators and users with a new, cost-effective tool for HAP and VOC compliance. Unlike other VOC-exempt solvents, TBAC has an intermediate evaporation rate and broad solvency for greases and resins, yet it is less aggressive than acetone on plastic and rubber substrates. Several cleaner formulators and users are evaluating it in hand-wipe, cold cleaning, and vapor degreasing operations.

By the end of 2007, most states and possibly Canada are expected to have exempted TBAC from VOC regulations. This will allow manufacturers to formulate compliant solvent-borne cleaners for precision cleaning applications for which current low-VOC technologies cannot be used or do not meet basic performance standards. **PCM**

Daniel B. Pourreau is currently a Technical Advisor for Lyondell Chemical Company (Lyondell Technology Center—Newtown Square, PA). Dan holds a Ph.D. in Chemistry from Penn State University and has held technical, management and business development positions at Lyondell. He holds more than 20 U.S. patents and has co-authored numerous articles on solvents.

He is a frequent speaker at national and international conferences. Dan can be reached at (610) 359-6837 or via e-mail at dan.pourreau@lyondell.com.

**Notes:**
1. Product of Lyondell Chemical
2. www.epa.gov/ttncca1/t1/lr_notices/tbac.pdf
3. www.arb.ca.gov/research/reactivity/tbac0.pdf
8. MEX was removed from the HAP list in December 2005 but is still a VOC.
9. www.tbac.com
Swell Test of T-butyl Acetate and Acetone mixed with Mineral Spirits

Lyondell
Dan Pourreau

Lindsay Ferrari
TLS 5402.001

August 31, 2005

About PIA/GATF
Printing Industries of America / Graphic Arts Technical Foundation (PIA/GATF) is the world's largest graphic arts trade association representing an industry with more than 1.2 million employees. It serves the interests of more than 12,000 member companies. PIA/GATF, along with its affiliates, delivers products and services that enhance the growth, efficiency, and profitability of its members and the industry through advocacy, education, research, and technical information.

About PIA/GATF Research
PIA/GATF is at the forefront of research and development for the printing industry, helping the industry with day-to-day operations. We can provide you with unbiased, respected, scientific, trustworthy, third-party results. Our experts help printers achieve consistent quality and manufacturers test and benchmark products. For further information contact Dr. Mark Bohan, Director, Research and Integrated Technology, at (412) 259-1782.

000290
Executive Summary

Lyondell Chemical Company has requested that PIA/GATF determine the degree of blanket swell using a t-butyl acetate/mineral spirits mixture and an acetone/mineral spirits mixture.

Tests Performed

PIA/GATF Degree of Swell test

Results

The t-butyl acetate/mineral spirits mix swells less than the acetone/mineral spirits mix. The t-butyl acetate/mineral spirits mix swell was similar to t-butyl straight. Straight acetone swell less than the acetone/mineral spirits mix.

Recommendations

The t-butyl acetate/mineral spirit mixture interacts with the blanket in an acceptable manner for lithographic cleaning applications. This cannot be said for the acetone mixture.

NOTICE: The conclusions drawn in this report are based on the facts and conditions that were observed by or reported to us. They include PIA/GATF test results and/or information believed to be reliable. Since there are so many variables in the process, these conclusions might not remain valid if the information given to us was incorrect and/or incomplete. We do not assume any responsibility for the use of this report. It is considered to be altered, quoted or published.
Degree of Swell Test

Background
The degree of swell is a very important test for blankets and blanket washes. The blanket is soft and porous and washed frequently. The degree of swell is more difficult to perform with rollers. According to best practices, an adverse swelling of a blanket suggests swelling of rollers on the press. Industry guidelines suggest that percent swell should be less than 5%. The objective of this test is to determine under laboratory conditions the degree of swell of a blanket.

Methodology
A three inch square piece of blanket was cut from a larger blanket, then measured with a Cady gauge for initial caliper. Twenty-six milliliters of cleaning solution were placed in a glass crystallization dish. The blanket was placed over the top of the dish, blanket printing face pointing toward the liquid cleaner. The dish and blanket were placed in a clamping device and inverted such that the liquid was in contact with the blanket face. After one hour, the blanket was removed from the cell, the solvent was wiped from the surface, and the caliper of the blanket was measured. The blanket was returned to contact with the liquid for an additional four hours. Again, the caliper was measured. Percent swell was calculated according to the following equation:

\[ \text{Percent Swell} = \frac{\text{Final Caliper} - \text{Initial Caliper}}{\text{Initial Caliper}} \times 100 \]

Results and Conclusion
The chart below shows the actual values from the swell test. The t-butyl acetate/mineral spirits mix swells less than the acetone/mineral spirits mix.

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<th>T-butyl</th>
<th>Acetone/MS 75/25</th>
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<tr>
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<td>After 4 hours</td>
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NOTICE: The conclusions drawn in this report are based on the facts and conditions that were observed by or reported to us. They include PIA/GATF test results and/or information believed to be reliable. Since there are so many variables in the process, these conclusions might not remain valid if the information given to us was incorrect and/or incomplete. We do no assume any responsibility for the use of this report. It is confidential and is not to be altered, quoted or published.
Table 1: t-butyl acetate and acetone mix swell test results

Table 2: t-butyl acetate swell test results

NOTICE: The conclusions drawn in this report are based on the facts and conditions that were observed by or reported to us. They include PIA/GATF test results and/or information believed to be reliable. Since there are so many variables in the process, these conclusions might not remain valid if the information given to us was incorrect and/or incomplete. We do not assume any responsibility for the use of this report. It is confidential and is not to be altered, quoted or published.
Table 3 acetone swell test results

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<td>75% Acetone 25% mineral spirits</td>
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<tr>
<td>Acetone</td>
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<td></td>
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</tbody>
</table>

NOTICE: The conclusions drawn in this report are based on the facts and conditions that were observed by or reported to us. They include PIA/GATF test results and/or information believed to be reliable. Since there are so many variables in the process, these conclusions might not remain valid if the information given to us was incorrect and/or incomplete. We do no assume any responsibility for the use of this report. It is confidential and is not to be altered, quoted or published.
May 7, 2008

Dr. Kevin J. Williams
Program Coordinator
Rule Development
Sacramento Metropolitan AQMD
777 12th St, 3rd Floor
Sacramento, California 95814-1908

Dear Dr. Williams:

This statement is respectfully submitted to the Sacramento Metropolitan Air Quality Management District (SMAQMD) by the Printing Industries of California in response to proposed amended Rule 450 ("Graphic Arts").

By way of introduction, Printing Industries of California (PIC) is the government affairs office of three printing industry trade associations in the state. The combined membership of the three affiliates is approximately 3,000 companies. Within SMAQMD jurisdiction, there are around 150 graphic arts firms, employing over 3,500 workers, and generating $514 million in sales. Roughly twenty-five percent of these firms don’t put ink on paper; they provide a variety of ancillary printing services, such as prepress, binding, other finishing services (e.g., embossing, foil), and fulfillment.

General Comments

SMAQMD’s bases the proposed cleanup solvent standards for printing on South Coast Air Quality Management District’s Technology Assessments for Lithographic, Screen and UV Printing Operations. I would be remiss, therefore, if I didn’t comment on that study. I will limit my comments to the treatment of lithographic and UV printing operations.

PIC was involved with the study from beginning to end, from identifying facilities to test new formulations, witnessing many of the tests, and interviewing representatives of these facilities on the performance of these formulations.
Dr. Kevin J. Williams  
Program Coordinator  
May 7, 2008  
Page 2

There was and still is strong disagreement between PIC, the SCAQMD, and its solvent formulator, the Institute for Research and Technology Assistance (IRTA) on the results of the Technology Assessment. IRTA formulated on the fly, testing solvents in its offices to see if they cleaned ink and, if so, taking the chemical to mix at printing facilities to test on press. Most of the firms that tested IRTA’s formulations did not perform extended tests of the formulations, but those that did perform extended tests found the formulations caused a number of “lithographic” (i.e. printing) problems.

IRTA final report is entitled Assessment, Development, and Demonstration of Low-VOC Solvents for Cleaning of Lithographic Ink Application Equipment (May 2006). I have attached the summary page (page 59) of companies involved in its assessment project (Exhibit A). The summary page identifies 21 companies as participants in the project.

Here is our assessment of the results:

1. L.A. Times, San Bernardino Sun, Vertis, J.S. Paluch—Each of these companies prints on newsprint or super-calendar (Vertis) substrates. The first three use soy ink. There are no or very limited color changes, and the press is cleaned on the fly (i.e., while it is running). The substrate absorbs much of the oil in the cleanup solvent so that the issue of residue is generally avoided. Each of these facilities was already using a low-VOC solvent before the testing (of IRTA’s formulation took place). None converted to the IRTA’s test formulations, nor did they use them for any extended time. On the other hand, J.S. Paluch used conventional ink formulations. It tested the soy ink, which left residue, and the company never completed other testing.

2. Nelson Nameplate—Nelson has two manual presses that print on metal and plastic, one sheet at a time. While they are classified as lithographic presses, they don’t perform as an ordinary lithograph press. Nelson did convert to an acetone-based product.

3. PIP Printing, SCAQMD Print Shop, City of Santa Monica, Presslink. Each of these companies runs a small press (e.g., AB Dick, Ryobi). PIP Printing and Presslink tried various test formulations (e.g., acetone-based and soy-based). None of the formulations worked, and the firms never performed into extended testing.

4. Western Metal Decorating—Print for metal cans, the last of such printers in the region. Never complete extended testing.

5. Tedco Printing Company and Oberthur Card Systems—UV printing on plastic. Never found adequate solvent, and therefore neither firm completed extended testing.
6. Huhtamaki—UV/EB printing for ice cream cartons. Never found adequate formulation, and therefore never entered into extended testing.

7. Fanfare Media Works—no information

8. R.R. Donnelley & Sons Co., The Castle Press, Print 2000 Graphics, The Dot Printer, Lithographix, Anderson Lithograph, The Printery. These firms are traditional lithographic printers, printing on paper substrate, employing either or both web and sheetfed presses, with two (Lithographix and Anderson Lithograph) running both conventional and UV ink. None of these firms completed extended testing.

The formulations tested by IRTA are attached under Exhibit B. As you can see, there were several versions of Soy Gold and acetone-laden formulations. The former failed, and continues to fail, in production situations. The later can be used to clean blankets, but a concentration above 30 percent swell the blankets. (See University of Tennessee's Center for Clean Products and Clean Technologies study entitled Compatibility Testing of Low-VOCAnterior Cleaning Solvents for Lithographic Printing Application (April 12, 2006).

PIC initiated parallel testing of Soy Gold 2500. The results confirmed what we culled from the IRTA field tests (Exhibit C). Soy Gold 2500, the preferred low-VOCl solvent of IRTA, fails in production situations.

Because of the controversy over IRTA's results, PIC submitted its own protocol to the SCAQMD for cleanup solvent testing (Exhibit D)—and the SCAQMD extended the 100 gram per liter target for an additional eighteen months.

PIC hired Mr. John McPhee well-known technical expert on lithographic printing. His resume, publications, and inventions are attached as Exhibit E.

I have included PowerPoint presentation that Mr. McPhee made to the SCAQMD on the results of his work (Exhibit F). As you will note, it's a much more technical approach than mixing and testing formulation at the press. Much of Mr. McPhee's work was performed on a Tackmaster 92 (See photo on the next page). This instrument consists of four rubber rollers and a chrome roller behind the top rubber roller. The device is hook up to a computer through which a special program reads the tack of ink over time (12 minutes in the test runs).

I have attached the protocol that is followed for inking and cleaning to test the influence of solvent on tack (Exhibit G). I have also attached the reading from three specifically chosen tests: Bottcher Bio 3 (Exhibit H) and Soy Gold 2500 with two different ink colors(Exhibits I and J). These ample are purposely chosen since Soy Gold 2500 is the
cleanup solvent of choice by IRTA and Bottcher Bio 3 is a low-VOC alternative European solvent (coconut oil).

The graphs should be read as follows. The tack is measures on the vertical line and the time of the run on the horizontal line (12 minutes). The rollers are first cleaned with high VOC solvent—around 700 grams per liter, and then inked and read for tack. The first graph line is positive (upward slopping) and shows an increase of tack. This is good since the more tack the ink has (up to a certain point), the sharper the dot pattern. After 12 minutes the rollers are cleaned with the test solvent, inked, and read for tack. This is done three or more times. Note that on each subsequent run the tack declines more and recovers less. This indicates that there is residue on the rollers—residue for the cleanup solvent—that attacks the ink. In a production situation, this would cause all kinds of printing problems.

In the Bottcher Bio 3 test, we ran the test and followed the cleanup with a rinse (Aqualux), then with vinegar and water, and lastly with vinegar. These materials help get residue out of the rollers.

In the June 28-29, 2006, Soy Gold 2500 test, we also measured for misting of flying of ink, which occurs when the ink emulsify or takes on residue from the rollers. All ink has
some fly, as seen in the second sheet of this test. However, after only three wash-ups, the misting with Soy Gold 2500 is very excessive—and indicates that the ink is taking on the oils from the cleanup solvent.

This discussion can’t reverse the decision at the SCAQMD, or the decisions of other air quality management districts.

I want to point out, however, the weak foundation on which the SCAQMD based its decision. The Technology Assessment is non-technical in approach and incomplete in field testing. Unfortunately, many local air districts—and CARB—spend little or no time reviewing the content of this document, but defer to its authority without even examining the document.

This SCAQMD’s approach, to say the least, is non-technical but authoritative. That is, there was no protocol, except the anecdotal evidence presented by the consultant, to verify test results. Yet the results became authoritative. Now other districts follow along without review or questioning the results.

Rule 450

Definitions

Proposed Definition:

**239 Other On-Press Components** A part, component, or accessory of a press that is cleaned while still be physically attached to the press, excluding blankets, rollers, metering rollers, and printing plates.

Comment:

The definition in **246 Removable Press Components** states that “rollers, blankets, metering rollers, dampening rollers, printing plates, fountains, impression cylinders and plates shall not be considered as removable press components.”

At the very least, the clause identifying those items excluded from **239 Other On-Press Components** should include the same laundry list of items as **246 Removable Press Components**.
Dr. Kevin J. Williams  
Program Coordinator  
May 7, 2008  
Page 6

Thus the statement in **239 Other On-Press Components** should read “excluding rollers, blankets, metering rollers, dampening rollers, printing plates, fountains, impression cylinders and plates.”

**Cleaning and Storage Requirements**

I want to reiterate the request that I made in our meeting of April 18th: the limits be reduced in two steps, first to less than 500 grams per liter one year after the effective date, and then at 100 grams per liter one year after the first date.

This would give printers time to adjust to working with these low-VOC solvents. **No other district attempted to move from the current limit to less than 100 grams per liter.** SMAQMD had no idea how hard it is to get these low-VOC solvents to work. The stepping down allows printers to become familiar with how lower solvent work and prepares them for the less than 100 gram per liter limit. In so doing, SMAQMD would have extended the Effective Date of the less than 100 gram per liter limit by only six months to around July 2010.

Please seriously consider this request.

**302.2 Lithographic and Letter Press Printing, Cleaning of Metering Rollers and Printing Plates**

This section should be deleted. No other district in the nation, let alone the state, has this standard. It’s a trap. For example, a printer in SMAQMD jurisdiction adopted a cleanup solvent in the 500 grams per liter range. However, it continued to use a higher VOC metering roller. The VOC from the metering roller cleaner exceed 15 percent by .5 percent. The printer is out of compliance.

I understand that SMAQMD wants to make sure that the metering roller cleaner is not used for other cleaning processes. However, it’s harder to find an effective metering roller cleaner at low-VOC limits than even roller and blanket wash. In this scenario, there is no incentive for the printer to try to use lower VOC solvents because it will exceed the usage percentage of metering roller.

I suggest the metering roller VOC limit be set at the same as the On-Press Components.

000300
Monitoring and Records

501.3 (b)(4). Delete this section. See comments for rationale above under Section 302.2 Lithographic and Letter Press Printing, Cleaning of Metering Rollers and Printing Plates.

501.5. Records should not have to be kept for more than 2 years. The only firms that the U.S. Environmental Protection Agency requires to keep records this long are Title V firms. This is just another burdensome requirement for small business. Ninety percent of all printing companies in SMAQMD have less than 15 employees. There are no engineers, nor do they have environmental and safety officers whose duty it is to perform these functions.

502.7. Since SMAQMD is proposing to delete the vapor pressure requirement on January 1, 2010, this section should also be deleted. The less formulae and references to formulae there are in the rule, the better.

I would be negligent if I didn’t address the vapor pressure issue. The issue of low vapor pressure materials (under 5 mm) was summarily dismissed as an alternative to low VOC materials before, during, and after, the requirement, as part of the SCAQMD’s Technology Assessment.

PIC and SCAQMD staff had agreed in discussions on the October 8, 1999, amendments to Rule 1171 that a study would be done on the relations between vapor pressure and VOC emission rates. To memorialize our agreement, the following language was incorporated in (d)(6) of Rule 1171: “The technology assessment shall include a study of the effect of total mass emissions of VOC from the use of cleaning solvents.”

Little did we know that this language would redirect the focus of the study? Perhaps the fault was ours. In the end, to make the long story short, the study did not evaluate the “relationship between vapor pressure and emission rates.”

In e-mail correspondence with Dr. Chung Liu July 30, 2003, regarding the study, he conceded the following: “However, the AQMD study as conducted does provide data to evaluate both. It is the belief of the AQMD that while the emissions rate may vary as a function of time, the mass emissions over time do not.” Dr. Liu’s further states: “Low vapor pressure solvents do have lower mass emission rates.” Exactly! That’s what we have been saying.
Dr. Kevin J. Williams  
Program Coordinator  
May 7, 2008  
Page 8  

U.S. EPA recognizes this fact and supports the use of low vapor cleanup solvents as a way to reduce emissions in the printing industry. See, for example, the following U.S. EPA documents: Control of Volatile Organic Compounds Emissions from Offset Lithographic Printing (September 1993); Alternative Control Techniques Document: Offset Lithographic Printing (1994), and the recently released Technical Support Document (TSD) for Title V Permitting of Printing Facilities (January 2005.). In the Title V document it says:

As a means to reduce VOC emissions from printing facilities, alternative cleaning solvent products have been formulated. The distinguishing characteristic of many of these alternative products is low vapor pressure. We encourage the use of these low vapor pressure products to reduce emissions at the source. We first became aware of low vapor pressure cleaning materials in the context of lithographic printing, and provided a 50 percent retention factor for certain uses of low vapor pressure cleaning materials. Low vapor pressure cleaning materials are now being used by other types of printers. (p. 61)

It’s mind boggling that SCAQMD didn’t follow EPA guideline. The results of looking at just VOC content may likely result in higher consumption of materials and, consequently, the creating of greater waste streams.

I have included a letter to Ms. Lee Lockie, Program Manager, SCAQMD on this issue as Exhibit K.

Thank you in advance for the consideration you may give my requests.

Sincerely,

G. M. Bonetto, Ph.D.  
VP Government Affairs

000302
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<td><strong>High VOC Solvent</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SB Sun</td>
<td>Pressroom Solutions</td>
<td>Blanket/Roller Wash</td>
<td>6.5 lbs/gal (773 g/l)</td>
</tr>
<tr>
<td>J.S. Poluch</td>
<td>Allied Photo Offset</td>
<td>Allied Hydrowash</td>
<td>5.82 lbs/gal</td>
</tr>
<tr>
<td>PIP Printing</td>
<td>A.G. Layne, Inc.</td>
<td>Low VOC Blanket</td>
<td>1.6 lbs/gal</td>
</tr>
<tr>
<td>Press Link</td>
<td>IC Compound</td>
<td>IC All Pro</td>
<td>6.6 lbs/gal</td>
</tr>
<tr>
<td>Litho-Chem</td>
<td>1700</td>
<td>5.5 lbs/gal (663 g/l)</td>
<td>(roller)</td>
</tr>
<tr>
<td>Litho-Chem</td>
<td>AQ 1301</td>
<td>4.7 lbs/gal (554 g/l)</td>
<td>(roller wash-step one)</td>
</tr>
<tr>
<td>Litho-Chem</td>
<td>AQ 1302</td>
<td>6.6 lbs/gal (792 g/l)</td>
<td>(roller wash-step two)</td>
</tr>
<tr>
<td>R.R. Donnelley</td>
<td>Anchor</td>
<td>EnviroWash 220</td>
<td>2.2 lbs/gal</td>
</tr>
<tr>
<td>Castle Press</td>
<td>A.G. Layne, Inc.</td>
<td>Shell Mineral Sprits</td>
<td>6.6 lbs/gal</td>
</tr>
<tr>
<td>Print 2000</td>
<td>Printers' Service</td>
<td>Powerklene VC</td>
<td>6.6 lbs/gal</td>
</tr>
<tr>
<td>The Dot Printer</td>
<td>Printers' Service</td>
<td>Autowash 6000</td>
<td>5.45 lbs/gal</td>
</tr>
<tr>
<td>Lithographix</td>
<td>Printers' Service</td>
<td>Superkleene 1 IC</td>
<td>5.40 lbs/gal</td>
</tr>
<tr>
<td>Anderson Litho</td>
<td>Printers' Service</td>
<td>Superkleene 2 R</td>
<td>6.65 lbs/gal</td>
</tr>
<tr>
<td>Anderson Litho</td>
<td>A.G. Layne, Inc.</td>
<td>Step 2 Roller Wash</td>
<td>6.6 lbs/gal</td>
</tr>
<tr>
<td>Tedco</td>
<td>Day International</td>
<td>Blanket Wash</td>
<td>6.6 lbs/gal</td>
</tr>
<tr>
<td>Huhtamaki</td>
<td>Tower Products</td>
<td>396 UV Wash</td>
<td>795 lbs/gal (900 g/l)</td>
</tr>
<tr>
<td></td>
<td>Anchor</td>
<td>EnviroWash 220</td>
<td>2.2 lbs/gal</td>
</tr>
<tr>
<td></td>
<td>Varn Products</td>
<td>CP 580 Hybrid Wash</td>
<td>7.39 lbs/gal</td>
</tr>
<tr>
<td></td>
<td>Litho-Chem</td>
<td>UV Roller Wash</td>
<td>6.7 lbs/gal (799 g/l)</td>
</tr>
<tr>
<td></td>
<td>Printers' Service</td>
<td>Wash EB</td>
<td>7.35 lbs/gal</td>
</tr>
<tr>
<td><strong>Low VOC Solvent</strong></td>
<td>Super Clean Corp.</td>
<td>Super Clean BW</td>
<td>3.65 lbs/gal (485 g/l)</td>
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<tr>
<td>Los Angeles Times</td>
<td>Magnaflux</td>
<td>Daraclean 236</td>
<td>less than 1%</td>
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<tr>
<td>Siebert</td>
<td>ES-219</td>
<td>Pressroom Cleaner</td>
<td>(fatty acid methyl esters)</td>
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<tr>
<td>Mirachem</td>
<td>AG Environmental</td>
<td>Soy Gold 1000</td>
<td></td>
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<td>Soy Gold 2000</td>
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<tr>
<td>J.S. Poluch</td>
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<td>Soy Gold 2000</td>
<td></td>
</tr>
<tr>
<td>PIP Printing</td>
<td>AG Environmental</td>
<td>Soy Gold 2000</td>
<td></td>
</tr>
<tr>
<td>Press Link</td>
<td>AG Environmental</td>
<td>Soy Gold 2000</td>
<td></td>
</tr>
<tr>
<td>R.R. Donnelley</td>
<td>AG Environmental</td>
<td>Soy Gold 2000</td>
<td></td>
</tr>
<tr>
<td>City of Santa Monica</td>
<td>AG Environmental</td>
<td>Soy Gold 2000</td>
<td></td>
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<td>Low VOC Solvent (continued)</td>
<td>Vertis</td>
<td>AG Environmental</td>
<td>Soy Gold 2000</td>
</tr>
<tr>
<td>------------------------------</td>
<td>-----------------</td>
<td>------------------</td>
<td>--------------</td>
</tr>
<tr>
<td>R.R. Donnelley</td>
<td>AG Environmental</td>
<td>Soy Gold 2000</td>
<td></td>
</tr>
<tr>
<td>Nelson Nameplate</td>
<td>JT Baker</td>
<td>Low VOC - Acetone</td>
<td></td>
</tr>
<tr>
<td>SCAQMD Print Shop</td>
<td>JT Baker</td>
<td>Low VOC - Acetone</td>
<td></td>
</tr>
<tr>
<td>Castle Press</td>
<td>JT Baker</td>
<td>Low VOC - Acetone</td>
<td></td>
</tr>
<tr>
<td>Print 2000</td>
<td>JT Baker</td>
<td>Low VOC - Acetone</td>
<td></td>
</tr>
<tr>
<td>Western Metal Décorating</td>
<td>JT Baker</td>
<td>Low VOC - Acetone</td>
<td></td>
</tr>
<tr>
<td>The Dot Printer</td>
<td>JT Baker</td>
<td>Low VOC - Acetone</td>
<td></td>
</tr>
<tr>
<td>Lithographix</td>
<td>JT Baker</td>
<td>Low VOC - Acetone</td>
<td></td>
</tr>
<tr>
<td>The Printery</td>
<td>JT Baker</td>
<td>Low VOC - Acetone</td>
<td></td>
</tr>
<tr>
<td>Tedco</td>
<td>JT Baker</td>
<td>Low VOC - Acetone</td>
<td></td>
</tr>
<tr>
<td>Oberthur Card System</td>
<td>JT Baker</td>
<td>Low VOC - Acetone</td>
<td></td>
</tr>
<tr>
<td>Huhtamaki</td>
<td>JT Baker</td>
<td>Low VOC - Acetone</td>
<td></td>
</tr>
<tr>
<td>Nelson Nameplate</td>
<td>Rho-Corporation</td>
<td>Rhosolv-7248</td>
<td></td>
</tr>
<tr>
<td>Several Facilities</td>
<td>Rho-Corporation</td>
<td>Rhosolv-7248</td>
<td></td>
</tr>
<tr>
<td>SCAQMD Print Shop</td>
<td>Rho-Corporation</td>
<td>Rho-Wash 100</td>
<td>98 g/l</td>
</tr>
</tbody>
</table>

| Acetone-Mineral Spirits      |
| Acetone-Mineral Spirits      |
| (metering roller cleaner)    |
| Acetone/Mineral Spirits/1,2,4|
| Trimethylbenzene             |
| (fatty acid methyl esters)   |

<table>
<thead>
<tr>
<th>000500</th>
<th>AG Environmental</th>
<th>Soy Gold 2500</th>
</tr>
</thead>
<tbody>
<tr>
<td>000500 Western Metal Decorating</td>
<td>AG Environmental</td>
<td>Soy Gold 2500</td>
</tr>
<tr>
<td>000500 The Printery</td>
<td>AG Environmental</td>
<td>Soy Gold 2500</td>
</tr>
<tr>
<td>000500 Tedco</td>
<td>AG Environmental</td>
<td>Soy Gold 2500</td>
</tr>
<tr>
<td>000500 Castle Press</td>
<td>Siebert</td>
<td>Magic Wash 522C</td>
</tr>
<tr>
<td>000500 Dot Printer</td>
<td>Siebert</td>
<td>Magic Wash 522C</td>
</tr>
<tr>
<td>000500 Lithographix</td>
<td>Seibert</td>
<td>Magic UV</td>
</tr>
<tr>
<td>000500 Tedco</td>
<td>Seibert</td>
<td>Magic UV</td>
</tr>
<tr>
<td>000500 Oberthur Card Systems</td>
<td>Seibert</td>
<td>Magic UV</td>
</tr>
<tr>
<td>000500 Huhtamaki</td>
<td>Seibert</td>
<td>Magic UV</td>
</tr>
<tr>
<td>000500 Anderson Litho</td>
<td>Benco Sales</td>
<td>Dipropylene Glycol Monomethyl Ether</td>
</tr>
<tr>
<td>000500 Oberthur Card Systems</td>
<td>Benco Sales</td>
<td>Dipropylene Glycol Monomethyl Ether</td>
</tr>
<tr>
<td>000500 Anderson Litho</td>
<td>Eastman</td>
<td>EEP Solvent</td>
</tr>
<tr>
<td>000500 The Printery</td>
<td>Rho-Corporation</td>
<td>Rhosolv 7150 Blanket Wash 114.4 g/l</td>
</tr>
<tr>
<td>000500 Tedco</td>
<td>Van Water &amp; Roger</td>
<td>6.6 lbs/gal</td>
</tr>
</tbody>
</table>

(acetone, diethylene glycol ether (hand clean))
(isopropyl alcohol)
<table>
<thead>
<tr>
<th>Company</th>
<th>Press</th>
<th>Ink</th>
<th>Application</th>
<th>Products (Very General)</th>
<th>Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bert-Co Industries</td>
<td>Man Roland 44&quot;x 63&quot;</td>
<td>conventional</td>
<td>blankets</td>
<td>publications/direct mail</td>
<td>oil residue/blinding of the plates</td>
</tr>
<tr>
<td>Bert-Co Industries</td>
<td>5/c</td>
<td>uv</td>
<td>blankets</td>
<td>publications/direct mail</td>
<td>too oily, harmed screens</td>
</tr>
<tr>
<td>Best Label</td>
<td>Gallus R160</td>
<td>uv</td>
<td>rollers</td>
<td>labels</td>
<td>too oily</td>
</tr>
<tr>
<td>Best Label</td>
<td>Gallus R160</td>
<td>uv</td>
<td>rollers</td>
<td>labels</td>
<td></td>
</tr>
<tr>
<td>Castle Press</td>
<td>Heidelberg 6/40&quot;</td>
<td>conventional</td>
<td>rollers/blankets</td>
<td>catalogues/direct mail</td>
<td>too slow; too oily</td>
</tr>
<tr>
<td>Crown Printers</td>
<td>Kamori 6/40&quot;</td>
<td>conventional</td>
<td>rollers/blankets</td>
<td>flyers/catalogues/direct mail</td>
<td>oil residue/blinding plates</td>
</tr>
<tr>
<td>Delta Printing Solutions</td>
<td>Heidelberg 6/40&quot;</td>
<td>conventional</td>
<td>rollers/blankets</td>
<td>catalogues/direct mail</td>
<td>oily rollers; sensitized plates</td>
</tr>
<tr>
<td>Doyle &amp; Sons</td>
<td>Akiyama 6/40&quot;</td>
<td>conventional</td>
<td>rollers/blankets</td>
<td>flyers/direct mail/newsletters</td>
<td>oily residue left on rollers</td>
</tr>
<tr>
<td>Green's Inc.</td>
<td>Heidelberg 5/40&quot;</td>
<td>conventional</td>
<td>blankets</td>
<td>flyers/direct mail/newsletters</td>
<td>oily-more waste to get to color</td>
</tr>
<tr>
<td>Lester Litho</td>
<td>Miller 6/28&quot;x40&quot;</td>
<td>conventional</td>
<td>rollers</td>
<td>flyers/direct mail/newsletters</td>
<td>oily residue left on rollers</td>
</tr>
<tr>
<td>Trend Offset</td>
<td>Man Roland Web</td>
<td>conventional</td>
<td>rollers/blankets</td>
<td>newspaper inserts</td>
<td>seemed to work fine; web pick off any oily residue</td>
</tr>
</tbody>
</table>

Conclusion: All the printers except Trend Offset (non-heatset web-newsprint) stated that the solvent immediately left a residue on the rollers. Almost all of them believed it was the soy oil. The soy oil on the rollers appears to hold the surfactant (and fountain solution) on the rollers that carries over from job to job. It would appear that the surfactant package might be too aggressive (strong). The cleanup solvent also had a deleterious effect on the blankets—blinding the plates (they hold the image). Again it's probably because of the surfactants in the formulation.
DRAFT PROGRAM PLAN

Introduction

Objective. The objective of this project will be to qualify by January 1, 2008, at least three low-VOC solvents for use in cleaning the rollers and blankets of lithographic printing presses.

Scope. The focus of this project will be to foster the development of low-VOC solvents by industry manufacturers and supervise the selection and testing of these solvents by lithographic printing companies. Based on experience with low VOC solvents to date, it is expected that it may be necessary to improve not only (1) the solvents that have been tried to date, but also (2) the existing equipment and procedures used to deliver and apply the solvents during the cleaning process.

In order to employ our resources most effectively, however, the scope of the work to be carried out under this plan will be concentrated in two ways. First, the printers to be used as test sites will be selected from a single segment of the industry that accounts for a significant fraction of the total amount of solvent consumed by all lithographic printers. Second, the task of developing whatever equipment improvements are necessary will be limited to identifying and publicizing those needs, with the expectation that the equipment manufacturers will do the actual development.

Project Plan

The project will involve at least six tasks that will be carried out more or less in sequence. The following paragraphs provide a brief description of each task, with more detailed descriptions to be provided as work progresses. The corresponding timeline for each task listed below is depicted in Figure 1 on page 3.

Task 1. Identify Industry Segment. Data on lithographic printers, including SCAQMD emission inventory records, will be analyzed to determine what lithographic segment accounts for the most significant fraction of total VOC emissions. A report will be issued profiling this segment. The report will also define a typical printer for this group, and present statistics on the solvent usage of this printer. Copies of the report will be sent to a dozen PIA members who are judged to be members of the defined segment, with a request for comments. These comments will help us authenticate the cleanup practices and requirements of a typical printer.

Task 2. Establish Solvent Performance Specifications. The purpose of this task will be to draft a set of target cleanup specifications for the low-VOC solvents. To accomplish this, a small group of representative members of the selected industry segment will be invited to a meeting to discuss solvent problems and performance requirements. Aside from the low-VOC limit of 100 grams/liter, these specifications will include an acceptable cost target and performance targets such as productivity and print quality requirements. A
report will be issued on these specifications, and it will include a description of our understanding of the specific problems experienced with the low-VOC solvents to date. Copies of this report will be sent to known solvent manufacturers with a call for new or reformulated solvents to meet the requirements set forth in the specifications. This call will also request the name of a person who can be contacted to discuss their recommendations regarding test conditions to be included in the protocols to be developed in Task 3.

**Task 3. Draft Test Protocols.** As presently envisioned, candidate solvents will be first screened by subjecting them to laboratory tests. Solvents that perform satisfactorily in the laboratory will then be tested at member companies as part of daily printing operations. During this stage, protocols for both the laboratory tests and the field tests will be developed. As part of this work, solvent manufacturers will be surveyed to determine what test conditions are necessary to a good test in both categories, e.g., should rollers be preconditioned in a certain manner prior to the test. These protocols will be treated as drafts because we have not yet been able to firmly establish a correlation between laboratory test results and successful performance in the field.

**Task 4. Verify Test Protocol.** The first few candidate solvents selected for testing, as obtained following the draft test proposals, will also be used to verify the correspondence of laboratory test results to field performance. For this reason, the initial testing of solvents will involve some trial and error involving redrafting of the test protocols and/or retesting.

**Task 5. Qualify at Least Three Solvents.** Following verification of the test protocols, testing of solvents will be continued until solvents from at least three different manufacturers have been identified. Once the solvents are identified, we will make our results known to the industry and urge printers in this major segment to begin making conversion to these low-VOC solvents.

**Task 6. Application to Other Lithographic Segments.** Those low-VOC solvents that are identified as acceptable for cleanup for the most prominent segment of lithographic printing will then be reviewed for their applicability to other segments. We will ask printers in these other segments to test the solvents and evaluate them for their particular process.
Meetings and Testing

PIA will interact with the following groups to foster a viable project:

(1) Manufacturers and Formulators. We will hold one general meeting and individual meetings on a quarterly basis to assess the progress each vendor has made. In meeting individually with vendors, we believe vendors and formulators will be more willing to share their progress—and test results—than in a group meeting.

(2) SCAQMD Staff. We will meet with staff at the end of each phase of the project. Since Phase V runs an additional 6 months from the end of Phase IV, we will meet with staff at the end of the 12 and 15 months since this is a critical phase of the project—on-press testing of alternative low-VOC solvents.

(3) SCAQMD Staff. We will invite district staff to view the field testing of alternative low-VOC solvents.

(4) ChemPoint Formulations. In Phase V testing, we will include Soy Gold and other soy-based formulations that may be viable low-VOC cleanup solvents for roller and blanket cleaning.
Notes on Program Requirements

In order for this proposed program to succeed, two different types of resources will be required: laboratory test facilities and printing companies that are willing to test solvents. The major problem in obtaining access to a laboratory is funds. Printers will probably require a different type of incentive. That is, it is anticipated that printers will be reluctant to test VOC solvents at or under 100 g/l given the press contamination problems already experienced with such solvents. One way to overcome this reluctance would be to have an agreement with the SCAQMD that would allow a selected test site to use a high VOC solvent to clean a contaminated press. Thus, as part of an agreement to test, a printer must be allowed to use a high VOC solvent under the condition that he only use the solvent to reverse an adverse affect that a test solvent may have on his equipment, provided he first notify SCAQMD of his need to do so, by e-mail to a designated person at the SCAQMD.

Another printer inducement would be the willingness of roller manufacturers to contribute small roller samples to be used by test laboratories in their screening of low-VOC solvents. This will give the printer some reassurance that the test solvents have been screened for any deleterious effect it may have on rollers and blankets. Finally, if, during the development of the test protocols, a costly test condition is identified, such as the refurbishment of rollers, or the installation of new ones, some additional funding may be required.

PIC will explore the feasibility of reimbursing lithographic printers for testing. The compensation would be a set predetermined fixed sum for all the initial testing of a low-VOC solvent. If the solvent performs well and the printer is willing to continue testing, the printer will then do so without compensation.

In order to help PIA offset some of the cost for purchasing press time, we request that the SCAQMD make a grant to the association of $25,000.
RESUME OF JOHN MacPHEE

Personal Data

Born: March 12, 1928 in Port Chester, NY
Married, with three grown children
Home: 6 Nylked Terrace, Rowayton, CT

Education

Columbia University: graduated in 1983 with Master’s Degree in Business policy.

Oak Ridge School Of Reactor Technology: completed 12-month course in 1954, equivalent to Master’s Degree in Nuclear Engineering.

Rensselaer Polytechnic Institute: graduated in 1952 with BEE Degree.

Univ. Conn./Polytechnic Inst. Of NY: completed six graduate courses in materials science and feedback systems theory.

Short Courses: completed sixteen short courses, including two each on surface chemistry and mini/micro computers.


Honors and Awards

Presented with Pioneer of the Year Award by PIA of Southern California in 2003
Won First Prize for best paper at 45th NAPIM Annual Technical Conference, 2001
Presented with NAPL Craftsman Award, 1989
Presented with TAGA Honors Award, 1986
Elected to Beta Gamma Sigma, honorary business society, 1983
Awarded Harold W. Gegenheimer Technical Achievement Award in 1983 and 1988
Elected President of TAGA, 1983 (Technical Association of the Graphic Arts)
Voted Employee of the Year, AMF Atomics, 1960
Received Professional Engineer’s License (NY), 1957
Elected to Tau Beta Pi, honorary engineering society, 1952
Elected Eta Kappa Nu, honorary electrical engineering society, 1952
Awarded Rensselaer Medal for Math, 1945

Patents

Over 100 patents on twenty inventions, as listed on attached sheet. Majority of these inventions are of products for the graphic arts field.

Publications

Work Experience

1972 to present: Baldwin Technology Company, Inc., Shelton CT. From 1972-82 was Vice President of Engineering for the Stamford division, responsible for product engineering and product development. In 1982, was promoted to Vice President of Research and Technology for the corporation where he was concerned with product development and long range planning on a worldwide basis. Semi-retired in 1998 with title of Senior Scientist.

1967-1972: AMF Thermatool, New Rochelle, NY. Hired as Chief Engineer for Versatran line of industrial robots. In 1969 was promoted to Vice President of Engineering, responsible for both Versatran and the Thermatool product line of radio frequency welding generators and mechanical handling equipment for new welding processes.


1955-1966: AMF Atomics, Greenwich, CT. Hired as nuclear engineer. After several promotions, was made Manager, Nuclear Systems Department. Responsible for work on variety of projects involving the design, developmental testing, and construction of nuclear reactors and associated systems.


1949-1952: General Electric Company, Schenectady, NY. Co-op student employed as test engineer for three different divisions.


Activities in Societies and Industry Organizations

PIA Web Offset Section: Member of Supplier’s Advisory Board; Chairman, 1987–8.
TAGA: Member, and President from 1984 to 1985.
ASME: Life Member.
IEEE: Life Member.
American Nuclear Society: Charter Member.

August 17, 2001
Updated on February 20, 2004
Chronological Listing of Some Technical Publications
Written By John MacPhee


JMP661
2/22/04
9/27/04

000315
INVENTIONS OF JOHN MacPHEE

19. "Nuclear Reactor Fuel Bundle", patented February 6, 1968 in the U.S. (3,687,840). Also in Italy, Argentina, Australia, Belgium, Canada, France, Germany, Great Britain, Japan and Switzerland.

8/17/01

JMP526

000316
PIASC's Understanding of the Problems Stemming From the Use of Low VOC Solvents on Lithographic Printing Presses

By
John MacPhee

JMacPhee@UNO.com Not for publication

Scope of Presentation

1. Describe the four most prominent problems and explain why they occur.
2. Identify possible remedies.
3. Discuss impact of the remedies on pressroom activities.

Two ways in which solvents can be absorbed by rubber

Caustive action

Results

Some of the absorbed solvent remains unoxidized and is released to the environment as being reasonably absorbed.

Consequences

When exposed to oxidizing environments the unoxidized material may slowly decompose.


000317
The different absorption of high and low VOC solvents by a compound used in sheetfed press rollers

<table>
<thead>
<tr>
<th>Type of solvent</th>
<th>After mixing 24 hours</th>
<th>After mixing 24 hours at 23°F</th>
<th>Volume solvent reduced with rubber</th>
<th>Volume solvent released by rubber</th>
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</thead>
<tbody>
<tr>
<td>High VOC</td>
<td>+32.4%</td>
<td>-8</td>
<td>+14</td>
<td>32.4%</td>
</tr>
<tr>
<td>Low VOC*</td>
<td>+19.4%</td>
<td>-5</td>
<td>+11.3%</td>
<td>11.3%</td>
</tr>
</tbody>
</table>

* Soy Gold

Data provided by Rotodynamic

Problem #1, Description

Some solvent is reversibly absorbed by rubber rollers during wadups and subsequently released to ink during make-ready. The released solvent does not evaporate and therefore contaminates the ink, producing the following printing problems:

1. Toning
2. Reduced water pickup by ink
3. Color variations
4. Increased ink drying time
5. Ink misting

Effect on ink tack of contamination by solvent released from rubber roller as measured on an inkometer type instrument
Effect on drying time of contamination from solvent released by rubber roller

![Graph showing the effect of ink contamination on drying time.](image)

Effect of ink contamination on the water pickup by ink as measured on a Litho Break Tester

![Graph showing water pickup by ink.](image)

Data provided by INX

Problem #1, Possible Remedies and Their Impacts

1. Use special rinses/solvent in one or more extra washups to remove low VOC solvent absorbed by rollers. When feasible, this has had a significant impact on productivity.
Problem #1, Possible Remedies and Their Impacts

1. Use special rinses/solvent in one or more extra washups to remove low VOC solvent absorbed by rollers. When feasible, this has had a significant impact on productivity.

2. Develop a rubber that is impervious to solvent. If feasible, this would require years to accomplish.
Problem #2, Description

Some low VOC Solvent is irreversibly absorbed by rubber rollers during washups because it chemically reacts with the rubber. As a result of the chemical bonding, the roller swells and hardens non-uniformly, producing the following problems:

1. Inability to maintain uniform roller stripes, leading to printing problems.
2. Excessive roller heating and premature roller failure in local spots (like roller ends).

Problem #2, Possible Remedies and Their Impacts

1. Develop a rubber that is impervious to low VOC solvents. If feasible, this would require years to accomplish.

2. Develop a low VOC solvent that is not absorbed by rubber. If feasible, this would require years to accomplish.

Problem #3, Description

Some automatic wash-up systems produce fugitive solvent that builds up on press components, resulting in drips that cast:

1. Fall on rollers or paper causing print defects, reject of job, or loss of customer.
2. Fall and collect on walk-ways, creating a safety hazard.
Efficiency of One Type of Automatic Blanket Cleaning System

**Efficiency** = \( \frac{\text{Required volume of solvent}}{\text{Total volume of solvent used}} \)

<table>
<thead>
<tr>
<th>Type of Cleaner</th>
<th>Type of Solvent</th>
<th>Volume solvent used*</th>
<th>Efficiency of system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cloth, presoaked</td>
<td>Low VOC</td>
<td>5 cc (0.2 oz)</td>
<td>100 %</td>
</tr>
<tr>
<td>Cloth, spray</td>
<td>Low VOC</td>
<td>66 cc (2.2 oz)</td>
<td>7.6 %</td>
</tr>
<tr>
<td>Cloth, spray</td>
<td>High VOC</td>
<td>90 cc (6.0 oz)</td>
<td>5.6 %</td>
</tr>
</tbody>
</table>

* One 40 inch shooed blanket cylinder

Problem #3, Possible Remedies and Their Impacts

1. Upgrade or replace offending automatic system. While effective, this remedy can be very expensive.

2. Follow automatic wash with hand wipes of areas where solvent is known to build up. While also effective, this remedy reduces press productivity.

Performance data, typical 40 inch press

<table>
<thead>
<tr>
<th>Process step</th>
<th>Hours per week</th>
<th>Hours per month</th>
</tr>
</thead>
<tbody>
<tr>
<td>Press down</td>
<td>4</td>
<td>16</td>
</tr>
<tr>
<td>Press up</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>Trim</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>Oiler</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>Lint catcher</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>Inspect</td>
<td>1</td>
<td>4</td>
</tr>
</tbody>
</table>

* Does not include time and maintenance, which is exponentially.
Corresponding productivity data

<table>
<thead>
<tr>
<th>Source: Productivity Calculated by FHA</th>
<th>New grant vol solvent 500</th>
<th>New grant vol solvent 1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>13. Total number of jobs run per year</td>
<td>1210</td>
<td>1635</td>
</tr>
<tr>
<td>14. Number one-sided jobs run per year</td>
<td>462</td>
<td>600</td>
</tr>
<tr>
<td>15. Number two-sided jobs run per year</td>
<td>1577</td>
<td>1936</td>
</tr>
<tr>
<td>16. Productive hours per year</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) Doing undercuts</td>
<td>3170</td>
<td>1941</td>
</tr>
<tr>
<td>(b) Printing</td>
<td>1320</td>
<td>1192</td>
</tr>
<tr>
<td>(c) Total productive hours</td>
<td>3448</td>
<td>3123</td>
</tr>
<tr>
<td>17. Non-productive hours per year</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) Washing blankets</td>
<td>110</td>
<td>412</td>
</tr>
<tr>
<td>(b) Washing rotogravure fountains</td>
<td>98</td>
<td>140</td>
</tr>
<tr>
<td>(c) Washing back cylinders</td>
<td>80</td>
<td>136</td>
</tr>
<tr>
<td>(d) Total non-productive hours</td>
<td>372</td>
<td>702</td>
</tr>
</tbody>
</table>

Problem 4, Description

Rags employed to soak up ink and solvent during washups of inking rollers and fountains retain low VOC solvents because they do not evaporate. Because most low VOC solvents contain drying oils, this increases the probability of fires caused by spontaneous combustion.

Conditions Necessary for Spontaneous Combustion

- A source of oxygen
- A material with a low burning temperature
- A material that evolves a heat source

Probability of spontaneous combustion = Probability of spontaneous combustion
Problem #4, Possible Remedies and Their Impacts

Enforce use of existing equipment and procedures for storing used tags to prevent spontaneous combustion. This remedy should not have a significant impact on pressroom activities.
Although it is know that the principal behind lithographic printing is that oil and water don’t mix at all, in reality lithographic inks must be formulated to absorb or pick up some water. Totally water repellant inks do not work well in lithographic printing. Nor can inks printing on a surface wet with water, and this is the mechanism by which water keeps the non-image area of the offset plate clean. However, if the image area becomes wet with water, then the ink will fail to adhere to the image. This problem is called gum blinding. The image can be seen on the plate, but the plate does not printing the image onto the substrate.

Lithographic printing thus requires tackier inks than do other printing processes to avoid excessive emulsification of the ink by the fountain solution (water and etch), and to print sharp half-tone images. The tack of the ink should not exceed the surface strength of the paper, or picking, splitting, and tearing of the paper will occur.

TACKMASTER ILLUSTRATION (four rollers: bottom roller—distribution roller; behind the bottom—distribution roller there another roller; cooper roller—takes in from the distribution roller; third roller (takes ink from cooper roller—not used in these tests; top roller—reading roller)

1. Start out with neat ink.
2. Measure the tack of neat ink—1½ minutes to evenly distribute the ink.
3. Introduce water and etch so that the ink doesn’t dry up, to attain optimum task (small beads of water on ink)—roughly 2 minutes.
4. Stop introducing water and etch. This determines if ink comes back to original tack.
5. Stop the machine and clean the rollers with predetermined cleanup solvent.
6. Repeat the process beginning with Step 1 above. If tack reading drops means some contamination. Consistent tack reading at the beginning is important. Look at the tack reading and bottom line (which is spikes show that the ink is not be transferred from the distribution roller to the cooper roller to the reading roller).
Bottcher BIO-3

Wash – 1 through 3 rinsed with Aqualux
Wash – 4 & 5 rinsed with water and 20% vinegar
Wash – 6 & 7 rinsed with 100 vinegar
Minimum | Maximum | Average | Std Dev | Slope | @Max | Total | File
11.4    | 12.6    | 11.6    | 0.3     | -0.0  | 0.33 | 12.07 | a4616 wash bio 3 Ving
Bottcher BIO-3  6082811-02 (Liquid)

*** DEFAULT GENERAL METHOD ***

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Result</th>
<th>Units</th>
<th>Reporting Dilution Limit</th>
<th>Factor</th>
<th>Method</th>
<th>Batch Number</th>
<th>Date Prepared</th>
<th>Date Analyzed</th>
<th>Data Qualifiers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density by ASTM D1475</td>
<td>0.8575</td>
<td>g/ml</td>
<td>1</td>
<td></td>
<td>EPA 24</td>
<td>W6H1204</td>
<td>08/29/06</td>
<td>08/29/06 sm</td>
<td>O-09</td>
</tr>
<tr>
<td>Total VOC</td>
<td>246</td>
<td>g/L</td>
<td>1.00</td>
<td>1</td>
<td>EPA 24</td>
<td>W6H1204</td>
<td>08/29/06</td>
<td>08/29/06 sm</td>
<td>O-09</td>
</tr>
<tr>
<td>VOC less Water</td>
<td>246</td>
<td>g/L</td>
<td>1.00</td>
<td>1</td>
<td>EPA 24</td>
<td>W6H1204</td>
<td>08/29/06</td>
<td>08/29/06 sm</td>
<td>O-09</td>
</tr>
<tr>
<td>Volatile Content by ASTM D2369</td>
<td>28.7</td>
<td>%w/w</td>
<td>1.00</td>
<td>1</td>
<td>EPA 24</td>
<td>W6H1204</td>
<td>08/29/06</td>
<td>08/29/06 sm</td>
<td>O-09</td>
</tr>
</tbody>
</table>

Conventional Chemistry/Physical Parameters by APHA/EPA/ASTM Methods

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Result</th>
<th>Units</th>
<th>Reporting Dilution Limit</th>
<th>Factor</th>
<th>Method</th>
<th>Batch Number</th>
<th>Date Prepared</th>
<th>Date Analyzed</th>
<th>Data Qualifiers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Content by GC</td>
<td>ND</td>
<td>%w/w</td>
<td>1.00</td>
<td>1</td>
<td>EPA 24</td>
<td>W6H1204</td>
<td>08/29/06</td>
<td>08/29/06 sm</td>
<td>O-09</td>
</tr>
</tbody>
</table>
1.) **Identification of the substance/preparation and company**

**Product details**

**Trade name**

_Böttcherin Aqualux_

**Use**

auxiliary for press clean-up

**Identification of the manufacturer / supplier**

**Address**

Felix Böttcher GmbH & Co. KG
Stolberger Str. 351-353
D-50933 Köln

**Telephone no.** +49 (0) 221 4907-1

**Fax no.** +49 (0) 221 4907-444

**Emergency telephone number**

+49 (0)221 / 4907-1

2.) **Composition / information on ingredients**

**Chemical characterization**

Aqueous solution of non-ionic surface-active agents and corrosion inhibitors

**Hazardous ingredients**

CAPRYL/CAPRILYL GLUCOSIDE

<table>
<thead>
<tr>
<th>EC no.</th>
<th>Index no.</th>
<th>CAS no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>1</td>
<td>161074-97-1</td>
</tr>
</tbody>
</table>

**Concentration** > 1 < 5 %-b.w.

**Classification** Xi; R41

**Hazard symbols** Xi

**R phrases** 41

**Other information (chapter 2.)**

The product does not require a hazard warning label in accordance with EC Directive 1999/45.

3.) **Hazards identification**

**Hazard symbols**

NONE

**R phrases**

NONE

4.) **First aid measures**

**General information**

In case of persisting adverse effects consult a physician. Remove contaminated clothing and shoes immediately, and launder thoroughly before reusing.

**After skin contact**

In case of contact with skin wash off immediately with copious amounts of water.

**After eye contact**

Separate eyelids, wash the eyes thoroughly with water (15 min.).

**After ingestion**

Do not induce vomiting. Seek medical advice.

5.) **Fire-fighting measures**

**Suitable extinguishing media**

Product itself is non-combustible; adapt fire extinguishing measures to surrounding areas.

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000336
6.) **Accidental release measures**

**Personal precautions**
- Refer to protective measures listed in sections 7 and 8. Ensure adequate ventilation.

**Environmental precautions**
- Do not discharge into the drains/surface waters/groundwater.

**Methods for cleaning up/taking up**
- Pick up with absorbent material (e.g., sand, sawdust, general-purpose binder). Send in suitable containers for recovery or disposal.

7.) **Handling and storage**

**Handling**
- **Advice on safe handling**
  - Ensure adequate ventilation.
- **Advice on protection against fire and explosion**
  - No special measures necessary.

**Storage**
- **Requirements for storage rooms and vessels**
  - Containers which are opened must be carefully resealed and kept upright to prevent leakage. Always keep in containers of same material as the original one.
- **Advice on storage assembly**
  - None known
- **Further information on storage conditions**
  - Keep container tightly closed in a cool, well-ventilated place.

8.) **Exposure controls / personal protection**

**Exposure limit values**
- **NONE**

**Personal protective equipment**

**Respiratory protection**
- If workplace exposure limits are exceeded, a respirations protection approved for this particular job must be worn. In case of aerosol and mist formation, take appropriate measures for breathing protection in the event workplace threshold values are not specified. Short term: filter apparatus, Filter A/P

**Hand protection**
- Sufficient protection is given wearing suitable protective gloves checked according to e.g. EN 374, in the event of risk of skin contact with the product. Before use, the protective glove should be tested in any case for its specific work-station suitability (i.e. mechanical resistance, product compatibility and antistatic properties). Adhere to the manufacturer's instructions and information relating to the use, storage, care and replacement of protective gloves. Protective gloves shall be replaced immediately when physically damaged or worn. Design operations thus to avoid permanent use of protective gloves.

**Eye protection**
- Safety glasses (EN 166)
Skin protection
Clothing as usual in the chemical industry.

General protective and hygiene measures
Do not eat, drink or smoke during work time. Keep away from foodstuffs and beverages. Avoid contact with eyes and skin. Remove soiled or soaked clothing immediately. Wash hands before breaks and after work.

9.) Physical and chemical properties

General information
Form liquid
Colour colourless
Odour characteristic

Important health, safety and environmental information
Changes in physical state
Type Boiling point
Value 100 °C

Flash point
Remarks not applicable

Density
Value 1,01 g/ml

Solubility in water
Remarks soluble

pH value
Value 5,0

Concentration 5 % H2O

10.) Stability and reactivity

Conditions to avoid
None known

Materials to avoid
None known

Hazardous decomposition products
No hazardous decomposition products known.

Thermal decomposition
Remarks No decomposition if used as prescribed.

11.) Toxicological information

Other information (chapter 11.)
Product specific toxicological data are not known.

12.) Ecological information

General information / ecology
Do not discharge into the drains or waters and do not store on public depositories.

13.) Disposal considerations

Product
Allocation of a waste code number, according to the European Waste Catalogue, should be carried out in agreement with the regional waste disposal company.
Packaging
Residuals must be removed from packaging and when emptied completely disposed of in accordance with the regulations for waste removal. Incompletely emptied packaging must be disposed of in the form of disposal specified by the regional disposer.

14.) Transport information
Other information (chapter 14.)
The product does not constitute a hazardous substance in national / international road, rail, sea and air transport.

15.) Regulatory information
Labelling in accordance with EC directives
The product does not require a hazard warning label in accordance with EC Directives.

Hazard symbols
- NONE
R phrases
- NONE
S phrases
- NONE

Remarks
Annex I, part 1 + 2: not mentioned. With regard to possibly appropriate decomposition products see Chapter 10.

National regulations

Other regulations, restrictions and prohibition regulations
VOC 0 %

16.) Other information
Relevant R-phrases (chapter 2): 41 Risk of serious damage to eyes.

Department issuing safety data sheet
UMCO Umwelt Consult GmbH
Georg-Wilhelm-Str. 183 b, D-21107 Hamburg
Tel.: +49 40 / 41 92 13 00 Fax: +49 40 / 41 92 13 57 e-mail: umco@umco.de

This information is based on our present state of knowledge. However, it should not constitute a guarantee for any specific product properties and shall not establish a legally valid relationship.
Soy Gold 2500 (5/03/06)

This test is on Horstmann-Steinberg inks that are cleaned with Soy Gold 2500. We received two different series of inks. The tests were conducted on the Reflex Pro Magenta.
Tack Measuring System Test Performed On Wed May 03 11:18:10 2006

Product Number: Huber Ref Pro Mag 5 3
Lot Number: Third soy 2500 5 3
File Name: 3 regpromagHS soy 2500 5 3
Project: C:\Program Files\TMS\projects\12 min washup

Kershaw Instrumentation, Inc  Tack Measuring System Version 1.02 Built On Jul 02 2003

<table>
<thead>
<tr>
<th>Minimum</th>
<th>Maximum</th>
<th>Average</th>
<th>Std Dev</th>
<th>Slope</th>
<th>@Max</th>
<th>Total</th>
<th>File</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.8</td>
<td>10.2</td>
<td>8.2</td>
<td>0.5</td>
<td>-0.1</td>
<td>0.16</td>
<td>12.07</td>
<td>3 regpromagHS soy 2500 3</td>
</tr>
</tbody>
</table>
Soy Gold 2500 (6/28-29/06)

This test is on Horstmann-Steinberg inks that are cleaned with Soy Gold 2500. We received two different series of inks. The tests were conducted on the Alpha (Black)(check sheet for misting).
Product Number: Alpha Veg Blk R LC258 800gm  Lot Number: start 2500 6/29/06
File Name: start Alpha V K blk R 2500 6 29
Project: C:\Program Files\TMS\projects\12 min black rollers
Kershev Instrumentation, Inc. Tack Measuring System Version 1.02 Built On Jul 02 2003

<table>
<thead>
<tr>
<th>Minimum</th>
<th>Maximum</th>
<th>Average</th>
<th>Std Dev</th>
<th>Slope</th>
<th>@Max</th>
<th>Total</th>
<th>File</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.6</td>
<td>21.0</td>
<td>18.2</td>
<td>1.9</td>
<td>0.5</td>
<td>12.05</td>
<td>12.07</td>
<td>start Alpha V K blk R</td>
</tr>
</tbody>
</table>
START LC258 800QM 450k
ALPHA VEL LACK H.S 6/29/06 BLACK ROLLERS
May 16, 2002

Ms. Lee Lockie

SCAQMD
21865 Copley Drive
Diamond Bar, CA 91765

Dear Ms. Lockie:

The following comments are respectfully submitted to the South Coast Air Quality Management District ("District") on behalf of the Screenprinting and Graphic Imaging Association and Printing Industries of California on the Draft Technology Assessment to Determine the Relationship of Solvent Vapor Pressure and Mass VOC Emissions. Based on a review of results and methodology, we believe that the assessment does not substantiate the removal of vapor pressure as a control technology option for solvent cleaning operations.

The methodology did not address the stated purpose of the study, nor did it adequately represent hand-cleaning operations as they occur in the printing industry. The assumptions and approach suffered from several deficiencies, the most obvious of which are as follows:

- The evaluation did not take into account the various phases of hand cleaning operations. It focused on only one factor, the evaporation of a thin film of solvent, and neglects the importance of the retention and evaporation of solvent in hand wipe towels.

- The method employed in the assessment deviated from that listed in Rule 1171. While the assessment measured total vapor pressure, Rule 1171 focuses on the composite VOC vapor pressure.

- The assumption that no water is present in cleaning solvents or that water could not be absorbed by the cleaning solvents exposure to the atmosphere can lead to erroneous results in both the vapor pressure and weight loss determinations—especially if water is present.
Ms. Lee Lockie  
May 16, 2002  
Page 2

- This assessment tested cleanup solvents at a higher temperature (100°F) than the temperature at which the solvents are actually used (75-80°F). Since vapor pressure is a function of temperature, measuring them at 100°F will result in higher vapor pressures than would be experienced at 75-80°F.

- The assessment did not include the rationale for the conditions used in the thermogravimetric analyzer or the film thickness for the cleaning solvent.

- The conditions used in the thermogravimetric analyzer violated several basic scientific principles and include the following:
  - The definition of "ambient" temperature was not provided. It was not evident if the same temperature was used for each sample or it varied.
  - The temperature at which the evaporation rate was determined was not controlled.
  - The amount of cleanup solvent tested was not consistent from sample to sample. Fluctuations up to 50 percent occurred, and such differences will have a significant influence on the observed results.
  - Samples were not exposed to the conditions in the analyzer for the same amount of time.
  - Sample size was too small to accurately measure the quickly evaporating solvent blends.

- The assessment tested a small number of cleaning solvents used in lithographic printing. Additionally, the cleaning solvents evaluated do not necessarily reflect the range of different hand cleaning solvents used (and available) for lithographic printing.

- The assessment neglected to examine cleanup solvents used in other types of printing processes. The cleaning solvents tested include two that are not used for hand cleaning operations, and four that violated one of the parameters set by the assessment itself because it included the exempt compound acetone. In considering the disqualified sample (due to water), the two automatic washes, and four with acetone, only four cleaning solvents were true hand wipe solvents and are not representative of all hand wipe cleaning solvents.

In short, the assessment did not substantiate the claim that low vapor pressure products have no effect on mass VOC emissions because it did not examine the fundamental linkage between vapor pressure and VOC emission rate. The assessment further concluded that since low vapor pressure products have high VOC contents, they then must emit high amounts of VOCs. This is erroneous.

000350
Specific comments on the evaluation are presented below on a section-by-section basis.

PURPOSE

The printing industry agrees with the premise of the draft assessment, which was to determine the relationship between VOC composite vapor pressure and mass emission rate. Specifically, the provision in amended Rule 1171 read: “The technology assessment shall include a study of the effect of vapor pressure on the total mass emissions of VOCs from the use of cleaning solvents.” The printing industry also agrees with the statement that “only emissions from wiped surfaces will be considered in this evaluation,” since the low vapor pressure solvents specified first in the 1991 version of Rule 1171 were for hand cleaning operations.

The assessment only focused on one aspect of analysis, the evaporation of solvent from a thin film. It did not address the release or lack of release from shop towels or the impact of evaporation on the quantity of solvent required for cleaning operations. Simply pouring cleaning solvents on the surface of rollers or blankets and then waiting until the solvent evaporates does not mirror the hand cleaning operations. Reusable towels or other kinds of wipers are used in hand cleaning operations. The effect of absorption of solvent into towels on the total evaporation of solvents was not considered. In addition, experience has shown that the speed of the evaporation of the cleanup solvent will affect the quantity of solvent required to clean a surface—that is, the faster the solvent evaporates, the greater the consumption of the solvent. This effect was not considered in the assessment. To truly replicate hand cleaning operations, as they occur in production settings, the methodology must focus on role and effect of the shop towel regarding solvent application and evaporation.

TEST METHODS

It is not evident why a modified ASTM D 323-99a Standard Test Method for Vapor Pressure of Petroleum Products (Reid Method) was chosen to measure the vapor pressure of the sample cleaning solvent. The method is not appropriate, as it will result in the measurement of total vapor pressure of the cleaning solvent including water and exempt compounds. It will not provide a measure of the VOC composite fraction.

Since the District assumed that no water was present in the cleaning solvents evaluated, no attempt was made to measure the water content or even ascertain if water was present in the samples (except for the rejected Prisco Superklene 11C, which was “observed to have a high non-volatile content and appearance that suggested the presence of water.”). This assumption and failure to measure the water content results in vapor pressure data
that cannot be evaluated to determine its accuracy since even a small amount of water will affect both the vapor pressure readings and weight loss due to evaporation.

It is important to understand that many of the hand wipe solvents used in the lithographic printing industry are designed to be miscible with water. Some of the components in the solvents are capable of absorbing water from the air. If procedures are not taken to either measure the amount of water in the sample or keep it from absorbing water, the results for both the vapor pressure test and weight loss will not be accurate. Since not all cleanup solvents have the same composition, there may be varying degrees of impact due to the unknown presence of water.

It is also not evident as to why the vapor pressure of the cleanup solvent samples was measured at 100°F. The vapor pressure of the samples should be measured at the same temperature that the evaporation rate will be determined. Cleanup solvents for hand cleaning operations are used at room temperature, which is approximately 68-72°F. If the purpose of the evaluation is to determine the relationship between composite VOC vapor pressure and mass emission rate under normal conditions of use, then the vapor pressure needs to be determined at those conditions.

Moreover, the use of ASTM D 323-99a is not consistent with the vapor pressure test method specified in Rule 1171. Rule 1171, both the 1991 version and the amended 1999 version, contain specific directions for both the testing and calculation of vapor pressure for compliance purposes. The determination of vapor pressure for this study should be conducted via either method as listed in Rule 1171. Rule 1171 (I)(2) states:

The identity and quantity of components in solvents shall be determined by SCAQMD Method 308 (Quantitation of Compounds by Gas Chromatography) contained in the SCAQMD "Laboratory Methods of Analysis for Enforcement Samples" manual. The VOC composite partial pressure is calculated using the equation in paragraph (b)(55).

For compliance purposes, companies providing materials for use in the District, prior to December 2001, reported the vapor pressure of a given product based on the following calculation found in Rule 1171(b)(55):
(55) VOC COMPOSITE PARTIAL PRESSURE is the sum of the partial pressures of
the compounds defined as VOCs. VOC Composite Partial Pressure is calculated as
follows:

\[ PP_c = \sum_{i=1}^{n} \left( \frac{W_i}{MW_i} \frac{(VP_i)(VP_c)}{MW_c} + \frac{W_i}{MW_i} + \sum_{i=1}^{n} \frac{W_i}{MW_i} \right) \]

Where:
- \( W_i \) = Weight of the “i”th VOC compound, in grams
- \( W_w \) = Weight of water, in grams
- \( W_e \) = Weight of exempt compound, in grams
- \( MW_i \) = Molecular weight of the “i”th VOC compound, in g/g-mole
- \( MW_w \) = Molecular weight of water, in g/g-mole
- \( MW_e \) = Molecular weight of exempt compound, in g/g-mole
- \( PP_c \) = VOC composite partial pressure at 20°C, in mm Hg
- \( VP_i \) = Vapor pressure of the “i”th VOC compound at 20°C, in mm Hg

For the District to draw sound conclusions regarding the use of low VOC composite
vapor pressure products and mass VOC emission rate, the testing methods used for
compliance purposes must be consistent with those used in this assessment. To not
utilize either Rule 1171 testing methodology or the calculation method distorts the results
because it does not allow for a direct comparison to the VOC composite vapor pressures
reported on the Material Safety Data Sheets.

In order to simulate the conditions associated with hand cleaning activities in a printing
operation, evaporation times were measured using a Dupont 951 Thermogravimetric
Analyzer. A small amount of solvent (20-30 microliters) was placed on an empty
weighing pan. The TGA was programmed to run at ambient temperature with a linear air
velocity of 0.4 cm/seconds until the sample completely dried or reach a constant weight.

There are several flaws with the conditions used to simulate the environment in which the
solvent will be exposed. The parameters chosen do not represent the conditions that
would normally be experienced in a printing environment where hand wiping will occur.

From a pure analytical aspect, the definition of “ambient” in terms of temperature needs
to be provided. Ambient temperature is generally thought of as room temperature, and,
unless a temperature is specified, the data is meaningless. It is also not clear if the same
temperature was used for each sample or if it was varied.
It was not evident that the "ambient" temperature was monitored or controlled during the evaporation rate measurement phase of the evaluation. When solvents evaporate, there is a loss of heat from the surface, thus reducing the temperature of the remaining liquid. By not controlling the temperature at which the samples were evaporated the actual temperature is not known, which will dramatically impact the evaporation rate of the evaluated samples.

The amount of sample evaluated was not consistent from sample to sample. According to the protocol, "a sample of 20-30 microliters" was used in the evaluation. Given the extremely small amount of sample used, fluctuations of up to 50 percent of the total sample will have a significant influence on the film thickness, which will produce inconsistent results. A constant volume of sample needs to be evaluated to establish a basis for comparison.

A constant volume of sample will also ensure that variations due to sample size will be minimized. The size of the sample will affect the thickness and perhaps the surface area of evaporation. These changes will impact the observed evaporation rates.

In addition, the small sample size can produce measurement errors due to the inability to accurately measure the time it takes to evaporate the sample. For those samples that evaporate quickly, measuring the exact amount of time it takes to evaporate is quite challenging and can lead to errors, thus misrepresenting the true evaporation rate of the sample being evaluated.

It is not clear why each sample was not exposed to the conditions in the TGA for the same amount of time. In the study, the only reference to time states, on page 5, that "All ten samples evaporated within 70 minutes and half of them evaporated within 30 minutes." The District did not clearly establish a baseline against which to judge these evaporation rates. Unless each cleaning solution is exposed to the same conditions for the same period of time, comparisons as to the weight loss between the solvents cannot be made and conclusions as to the VOC emissions of each are impossible to quantify.

The assessment did not identify the rationale for selecting either the conditions, ambient temperature and 0.4 cm/sec linear air flow or amount of cleaning solution and how that compares to what actually occurs in a printing hand wipe operation. The conditions chosen do not represent field conditions in the printing industry when using cleaning solvents for hand cleaning operations. The industry uses either shop towels or hand held non-propellant spray bottles to apply the solvent to the surface being cleaned. If spray bottles are used, then shop towels are used to wipe the solvent from the surface. The solvent residue, left over from the wiping operation, would be the only portion of the
solvent product that is expected to evaporate over time. Therefore, only measuring the amount of solvent remaining on the equipment without consideration of the amount of solvent remaining in the towel not evaporating does not reflect the total loss of solvent due to hand wiping operations.

Furthermore, when an operator actually cleans a piece of equipment, they do not wait until all of the solvent evaporates from the surface to begin printing the next job. Any residual solvent remaining on equipment is wiped away with a shop towel. Since most cleaning operations occur in a 5-10 minute period, a 30-70 minute period far exceeds what would occur in a normal cleaning operation. This means that the towel would absorb the solvent that does not evaporated after 5-10 minute. The towel is then immediately placed in a closed container. The combined effect of the shop towel absorption and closed container will further impede evaporation.

It is not clear how it was determined that the 20-30 microliters of solvent represents the amount of residual solvent remaining on the cleaned equipment. It is also not clear how the 0.2-0.4 mm film thickness was determined. Since these are two critical parameters, information on why these were chosen is critical to understanding some of the derived results.

Lastly, the evaluation did not take into account the interaction of the cleaning solution with the material being cleaned. In many instances, hand wipe cleaning involves the removal of ink from equipment. The influence of the material being removed will also greatly change the evaporative loss characteristics of the cleaning solutions due to both physical and chemical interactions.

RESULTS

Samples

The selection of solvents for the study is very questionable. The District stated on page 1 that the submitted samples should contain no exempt solvents; however, several products contained acetone. These products should not have been included in the overall assessment.

The District states that an attempt was made to subtract the acetone vapor pressure from the measured vapor pressure based on the amounts of acetone listed on the MSDS. Generally, the vapor pressure figure listed on the MSDS already represents the vapor pressure of the product as supplied, minus the acetone since it is an exempt compound.

It is also not clear as to why two of the cleaning solutions that are not typically used for hand cleaning operations were included in the assessment. The Prisco Autowash LA-3
and Prisco Autowash 6000 are typically used in automatic blanket wash systems. Both are specifically formulated for this particular application. They should not have been included in the overall evaluation. Without additional details regarding the other cleaning solvents used in the study, it is difficult to determine if any others should be excluded.

The study indicated, “an attempt will be made to study samples that meet the previous Rule 1171 limitations but still represent a range of vapor pressures.” It is not clear why the SCAQMD decided to limit the evaluation to only those materials that met the limits in Rule 1171. This choice immediately constrained the assessment, which would lead to the erroneous conclusions contained in it. The purpose of the study was to answer the question of the effect of vapor pressure on the total mass emissions of VOCs from the use of cleaning solvents, not those cleaning solutions that met the limits of the previous Rule 1171. While it is appropriate to include cleaning solutions that met the limits of the previous Rule 1171, using them exclusively does not allow for a complete evaluation of the relationship between composite VOC vapor pressure and mass emission rate.

Further, the products tested as part of this study do not represent the full range of low vapor pressure products used by the printing industry. Those evaluated within this draft report are only used in the offset lithographic industry. No products used for wipe cleaning operations in either screenprinting or specialty flexographic printing were identified and included in the study. The intent of the technical assessment is to review the use of low vapor pressure products for all printing processes.

Until the last amendment package in 1999, the printers in the District had utilized low vapor pressure products as a means to reduce emissions from solvent cleaning activities. Both the VOC content and vapor pressure requirements differ between print processes, confirming the necessity of culling out different control strategies by process type. The draft study did not recognize nor seek out products that were used by all printing types.

The study focused on cleaning solvents used in the offset lithographic process, and ignores those used by screenprinting and specialty flexographic operations. The conclusions cannot be extrapolated to cover the entire printing industry. In order for the District to be able to substantiate its claim regarding the removal of vapor pressure as a compliance strategy, the study needs to incorporate solvent cleaning products from all printing industry categories.

Products for all identified printing processes covered under Rule 1171 and meeting the limits established in 1991 were still available prior to December 2001. If the study were conducted after the December effective date, the District would still have been able to
Ms. Lee Lockie  
May 16, 2002  
Page 9  

obtain samples of previously compliant materials by contacting the industry trade Ms. associations. These materials are used extensively in other parts of the country and are readily available.

The 1991 limits set different limits for each printing process type. For example, screen printing operations were allowed the use of products with a VOC content of 1070 grams per liter and a vapor pressure of 5 mm Hg. Lithographic roller wash operations were allowed to use products with a VOC content of 900 grams per liter with a vapor pressure of 10 mmHg. Specialty flexographic operations were allowed products with no more than 801 grams per liter with a vapor pressure of 21 mm Hg.

The District has long recognized the need to allow industry sectors the ability to use technology that is developed specifically for that industry sector. The pre-1999 Rule 1171 was no exception. It is imperative that the study to determine the linkage between vapor pressure and mass VOC emissions look at all the product categories. Otherwise, a valid conclusion cannot be reached.

In addition, the draft assessment does not indicate if the solvents selected for evaluation were representative of those used by the majority of lithographic printing operations or if they are used as the primary “hand wipe” cleaning solutions. Printers can use a variety of cleaning solutions, some of which do not involve hand wiping. The study does not indicate the primary use of any of the evaluated products.

Vapor Pressure and Evaporation Rate

Despite the many flaws in the testing methodology, an obvious trend that can be seen in the data is that the emissions rate and vapor pressure correlate quite well, despite the claims in the report to the contrary. This correlation is clearly shown by the data in the TGA curves. However, the trend is masked by the procedure used in the report to evaluate evaporation rated based on time to total evaporation or to constant weight. Some of the solvent cleaners have components that do not completely evaporate due to the presence of low volatility compounds present in some of the solutions exhibiting higher vapor pressures.

In examining the time required for a percentage of the solvent film to evaporate versus the vapor pressure of the material, an obvious trend can be seen relating to vapor pressure and emission rate. This trend contradicts the stated conclusion in the report that “Vapor pressure does not appear to influence VOC mass emissions within the range of products and conditions that were studied...” (Note: only one set of conditions was included in the report, further questioning the validity this conclusion, no “range” of conditions was in fact studied.)

000357
Data from the TGA curves can be used to document the quantity of solvent evaporated in a fixed time period. Since hand cleaning generally only occurs for a few minutes, times of 5 and 10 minutes were evaluated. Summarized below is the data showing the percent solvent evaporation occurring during the first 5 minutes and 10 minutes of the TGA portion of the assessment.

<table>
<thead>
<tr>
<th>Product</th>
<th>Vapor Pressure (mm Hg)</th>
<th>Percentage of solvent evaporated in first 5 min</th>
<th>Percentage of solvent evaporated in first 10 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dowanol EB</td>
<td>23</td>
<td>6%</td>
<td>14%</td>
</tr>
<tr>
<td>Prisco UV #8</td>
<td>32</td>
<td>12%</td>
<td>26%</td>
</tr>
<tr>
<td>Prisco Powerclean VC</td>
<td>40</td>
<td>12%</td>
<td>25%</td>
</tr>
<tr>
<td>Star Ultra 2B</td>
<td>45</td>
<td>27%</td>
<td>50%</td>
</tr>
<tr>
<td>Superklene 2P</td>
<td>45</td>
<td>17%</td>
<td>36%</td>
</tr>
<tr>
<td>Autowash 6000</td>
<td>46</td>
<td>16%</td>
<td>32%</td>
</tr>
<tr>
<td>Toluene</td>
<td>92</td>
<td>89%</td>
<td>100%</td>
</tr>
<tr>
<td>IPA</td>
<td>116</td>
<td>75%</td>
<td>100%</td>
</tr>
<tr>
<td>Star #250 Wash</td>
<td>117</td>
<td>87%</td>
<td>100%</td>
</tr>
<tr>
<td>Star 1001</td>
<td>252</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>Autowash LA3</td>
<td>279</td>
<td>39%</td>
<td>62%</td>
</tr>
<tr>
<td>Star LVP 25</td>
<td>279</td>
<td>66%</td>
<td>100%</td>
</tr>
<tr>
<td>Prisco MRC-F</td>
<td>284</td>
<td>79%</td>
<td>94%</td>
</tr>
</tbody>
</table>

As the data shows, those materials with low vapor pressures (<50 mm Hg per the test protocol) showed limited evaporation over the 5 minute and 10 minute periods, with the highest percentage loss of 27% for the 5 minute period and 50% for 10 minutes. The average 5 minute loss for the 5 tested low vapor pressure materials and the reference materials Dowanol EB was 15%, with losses over the 10 minute period averaging 30.5%.

In sharp contrast, the high vapor pressure materials showed significantly higher initial evaporation rates and were, in most cases, totally evaporated within the 10 minute period. The average 5 minute loss for the 5 tested materials and the 2 reference materials toluene and IPA was 85.4%, with losses over the 10 minute period averaging 93.7%.

The impact of this significant difference in evaporation rates will manifest itself as a difference in VOC emissions from cleaning solutions for at least two reasons. First, the use of a higher vapor pressure, more rapidly evaporating solvent will likely require the use of more solvent for a given cleaning operation. The rapid evaporation of solvent from the surface being cleaned will mean that additional solvent will be required to replenish the solvent used to complete even short-term cleaning jobs. Second, with the use of towels or other wipers, the removal of excess solvent from the surface with the wiper and storage of the wiper in a closed container, will minimize the quantity of solvent
film on the surface for evaporations (unlike a high vapor pressure material that will Ms. quickly evaporate, leaving a dry surface with nor residual solvent that can be removed) and prevent additional evaporation once the wiper is placed in a container.

This trend is illustrated in the table below, where the time over which various percentages of solvent weight loss are tabulated for the various vapor pressure materials. For example, under the report test conditions, it takes approximately 7.9 minutes to achieve a 20% solvent loss from Prisco UV#8 (vapor pressure = 32 mm Hg) compared to only 1.3 minutes to evaporate the same percentage of Star #250 Wash (vapor pressure = 117 mm Hg). As described above, since cleaning occurs for periods of only a few minutes, this large difference in time required to achieve the same percentage solvent loss will equate to significant difference in evaporative losses from actual hand cleaning operations for low vs. high vapor pressure materials.

<table>
<thead>
<tr>
<th>Product</th>
<th>Vapor Pressure (mm Hg)</th>
<th>Time (minutes) required to achieve weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>20%</td>
</tr>
<tr>
<td>Dowanol EB</td>
<td>23</td>
<td>14.8</td>
</tr>
<tr>
<td>Prisco UV #8</td>
<td>32</td>
<td>7.9</td>
</tr>
<tr>
<td>Prisco Powerclean VC</td>
<td>40</td>
<td>8.4</td>
</tr>
<tr>
<td>Star Ultra 2B</td>
<td>45</td>
<td>4.0</td>
</tr>
<tr>
<td>Superkleene 2P</td>
<td>45</td>
<td>6.0</td>
</tr>
<tr>
<td>Autowash 6000</td>
<td>46</td>
<td>6.4</td>
</tr>
<tr>
<td>Toluene</td>
<td>92</td>
<td>1.2</td>
</tr>
<tr>
<td>IPA</td>
<td>116</td>
<td>1.5</td>
</tr>
<tr>
<td>Star #250 Wash</td>
<td>117</td>
<td>1.3</td>
</tr>
<tr>
<td>Star 1001</td>
<td>252</td>
<td>0.8</td>
</tr>
<tr>
<td>Autowash LA3</td>
<td>279</td>
<td>1.6</td>
</tr>
<tr>
<td>Star LVP 25</td>
<td>279</td>
<td>1.2</td>
</tr>
<tr>
<td>Prisco MRC-F</td>
<td>284</td>
<td>0.7</td>
</tr>
</tbody>
</table>

**Vapor Pressure and VOC**

On page 7 of the study, the District states that “There was no relationship between VOC content and vapor pressure.” The printing industry does not argue with this statement.

All cleaning solvent products, regardless of vapor pressure, are generally comprised of solvent products. Due to the conditions associated with ASTM D2369, high VOC contents are expected. The purpose of the study was to determine the linkage between composite VOC vapor pressure and mass VOC emission rate, not VOC content, so that a comparison between the two physical characteristics could be made.
The printing industry has submitted to the District testing data and a methodology that clearly shows that a link exists between lower vapor pressure and mass VOC emissions. Based on the review of the draft study, we find no indication that the information provided to the District was either used or referenced.

CONCLUSIONS

This section of the assessment consists of three sentences, all three of which we believe are inconsistent with the results and data reported in the report itself. It appears that this is the result of the authors equating “VOC mass emissions” with “VOC emissions rate.” These conclusions, therefore, misrepresent the report results and fail to recognize the significant effect of vapor pressure on VOC emissions rates.

Our comments on these sentences is as follows:

(1) “Vapor pressure has no effect on mass VOC emissions.”

This statement is a direct contradiction of the statement on page 5 of the report which stated “there is a positive correlation between vapor pressure and evaporation rate.” Further, the statement is totally inconsistent with the evaporation rate data found in the text and tables of the document, including the TGA curves in Attachment F and the results summary table in Attachment E.

All of these data show a strong, positive correlation between the rate of evaporation and the vapor pressure of the cleanup solvent. Whether this is measured in terms of the peak rate of weight loss (Attachment E), the time required for a fixed percentage weight loss (see our comments on this subject elsewhere), or the amount of solvent loss over a fixed, relatively short period of time (see our comments on this subject elsewhere), there can be no doubt that the rate of emissions will decrease significantly when the vapor pressure of the solvent is reduced. This results presented in this report strengthen and confirm this conclusion.

It appears, however, that the authors of this report have chosen to ignore this strong correlation between emissions rate and vapor pressure. Instead, they appear to conclude that, as would be expected and could have been easily predicted without conducting this study, given the right conditions and enough time, a solvent mixture will totally evaporate. What a revelation! Had the authors chosen to review the standard test methods that are used to determine VOC content of materials, such as USEPA Methods 24 or 24A or District Method 304, they would have learned that the technique used to
determine the VOC content of a material is to measure the weight loss of a sample after it has been heated under a prescribed set of conditions for a standard length of time. The premise of these methods is that all the VOC will evaporate under the test conditions. In effect, what the authors of this report have done is to modify these standard test methods by using a different temperature and a TGA apparatus and demonstrate that, given enough time, all of the VOC from the solvent samples studied will evaporate, resulting in 100% VOC emissions. This result does not demonstrate anything relative to evaporative losses from materials that are used for cleaning. It represents shoddy science and distorts the results of the study.

2. “Even samples with very low vapor pressure tested at nearly 100% VOC.”

Much like the statement above, this conclusion could have been drawn from a review of material safety data sheets and an understanding of the composition of cleaning solvents. No testing would have been required. However, that is not the point. The printing industry has never contended that vapor pressure has any direct correlation with VOC content. Organic materials, including pure compounds and solvent mixtures, have different vapor pressures even though they may be 100% VOC. This is a simple physical property of organic materials. In the category of straight-chain aliphatic hydrocarbons, for example, the vapor pressures range from 16.3 psi at 70°F for butane (i.e., it is a gas at ambient conditions) to 0.3 mm Hg at 20° for dodecane (equal to 0.0058 psi at 68°F). Both of these compounds are 100% VOC, yet the evaporative losses from these two materials will be markedly different, with 100% loss of butane instantaneously to a very slow, almost imperceptible evaporation of dodecane under ambient conditions.

Although this statement is true, it is totally irrelevant to the purported purpose of this report, which was to determine whether there is a relationship between vapor pressure and the VOC emissions (not VOC content) of solvents.

3. “Vapor pressure does not appear to influence VOC mass emissions within the range of products and conditions that were studied; therefore, it is concluded that lower vapor pressure limits will not result in further reduction of VOC emissions.”

This final sentence once again calls upon the faulty logic as expressed in the previous sentences to support the position that vapor pressure is not an important factor in evaporative losses from solvents. Once again, the conclusion is at odds with the data in the report.
Although a range of products was examined, only one condition (complete evaporation of solvent at a single temperature and air flow) was studied. As noted elsewhere in our comments, the impact of the use of shop towels (and storage of solvent contaminated towels) and the effect of solvent evaporation on solvent usage were not considered, nor were other parameters, such as realistic temperatures for cleaning, mixture of solvents with the less volatile components they are being used to remove, etc. So not only does the conclusion appear to be wrong in that the results do show vapor pressure having an influence on VOC emissions rates, the authors appear to want to extrapolate this single-condition test result to all conditions under which hand solvent cleaning is used. Unfortunately, the results cannot support either the conclusion or the extrapolation.

Based upon our review of the report, we suggest the following revision to the Conclusion section of this report:

“This report has shown that there is a positive correlation between vapor pressure and VOC emissions rate, with lower vapor pressure solvents having a lower mass VOC emissions rate. Since the scope of this project was to examine only materials that contain no exempt solvent, all of the samples (both with high and low vapor pressure) tested at nearly 100% VOC; however, the peak rate of VOC weight loss from the various solvents ranged over an order of magnitude, from a low of 2.65% per minute to a high of 26.84% per minute. Vapor pressure appears to strongly influence the VOC mass emissions rate within the range of products that were studied under this single test condition; therefore, it is concluded that lower vapor pressure limits will likely result in further reduction of VOC emissions.”

Finally, in its conclusions the District has not addressed the relationship between vapor pressure and VOC emissions. This evaluation does not substantiate the claim that low vapor pressure products have no effect on mass VOC emissions. The conclusion reached by the District is that since low vapor pressure produce has high VOC contents, then they must emit high levels of VOCs. In fact, the data in the assessment does not support this conclusion.

The ability to use alternative cleaning solvents that result in less VOC emissions is critical to the economic viability of the printing industry in the District and the topic deserves a well constructed evaluation strategy.

The inclusion of the technical assessment in Rule 1171 came as a result of discussions between the printing industry and the District. It is unfortunate that the District did not include the industry as a partner in this study. The use of low vapor pressure products as a compliance strategy was developed and adopted by the District in 1991. It behooves the District to substantiate its abandonment of a compliance option that it once supported.
The current study neither encourages nor discourages the use of low vapor pressure products as a viable compliance option. To resolve this critical compliance, and economic issue, the printing industry strongly encourages the District to work with the industry to develop a proper assessment that will adequately investigate the relationship between vapor pressure and VOC emissions.

Thank you in advance for the consideration you may give our comments.

Sincerely,

Marcia Y. Kinter
VP Government Affairs
Screenprinting & Graphic Imaging
Association International

Gerald M. Bonetto, Ph.D.
VP Government Affairs
Printing Industries of California

Cc: Dr. Barry Wallerstein
Executive Officer

Chung Liu
Deputy Executive Officer
Science and Technology Advancement
May 14, 2008

Kevin J. Williams, PhD
Program Coordinator – Rule Development
Sacramento Metropolitan Air Quality Management District
777 12th Street, Third Floor
Sacramento, CA 95814

Re: Comments on Rule 454 Amendments and Follow up to Request for Exemption from District Rule 454 for Teledyne MEC High Voltage Microwave Vacuum Tube Operations

Dear Dr. Williams:

Teledyne Wireless, Inc., doing business as Teledyne MEC has reviewed the District’s proposed amendments to Rule 454, Degreasing Operations, which do not include an exemption for high voltage microwave tubes. This letter expresses our interest in pursuing an exemption based on the specific details and information we provided to the District in a letter dated January 31, 2007, and the following:

Our small-scale operation in Rancho Cordova involves precision manufacturing, repair, and packaging of high voltage microwave vacuum tube assemblies. This is accomplished at various bench-top workstations that are located throughout our facility. Some aspects of the operation involve the assembly of very small ceramic and metal parts which must be cleaned with solvent to remove residue and other potential contaminants. At present, we use solvents that are Volatile Organic Compound-compliant as required in the District’s Rule 466; and we apply the solvents by wipe cleaning in accordance with the District’s Permit-To-Operate 19200. However, based on our assessment and failure analysis, we believe that soaking small parts in 100% anhydrous IPA for the purpose of removing residual material, such as adhesives or other contaminants that may be tightly bonded to the parts, would be much more effective than wipe cleaning. This, we believe, will improve reliability of our products which are used in United States Military aircraft and ships in defense measures.

In assessing other methods for improving our cleaning operations, we have reviewed the application of an “Airtight/Airless Cleaning” system as described in Rule 454; and based on our operational needs which involve hand manipulation of very small parts during cleaning and assembly, we have concluded that the application of such system would be impractical or not feasible. At this point, the most practical and effective approach for improving product cleaning would be soaking in 100% anhydrous IPA. We would propose to do this in small batches (< 1 liter) within closed containers such as beakers, jars, or small trays. This would occur only in
select areas that we believe to be critical for producing defect-free product. Although a slight increase of solvent usage could be expected, the overall emissions would not exceed current levels. This would be accomplished in accordance with the general operating requirements of Rule 454, in order to prevent solvent leakage and uncontrolled emissions.

Based on the information provided herein and in our January 31, 2007 letter, Teledyne MEC proposes the following comments be added to Rule 454, Section 110 “Exemptions”:

“The VOC content limits in Sections 302.2 and 302.3 do not apply to degreasing of high voltage microwave vacuum tube assemblies”; or

“Rule 107 alternative compliance from the VOC content limits in Sections 302.2 and 302.3, may be used for degreasing of high voltage microwave vacuum tube assemblies”

Please let me know if you need more information or if you would like to discuss in more detail any aspect of our request.

Thank you for your consideration.

Sincerely,

[Signature]

Hassan (Al) Bataki
Manager, Environmental, Health and Safety
Jimmy Cheng  
Sacramento Metropolitan Air Quality Management District  
777 12th Street, 3rd Floor  
Sacramento, CA  95814-1908

Subject: Comments from Aerojet, Sacramento to the Sacramento Metropolitan Air Quality Management District on the Proposed Changes to Rule 456

Dear Mr. Cheng:

Aerojet respectfully submits comments on the Sacramento Metropolitan Air Quality Management District’s (SMAQMD) proposed changes to Rule 456. Proposed rule amendments change how solvent cleaning for coating application equipment is performed under Rule 456 Aerospace Assembly and Component Coating Process. Specifically, Section 304.4 will lower the solvent Volatile Organic Compound (VOC) limits allowed for Application Equipment Cleanup from 200 grams of VOC per liter of material (g/l) or use of an enclosed gun cleaner to 25 g/l and the use of enclosed gun cleaners will no longer be permitted.

Aerojet is concerned about this change for the following reasons:
1. More heavily reliance on exempt solvents, such as Acetone, will have negative health and safety impacts and will be restricted based on Environmental Health and Safety risks.
2. A very limited number of substitute, compliant solvents are available that thoroughly clean the type of coatings, i.e. multi-part epoxies and polyurethane containing materials. These types of coatings are required for use by United States Government Contract Aerospace, Missile and Space Vehicle Specifications.
3. There is not enough time allotted by the SMAQMD to test and requalify substitute solvents by the effective date of the proposed rule changes.
4. Based on preliminary discussions with our suppliers (Deft and Sherwin-Williams), suitable replacements may not even exist.
5. A final factor is the cost that will be associated with the work to requalify and incorporate replacement solvents that are mandated by the proposed rule change.

Since there are no known commercially available products with 25 grams of VOC’s per liter, or less, that will be effective in cleaning aerospace coatings used at Aerojet, employees may rely on acetone, an exempt solvent, or an acetone-based material. However, the use of acetone will cause unacceptable flammable and safety risks within the process areas at Aerojet. Acetone’s high vapor pressure, toxicity,
and very low flashpoint increase the risk of damaging fires and personnel exposures. These risks are explained in more detail below.

Per Aerojet’s Fire Marshal, the use of acetone will be limited based on building code issues, fire code issues, and the cumulative higher vapor releases inside buildings will be limited by the Fire Marshall. The proposed rule change will encourage people to use acetone more but at the same time there will be additional restrictions. In the end, Aerojet will not be able to use our historical cleaning materials or the preferred exempt materials.

Regarding safety issues, using high volumes of acetone has a negative and costly affect. Increased use of Acetone could have adverse safety effects on some operations and increase the cost of controlling hazards in both explosive and inert operating areas. Acetone is significantly more volatile and flammable than many of solvents currently used in Aerojets processes.

Under Cal-Osha “Injury and Illness Prevention Program” and “Process Safety Management” regulations operations would need to be analyzed to identify potential hazards/controls. Following are a few examples of how operational costs may be affected from increased use of Acetone:

- Ventilation rates to keep Acetone/Air vapors below their lower flammability limits might need to be increased
- Build and Fire codes may require that EP rated electrical equipment be installed where Acetone/Air vapors could collect
- And some sensitive explosive operations may require that conductive floors and/or runners with antistatic shoes be employed to prevent ESD from igniting of Acetone/Air vapors and propagating to explosive materials

Each situation will need to be carefully evaluated if acetone is substituted.

If the proposed rule changes are adopted, and Aerojet selects acetone as a substitute; there is the possibility of equipment being corroded and breaking-down. For instance, rubber seals and gun cleaning devices have the potential to break down over time after repeated exposure to acetone. Another chemical property of acetone is that it is hydroscopic and water easily absorbs into the solvent. There is great concern of cross contamination with the introduction of water into the subsequent steps of the coating process. For instance, there cannot be any water contamination when adhesives, i.e. Chemlock, are applied and with acetone used in the previous cleaning stage, there is a significant risk of bonding failure with the presence of water contamination.

In SMAQMD’s Draft Staff Report (Staff Report), dated March 28, 2008, it states that:

Compliance costs are expected to decrease for the two sources that currently perform spray gun cleaning using noncompliant materials. The average cost of the noncompliant material is $23.40 per gallon, while the average cost of compliant material, as given in the November 2003 staff report for South Coast Air Quality Management District (SCAQMD) Rule 1171, is $11 per gallon.
Aerojet’s research and has found these statements are not completely accurate and cannot be applied to Aerojet Sacramento. The companies referenced in Section III—“Alternatives in Coating and Adhesive Application Equipment Cleaning” (Alternatives Study) of the August 2003 “Assessment, Development and Demonstration of Low-VOC Cleaning Systems for South Coast Air Quality Management District Rule 1171”, only evaluated acetone against their current cleaning solvent. For reasons discussed previously, Aerojet is strongly against increasing the use of acetone. The three aerospace companies, Hydro-Aire, Gulfstream and California Propeller, involved in the SCAQMD Alternatives Study are not comparable in size or magnitude to the Aerojet campus in Sacramento California. These companies are described as small and typically had one gun cleaning station. For example, Hydro-Aire was sited as using approximately 60 gallons per year of gun cleaning solvent whereas Aerojet has the potential to use up to 130 gallons per year (five gallons every two weeks) in one spray booth. Aerojet has over ten spray booths that would be affected by this rule change.

Aerojet would need adequate time to determine if substitute, compliant material would work with our complex processes and the variety of other materials that have the potential to come in contact with it. Finding an inexpensive alternative, as implied in the SMAQMD statement on cost savings, would not be as high on the priority list as finding a compliant material that is effective and safe in our processes. This alternative solvent will have to be based on product safety, effectiveness of cleanliness (determined by military specifications) and cost effectiveness and must go through a qualification process that will include a plan, budget and customer approval. The current allotted time proposed by the SMAQMD is simply not enough to go through all the stages of researching alternatives (including funding the for this research project) procuring the alternatives, testing the alternatives against all affected processes on plant, and finally choosing effective alternative. This research process has the potential to take a minimum of 36 months without any promise of successfully finding an alternative product. Aerojet is requesting a delay of the adoption of rule to allow for more time to accurately requalify solvent materials.

Aerojet inquired with our current suppliers within this very short comment period allotted by the SMAQMD and received no positive feedback. Bob Sypowicz from Deft Inc., which is the company Aerojet purchases many of our US Government Specification coatings from, states in an email dated May 9, 2008, that costs of alternative solvents will be a big drawback. In discussion with Mr. Sypowicz, Oxsol was recommended as a possible cleaning solvent but it is slow and would need to be combined with acetone. He goes on to state that “urethane grade acetone and Oxsol are typically 3-4 times more expensive than standard urethane reducers. The practicality of using these expensive solvents for gun cleaning is questionable.” Another statement from the Paints and Coatings Resource Center states that “Oxsol as many times more expensive than other solvents”.

There are other cleaning solvents such as acetone that are listed in the SMAQMD’s Rule 101, Section 204 Exempt Compound list, dated September 3, 1998, but Aerojet has made a commitment to restrict, or aggressively prohibit, some of these chemicals for Environmental Health and Safety risk reasons. These materials include but are not limited to EPA 17 materials, Ozone Depleting Substances (ODS), carcinogens, Occupational Safety and Health Administration (OSHA) regulated materials, National Emission Standards for Hazardous Air Pollutant’s (NESHAPs), and acutely hazardous materials. Due to Aerojet’s strict standards, many SMAQMD exempt compounds are prohibited from a wide range of applications, or completely restricted from use. The Sacramento-area sales representative from Sherwin
Williams has told Aerojet that they do not sell any cleaning solvents that would work for Aerojet’s coatings. The lowest effective VOC containing solvents Sherwin William offered Aerojet contains 250 g/l VOC.

While reviewing the SMAQMD’s Staff Report, it became clear that Aerojet was one of the two companies referenced for using non-compliant materials for spray gun cleaning. Aerojet quickly remedied the situation and purchased commercially available enclosed gun cleaners. The current enclosed gun cleaning process greatly reduces the amount of VOC’s emitted to the air in comparison to cleaning with solvents with no controls. By controlling the emissions to the environment, this achieves the same reductions as lowering the VOC limits contained in the rules.

Another variation of the coating process at Aerojet is to use long booms/wands to apply coating materials where a conventional High Vapor Low Pressure (HVLP) gun is not a feasible option. The alternative coating application has been approved by the Environmental Protection Agency (EPA) in early 1999’s, and is incorporated into four of Aerojet’s local permits and the Title V permit. Along with the EPA-approved boom/wand coating method, SMAQMD has approved an alternative method for cleaning the booms/wands that cannot be cleaned in a commercially available enclosed gun cleaner. The cleaning technique is generically described as a long wand with a rubber stopper affixed on the wand that is fed into a 5-gallon steel bung container. The solvent is loaded into the spray pot and pressurized through the pot, hoses and wand and is deposited into a properly labeled waste container. This has been accepted as an enclosed gun cleaner as well and is compliant with the SMAQMD rules.

The proposed version of Rule 456 assumes no controls are applied when cleaning coating application equipment. Aerojet proposes that the boom/wand cleaning technique be retained in Rule 456 as we are not sure this system can be effectively replaced. The coating applied using the booms/wands serves a critical function in propellant bonding. Failure of this bonding can be catastrophic. Aerojet also requests that the use of enclosed gun cleaners as a way to reduce VOC emissions be retained in Rule 456 to achieve the VOC reductions the SMAQMD is trying to achieve.

Aerojet is committed to the health and safety of our employees and the public. However, we believe that the proposed rules would place an undue burden on our local operations, which could threaten the viability of certain types of work currently being conducted at our Sacramento facility.

Aerojet is one of the nation’s leading aerospace and defense contractors and employs more than 1700 professionals at the Sacramento campus. The work we do at our facility is critical to our national security and continued involvement in space exploration. Our procedures, documentation and operations are closely monitored by our government and customers and have been the subject of rigorous qualification processes. Considering the myriad of applications Aerojet has we cannot easily switch to a water-based coating or low VOC solvents that are designed to clean water-based coatings. Alternative coatings and or solvents would need to go through a lengthy qualification and documentation process for each item that uses the solvents, which would result in significantly higher costs, as well as a considerable slowdown in operating efficiencies and throughput. This would be a burden to Aerojet because of time delays to qualify new products, as well as safety and quality issues that may Result.

In conclusion, the potential effects of the proposed rule changes cannot be properly researched in the allotted time frame. Aerojet is requesting a delay of the adoption of the rule to allow for additional time.
to adequately identify and qualify substitute solvent materials, and to estimate the financial burden placed upon the Sacramento Plant. Aerojet is requesting a minimum delay of two years from adoption. The enclosed gun cleaning technique used for application equipment cleaning is very effective way of reducing VOC emissions to the atmosphere. Aerojet requests that enclosed gun cleaning as well as the critical SMAQMD-approved enclosed wand/boom cleaning, be kept in Rule 456 as an alternative method to comply with the low proposed limits of 25 g/l VOC. If neither of the above options can be accepted, Aerojet respectfully requests the Board reject these proposed changes to Rule 456.

If you have any questions, please contact Chelsea Sand at (916) 355-2971.

Thank you,

Chelsea Sand
Environmental, Health and Safety
EPA

Region IX
75 Hawthorne Street
San Francisco, CA 94105-3901

August 18, 2008

Transmittal of EPA Rule Review Comments

To: Ms. Aleta Kennard, Sacramento Metropolitan Air Quality Management District
   akennard@airquality.org
   Mike Guzzetta, California Air Resources Board
   mguzzetti@arb.ca.gov

From: Andrew Steckel, Rulemaking Office Chief
      steckel.andrew@epa.gov

    Drafts

We are providing comments based on our preliminary review of the draft rules identified above. Please direct any questions about our comments to me at (415) 947-4115 or to Sona Chilingaryan at (415) 972-3368.

Potential Approvability Issues

Rule 450, Graphic Arts Operations

The 2006 CTG for Offset Lithographic Printing and Letterpress Printing recommends a 1.6 percent alcohol by weight fountain solution for heatset web offset lithographic printing, a 5 percent alcohol by weight for sheet-fed offset lithographic printing, and 5 percent alcohol substitute or less and no alcohol in the fountain solution for coldset web offset lithographic printing. For heatset web and sheet-fed printing, the CTG provides different approaches for achieving the recommended level of control. The 100 g/L VOC limit for chilled fountain solutions and 80 g/L limit for non-chilled fountain solutions in Section 301.2 are not as stringent as the CTG recommendations. Please include requirements that are as stringent as the CTG recommendations.

The 2006 CTG for Offset Lithographic Printing and Letterpress Printing recommends a control device with an overall control efficiency of 90% or 95% for heatset web offset lithographic printing depending on the first installation date of the control device, and also recommends that the dryer be operated at negative pressure. While Section

000371
303.2.a requires a control device efficiency of at least 95%, Section 303.2.b requires an emission collection efficiency of at least 70%. The 70% emission collection efficiency requirement is not as stringent as requiring the dryer to operate at negative pressure. Please include requirements that are as stringent as the CTG recommendations. Please note that the CTG does not recommend that heatset web sources be allowed to use graphic art printing materials (inks and varnishes) with a certain VOC content instead of using an add-on control device. Please change rule requirements to allow heatset web sources to comply only by using control technology that has an overall capture and control efficiency that’s equivalent to CTG recommendations or demonstrate that compliance with the VOC content limits is equally as stringent.

The 2006 CTG for Flexible Package Printing, depending on first installation date of the press and add-on control device, recommends an overall capture and control efficiency of up to 80%. Section 303.2 requires an overall capture and control efficiency of only 67%. As an alternative to meeting the applicable capture and control efficiency, the CTG recommends that materials be used that meet the following limits: .8 kg VOC/kg solids applied or .16 kg VOC/kg materials applied. Please include requirements that are as stringent as the CTG recommendations.

Rule 451, Surface Coating of Miscellaneous Metal Parts and Products

Section 111.9 exempts conformal coatings. This exemption is not recommended in applicable CTGs. Please demonstrate that Rule 451 meets RACT even though this exemption is not recommended in applicable CTGs.

We understand that Rule 451 includes coating emission limits for metal furniture operations. Please ensure that Rule 451 requirements are as stringent as the recommendations in the 2007 Metal Furniture Coatings CTG. Certain limits in the VOC content table in Section 301 are less stringent than the recommend emission limits for various coating categories in the 2007 Metal Furniture Coatings CTG (e.g., the VOC table in the rule has a 3.5 lb/gal air dried limit for extreme high gloss coatings whereas the CTG recommends a 2.8 lb/gal air dried limit for the same category). Moreover, the CTG recommends an overall capture and control efficiency of 90% whereas Section 305 only requires an overall capture and control efficiency of 85%. The CTG also recommends work practice standards for both coating and cleaning activities, whereas the rule only contains work practice standards for surface preparation and clean-up in Section 304.

Rule 452, Can Coating

Unlike similar rules in other areas, Rule 452 does not require sources to use specific coating application methods (see, for example, Section (c)(4) of South Coast Air Quality Management District (SCAQMD) Rule 1125 and Section 5.6.2 of San Joaquin Valley Air Pollution Control District (SJVAPCD) Rule 4604). Please add provisions to Rule 452 that specify appropriate coating application methods.
We noticed that there were several other California rules that had more stringent requirements than Rule 452. Please explain why each of the following more stringent requirements are not feasible in Sacramento or change Rule 452 to be equally as stringent:

The VOC limit for end sealing compound is 440 g/L. BAAQMD Rule 8-11 and SJVAPCD Rule 4604 have a 60 g/L limit for drum, pail and lid end sealing compounds, and a 20 g/L limit for end sealing compounds in all other categories.

SCAQMD Rule 1125 has a 20 g/L limit for end sealing compounds for food/beverage cans and a 0 limit for end sealing compounds for non-food containers.

The VOC limit for three piece can interior body spray is 510. BAAQMD Rule 8-11 and SJVAPCD Rule 4604 both have a 360 g/L limit for this category.

The VOC limit for two piece can interior body spray is 440. BAAQMD Rule 8-11 and SJVAPCD Rule 4604 both have a 420 g/L limit for this category.

Section 302.1 requires an overall 85% capture and control efficiency for add-on control devices. BAAQMD Rule 8-11 and SJVAPCD Rule 4604 both require an overall 90% capture and control efficiency.

Rule 463, Wood Product Coatings

Section 306 provides for a rolling 30 day averaging period for compliance with the rule’s emission limits. From conversations with the District, we understand that only one very small source that refinishes antiques is currently utilizing this averaging provision. We are aware of no other areas that have SIP approved rules with such an extensive compliance period for wood coatings. Though we recognize that rules in other areas that have daily or no averaging provisions might be less stringent than Rule 463 in some other respects, we recommend the District remove this provision. However, if the District significantly narrows the scope of the provision (e.g., to very small sources refinish ing antiques), we believe that the District can utilize our 1% Screening Analysis (see December 2002 Memo from Andrew Steckel) to demonstrate that the averaging provision does not cause the rule to deviate from RACT or affect attainment of the eight hour ozone standard.

Please demonstrate that Rule 463 meets RACT though the exemption for military stencil coatings in Section 110.5 is not in the 1996 Wood Furniture Manufacturing CTG.

Rule 465, Polyester Resin

We noticed several other California rules have more stringent requirements than Rule 465. Please explain why having the following more stringent requirements is not feasible or change Rule 465 to be equally as stringent:
Section 301.1.a.1 requires that general resins have a monomer content of no more than 35%. Ventura County Air Pollution Control District (VCAPCD) Rule 74.14 and SCAQMD Rule 1162 have replaced the general purpose resin category with four sub-categories: marble resins (10% monomer content or 32% as supplied, no fillers), solid surface resins (17% monomer content), tub/shower resins (24% monomer content or 35% as supplied, no fillers), and lamination resins (31% monomer content or 35% as supplied, no fillers).

Section 301.1.a.2 requires that pigmented gel coats have a monomer content of no more than 45%. VCAPCD Rule 74.14 and SCAQMD Rule 1162 have replaced the limit for pigmented gel coats with lower limits in three sub-categories: white and off white (30% monomer content), non-white (37% monomer content), and primer (28% monomer content).

Section 301.1.a.3 requires that specialty resins and clear gel coats have a monomer content of no more than 50%. Rule 74.14 and SCAQMD Rule 1162 have replaced the limit for clear gel coats with two sub-categories that have lower limits: marble resins (40% monomer content) and other resins (44% monomer content). Rule 465 defines specialty resins as "any...resin used to make product for exposure to one or more of the following extreme environmental conditions: acute or chronic exposure to corrosive agents, caustic agents, acidic agents, or flame." Both Rule 74.14 and SCAQMD Rule 1162 also have 38% monomer content limit for fire retardant resin, 48% monomer content limit for corrosion resistant resin, and 40% monomer content limit for high strength resin.

Section 301.2 requires that emission control systems have an overall 85% control efficiency. Rule 74.14 and SCAQMD Rule 1162 both require an overall capture and control efficiency of 90%.

Rule 466, Solvent Cleaning

The VOC standards table in Section 301 allows for different limits for the solvent cleaning of architectural coating application equipment for water based coatings and solvent based coatings. Until one year after rule adoption, for water based coatings, cleaning without an enclosed gun cleaner has a 50 g/L limit, whereas for solvent based coatings, cleaning without an enclosed gun cleaner can have a limit up to 300 g/L.

In order to ensure that these limits are enforceable, please define water based coating and solvent based coating. Also, under solvent based coatings, cleaning architectural coating equipment without an enclosed gun cleaner at the jobsite has a 300 g/L limit whereas cleaning architectural coating equipment without an enclosed gun cleaner not at the jobsite has a 50 g/L limit. In order to ensure that these limits are enforceable, please define job-site in the rule.

Additional Recommendations
Rule 450, Graphic Arts Operations

We noticed that several other California rules have more stringent requirements than Rule 450. Please consider making Rule 450 limits as stringent as the following limits from other rules.

Section 110.1 exempts any graphic art operation that has actual emissions of less than or equal to 60 pounds per calendar month. As noted in ARB’s April 24 comments, VCAPCD Rule 74.19 contains a current exemption limit of 200 pounds per rolling 12-month period. The SJVAPCD is currently working on their Rule 4607 and also intends to lower their exemption to graphic arts operations which emit less than 200 pounds per 12 rolling consecutive calendar months.

The VOC limit for “Extreme Performance Ink/Coating” for screen printing is currently 800 g/L. SJVAPCD Rule 4607 and BAAQMD Rule 8-20 both limit the VOC content for this category to 400 g/L.

The VOC limit for “Sign Ink/Coating” for screen printing is currently 500 g/L. Both SJVAPCD Rule 4607 and BAAQMD Rule 8-20 limit the VOC content for this category to 400 g/L.

Rule 451, Surface Coating of Miscellaneous Metal Parts and Products

SCAQMD Rule 1107 has lower limits for the extreme high gloss, extreme performance, pre-fabricated architectural component, and general one-component coating categories. Please consider making Rule 451 limits as stringent as Rule 1107 for these categories.

Rule 452, Can Coating

Section 302 allows sources to comply with the use of an add-on control device only if emissions do not exceed the level which would be achieved from the equivalent use of compliant coatings. However, Rule 452 does specify how to calculate whether the control device is achieving emission reductions that would be equivalent to using compliant coatings. We recommend adding a section that’s similar to SJVAPCD Rule 4604 Section 5.2.9.

Rule 454, Degreasing Operations

Section 304.1 gives sources the option of complying with rule requirements by operating a vapor degreaser with a water separator. We recommend adding a definition for water separator. See SCAQMD Rule 1122 Section (b)(40) for potential draft rule language.

Rule 454 requires that airtight/airless cleaning systems not have a vapor leak of more than 50 parts per million measured as methane at the outlet of the airtight/airless
cleaning system. SCAQMD Rule 1122 section (f)(4) requires that airless/air-tight equipment be maintained in a vapor-tight, leak-free condition and states that any leak is a violation. Please consider whether a similar provision would strengthen Rule 454.

Rule 456, Aerospace Assembly and Component Coating Operations

Section 302 limits the VOC content of strippers to 300 g/L of VOC per liter of material. Section B.6 of Imperial Rule 425 limits the VOC content of strippers to 200 g/L. Please consider inserting this lower limit into Rule 456.

The current limit for adhesives is 600 g/L. SJVAPCD Rule 4605 has three different categories for adhesives - non-structural adhesives with a 250 g/L limit, structural autoclavable adhesives with a 50 g/L limit, and structural nonautoclavable adhesives with a 850 g/L limit. Please consider whether including a category for non-structural adhesives or structural autoclavable adhesives would allow the District to obtain additional emission reductions.

The current limit for adhesive bonding agents is 780 g/L. SJVAPCD Rule 4605 has six different categories for adhesive bonding primer, three with a 250 g/L limit, and three with a 805 g/L limit. Please consider if including additional categories that have a 250 g/L limit would allow the District to obtain additional emission reductions.

Rule 463, Wood Product Coatings

Section 110.4 exempts the coating of architectural components or structures, not coated in a shop environment. We recommend that the District add rule language to Section 110.4 to clarify that the exempted wood products are still subject to the requirements in the District's architectural coatings rule.

The VOC limit for strippers is 350 g/l. San Diego County Air Pollution Control District (SDAPCD) Rule 67-11 Section (d)(5)(i) has a limit of 200 g/l for strippers. We recommend that the district include this lower limit in the rule.

Section 306 provides for a rolling 30 day averaging period for compliance with the rule's emission limits. Please confirm that District policy interprets any violation of the averaging period as a violation of each day of the averaged period. EPA recommends inserting language similar to the following to clarify this in the rule: "Any rolling 30-day averaged value which exceeds the applicable emission limit shall constitute a violation of the rule for each day of the averaged period."

Section 110.4 exempts the coating of architectural components or structures, not coated in a shop environment. We recommend that the District add rule language to Section 110.4 to clarify that the exempted wood products are still subject to the requirements in the District's architectural coatings rule.
We noticed that several other California rules have more stringent requirements than Rule 463. Please consider making Rule 463 limits as stringent as the following limits from other rules.

Sources using less than 55 gallons per year of wood product coatings and/or strippers are exempt from the requirements of this rule. BAAQMD Rule 8-32, SJVAPCD Rule 4606, and Santa Barbara County Air Pollution Control District (SBAPCD) Rule 351 limit this exemption to 20 gallons per year.

The VOC limit for “High-Solid Stain” in Section 302.2 is 350 g/l. SJVAPCD Rule 4606, SBAPCD Rule 351, and VCAPCD Rule 74-30 all have a limit of 240 g/l for this category.

The VOC limit for “Sealer” in Section 302.2 is 275 g/l. VCAPCD Rule 74-30 has a limit of 240 g/l for this category.

Rule 464, Organic Chemical Manufacturing

While the recordkeeping provisions in Section 501.4 through Section 501.7 require sources to keep daily records on-site of the types and amounts of organic compounds used for continuous processes as well as information about each production batch for batch processes, they do not specifically require sources to record the VOC content of the materials used. We recommend adding a recordkeeping requirement specifically for the VOC content of materials used.

Rule 466, Solvent Cleaning

Section 110.4 exempts the cleaning of the nozzle tips of automated spray equipment from the requirements of Section 302.2. Section 302.2 is one of many options that sources can pick from in order to be in compliance with the rule’s requirements for cleaning devices and methods. Please ensure that the reference in Section 110.4 to Section 302.2 is correct.

The District is widening the applicability of the rule by including VOC content limits for the sterilization of food manufacturing and processing equipment. We recommend clarifying this in Section 102, Applicability.

To further clarify the applicability of the VOC limits in table 301.1, we recommend adding a definition for pharmaceutical product and general work surfaces. Potential draft language can be found in SCAQMD Rule 1171.
August 20, 2008

Mr. Jimmy Cheng
SMAQMD
777 12th Street, 3rd Floor
Sacramento, CA 95814-1908

Subject: Proposed Revisions to SMAQMD Rule-450, Graphic Arts Operations

Subsequent circumstances since the public workshop on Rule-450 have raised a compliance issue relevant to section 302.2 of the rule. The Office of State Publishing (OSP) has discovered that a violation of section 302.2 can occur when the amount of blanket/roller wash usage is reduced but plate cleaner/metering roller cleaner usage remains steady. We request the SMAQMD consider deletion of the current usage ratio in section 302.2 all together instead of delaying the action until January of 2010 as proposed in the revisions.

The OSP has been using new lower-VOC (volatile organic compound) blanket wash for the last two months and discovered that smaller quantities of this wash are needed to do the job when compared to washes previously used. This factor has already made a substantial impact on reduction of VOC emissions and waste generation at OSP. Unfortunately, this situation creates solvent usage ratios that exceed the 15% limit in section 302.2 of Rule-450 because our plate cleaner and metering roller cleaner usage is relatively the same from month to month.

Contact me at (916) 327-4174, FAX (916) 323-4342 or e-mail don.eggleston@dgs.ca.gov if you have any questions.

Sincerely,

[Signature]

DONALD G. EGGLESTON
Environmental Coordinator