SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

Final Report for
2004 Technology Assessment for Small Degreaser Exemption
Under Rule 1122- Solvent Degreasers

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Background

Rule 1122 - Solvent Degreasers was adopted on March 2, 1979 primarily to control VOC emissions from solvent degreasing operations. The rule establishes both equipment and operating requirements for any type of solvent degreasing operation. Industries subject to the provisions of Rule 1122 include any industrial, commercial or institutional facility that operates degreasing equipment that removes contaminants as part of their production process.

During the last several years, the AQMD Governing Board approved sweeping changes to the way degreasing is conducted in the South Coast Air Basin. The 1997 and 2001 amendments to Rule 1122 significantly lowered VOC emissions from degreasing operations, and the rule now requires the use of ultra-low VOC cleaning materials (25 grams/liter or less VOC content) in batch-loaded cold cleaners. Batch-loaded cold cleaners are batch-operated degreasers that are designed to contain liquid solvent, and are always operated at a temperature below the solvent's boiling point. Today, aqueous cleaners and VOC-exempt solvents that meet the VOC requirements of the rule are being used in most degreasing applications.

However, Rule 1122 still provides a limited exemption, under section (k)(1)(D), that allows for the continued use of high-VOC solvents until January 1, 2005 for certain types of cleaning applications. The exemption applies only to small batch-loaded cold cleaners and vapor degreasers with open-top surface areas less than 1 square foot, or with a capacity of less than 2 gallons. In addition, such equipment must be used only for electrical, high precision optics or electronics applications; or aerospace and military applications for cleaning solar cells, laser hardware, space vehicle components, fluid systems, and components used solely in research and development programs, or laboratory tests in quality assurance laboratories. Solvent usage per piece of equipment subject to the exemption is limited to 5 gallons per month.

This exemption was added to the rule in 1997, and then extended for two years in 2002, to give industry additional time to research and test alternative cleaning technologies. In September 2002, AQMD staff completed a technology assessment, the results of which were used to justify the two-year extension of the exemption.

Currently, Rule 1122 requires that another technology assessment be performed in 2004 in order to evaluate the progress made by the affected industries in finding alternative cleaning systems. Furthermore, the study will determine whether it is necessary to continue the exemption identified in section (k)(1)(D) beyond the existing sunset date of January 1, 2005.

In the past several weeks, AQMD staff has conducted site visits (8) and telephone surveys (20) to facilities affected by the exemption to determine progress made in testing alternative cleaning methods and solvents that comply with the 25 gram per liter VOC limit in Rule 1122. A technical panel, comprised of representatives from various industries directly affected by the exemption, was also formed to assist AQMD staff in reviewing existing cleaning technologies as well as evaluating the need for the exemption for those cleaning applications identified in section (k)(1)(D).

This report updates the 2002 Technology Assessment and presents new information obtained from AQMD staff's fieldwork as well as input from the Technical Panel on available cleaning materials and technologies. In addition, data from research studies conducted by the Institute for Research and Technical Assistance (IRTA), an AQMD contractor, are also incorporated in this Technology Assessment report. The report concludes with a recommendation regarding the small-sized degreaser exemption.

Cleaning Effectiveness of Solvents

Immersion cleaning is the method widely used for the cleaning applications covered by the rule exemption. This cleaning method refers to dipping or soaking of parts in a liquid bath (usually organic solvent) at room temperature with no agitation and relies primarily on the solvent's cleaning effectiveness.

The cleaning effectiveness of an organic solvent relies heavily on three fundamental solvent properties: chemical solvency, polarity of the solvent, and surface tension. The chemical solvency of a solvent is measured by its Kauri-Butanol (KB) value. The KB value is an indication of the dissolving power of a solvent, and is used to compare the strength of organic solvents. The higher the KB value, the stronger the solvent's dissolving power or solvency to a specified oil or soil.

Solvent polarity is also an important factor in determining the effectiveness of the cleaning solvent for a particular type of soil or contaminant. As a general rule, a polar solvent will remove polar contaminants while a non-polar solvent removes non-polar contaminants. Water is a polar solvent, and therefore it will remove ionic contaminants.

Surface tension of a solvent is important when "blind holes" or very small gaps are part of the geometry of the part being cleaned, as in the precision cleaning of some high-tech electronics and aerospace parts. The lower the solvent surface tension, the more penetration the solvent will have. Water has a relatively high surface tension (0.00499 lb/ft at 68° F) compared to isopropyl alcohol (0.00149 lb/ft at 68° F). Surfactants, emulsifiers, saponifiers and other additives (along with heat) provide the cleaning mechanisms for most alkaline water-based materials. Surfactants lower the surface tension of water, and are used in aqueous cleaners to provide detergency and emulsification. Emulsifiers allow non-water-soluble soils to be cleaned with aqueous solutions and keep these soils dispersed throughout the cleaning fluid. Saponifiers are chemicals designed to react with organic fatty acids, such as rosin-based fluxes, to form a water-soluble soap. They also assist in surface tension reduction.

To improve cleaning effectiveness, heat is applied and/or agitation may be added to the water-based cleaning solutions provided the parts to be cleaned can withstand the agitation. The most common forms of agitation are high and low pressure sprays (from 40 psi to greater than 500 psi), and ultrasonic cavitation, which is produced by a transducer that can be mounted on the outside or inside of the cleaning equipment. Surfactants, emulsifiers and saponifiers are rinsed off in successively higher quality water so as to optimize the removal of contaminants. Once cleaned, the parts are dried. This is accomplished with air knife fans, heating in ovens, or simply using hot air.

The cold cleaning activities listed for the small-sized degreaser exemption in Rule 1122 (k)(1)(D) are referred to as precision cleaning activities. Precision cleaning reflects a specified level of contamination after cleaning. Different specifications are written for different manufactured parts. Although commercial components may have different cleanliness specifications, it is generally the military and NASA specifications that result in more demanding levels of cleanliness. These specifications, however, have become more tolerant of alternative cleaning materials and have recognized their effectiveness in cleaning to more precise specifications. In fact, many aerospace companies and their contractors have led the industry in advances in low-VOC cleaning technology.

Industries Subject to the Rule Exemption

Aerospace and military operations and their subcontractors use a variety of chemistries ranging from zero-VOC (exempt) solvents to high-VOC cleaning materials for their cleaning. Since the rule was last amended in December 2002, many companies have researched and converted to alternative cleaners such as acetone, aqueous, soy-based cleaners, etc. such that they no longer need to use this exemption. However, these conversions have not occurred across-the-board. Space vehicle components are particularly high–reliability electronics components and continue to present the greatest challenge to low-VOC cleaning. Cleaning practices for such applications have remained relatively unchanged in the industry. The obstacles are the same as those that justified the recent amendment found in Rule 1122 (k)(2) that exempts the cleaning of parts used for travel beyond the earth's atmosphere. These obstacles include the inability to perform repairs in space and a reluctance to change effective cleaning procedures where high-reliability is required.

Industries still using the (k)(1)(D) exemption are aerospace, military, electronics and communications manufacturing companies, and their subcontractors. Parts being cleaned include satellite circuit boards, microelectronics, hybrid circuit boards, electronic and electrical components, and high precision optics where high product reliability is of great importance.

The September 2002 Technology Assessment initially identified eleven (11) facilities utilizing the limited exemption in rule section (k)(1)(D). Most of these companies belong to the aerospace and optics industries. Subsequent to the 2002 rule amendment that extended the small-sized degreaser exemption, AQMD staff initiated a study to identify other facilities that may fall under the limited exemption in Rule 1122. As a result of the study, staff was able to identify twelve (12) additional facilities that use the exemption mostly for cleaning electrical or electronic components, and optics. Consequently, the VOC emissions inventory presented in the September 2002 Technology Assessment increased by six (6) pounds per day to thirty-seven (37) pounds per day.

However, the most recent data obtained from numerous site visits and telephone calls to facilities affected by the exemption indicate that the exemption for most of the cleaning applications identified in (k)(1)(D) is no longer needed. Many facilities (particularly in the optics industry and electrical component manufacturing) that used the exemption have successfully converted to alternative cleaners such as aqueous and soy-based cleaners, and/or VOC-exempt solvents since the last rule amendment in 2002. Other companies continue to test alternative cleaning systems. Because of such conversions, the number of facilities and associated emissions has decreased during the last two years.

Table 1 provides a list of known facilities that use high-VOC solvents in small batch-loaded cold cleaners as allowed under the exemption provision in Rule 1122 (k)(1)(D). The information presented for each facility includes the type of cleaning operation, contaminants removed, and cleaning solvents currently used. Many of the companies that continue to use high-VOC solvents are engaged in the manufacture of high-reliability electronic parts and components used in aerospace and military applications.

Table 1 – Facilities Using Rule Exemption

Company Name	Primary Operation	Types of Contaminants Removed	VOC Solvents Used Under Exemption
Boeing Satellite Systems	Satellite circuit boards; microelectronics	Rosin flux; plating residues; flux activators; particulates; oils	Isopropyl Alcohol (IPA)
Raytheon	Military microcircuit boards; high precision optics	Rosin flux; plating residues; flux activators; particulates; oils	IPA; Ethanol; Hexane
Northrop Grumman Space Technology (formerly TRW)	Space research and development; solar cells; electronics, housings for electronic chips	Rosin flux; plating residues; flux activators; particulates; oils	IPA; IPA/Methylene Chloride; Methanol
Teledyne Electronic Technologies	Microelectronics; custom hybrid circuit boards; fiber optics	Rosin flux; plating residues; flux activators	IPA; IPA/Cyclohexane, n-Propyl Acetate; n-Methyl Pyrrolidone
Union Technology Corp.	Capacitors	Rosin flux; plating residues; flux activators	Ultrasonic Ethyl Acetate; IPA rinse
Newport Optics	Prisms; lenses; mirrors; windows	Polishing and lapping compounds; pitch	Acetone/n-Propyl Bromide
Rand Precision Optics	Prisms; lenses; mirrors; windows	Polishing and lapping compounds; pitch	Citrus-based Cleaner

Table 1 - Continued

Company Name	Primary Operation	Types of Contaminants Removed	VOC Solvents Used Under Exemption
Matrix Systems	Circuit boards	Rosin Flux	Ultrasonic IPA
Southern Electronics Co.	Capacitors	Rosin flux	IPA
Customs Suppression	Capacitors	Rosin flux	IPA
Sota Corp	Fuel pump; circuit board	Rosin flux	IPA
CommOptics	Prisms; lenses; mirrors	Polishing compound; pitch	IPA
Rolyn Optics	Prisms; lenses; mirrors	Polishing compounds; pitch; wax	Citrus-based cleaner

The total VOC emissions associated with the (k)(1)(D) exemption are very low. This is primarily due to the recycling of spent solvents and current work practice of covering the containers during and after part soaking. The average daily emission rates, as provided by the affected facilities, represent the most current emissions data from small degreasers exempt under the rule. Table 2 summarizes the average daily emission rates for each facility.

Table 2 – Emissions Inventory

Company Name	Average Daily Emission Rate (lb/day)
Boeing Satellite Systems	5
Matrix Systems	0.5
Southern Electronics Co.	1

Table 2 - Continued

Company Name	Average Daily Emission Rate (lb/day)
Newport Optics	2
Customs Suppression	0.2
Sota Corp	0.3
CommOptics	1
Rand Precision Optics	2
Raytheon	3
Teledyne Electronic Technologies	2
Northrop Grumman Space Technology	1
Union Technology Corp.	5
Rolyn Optics	2
Total	**25 lbs/day (0.0125 ton/day)**

Current Cleaning Practices

The current cleaning practices of the majority of the industries subject to the Rule 1122 exemption have remained relatively unchanged since the 2002 rule amendment. Typically, bench-top cleaning occurs at specific work areas where parts are soaked in beakers, Pyrex "casserole" trays, or ultrasonic degreasing units containing VOC solvent. Such cleaning containers are situated in a clean room and under a hood for adequate ventilation of the vapors. While some aerospace companies already use water and waterborne chemistries to clean a variety of metal housings and circuit boards, cleaning with VOC organic solvents is often faster and simply more convenient than water. These organic chemicals are also perceived to be a more reliable mechanism for precision cleaning. Other concerns with aqueous or low-VOC cleaning for high-reliability applications expressed by some industries include the potential for contamination and corrosion.

Cleaning of high precision electronic circuit boards continue to be the greatest challenge to the aerospace and military industries in finding acceptable substitute cleaners. The industries' main concern with waterborne cleaning is the non-volatile residue (NVR) level and corrosion potential in high precision electronics application. NVR is determined through a cleanliness verification test that measures the non-volatile residue remaining on the part after cleaning. The higher the NVR, the more contaminated the part.

In high precision electronics, parts mounted on circuit boards are spaced closely between each other and the gap between the parts and the circuit board is very small (<3mm). Such tight spacing can be a source of problems because of the difficulty to flush “soils” out and obtain acceptable ionic contamination levels. According to Northrop Grumman Space Technology (formerly TRW), Boeing Satellite Systems (Boeing) and Raytheon Company (Raytheon), liquid entrapment and corrosion do occur when cleaning densely packed printed wire board components with aqueous cleaning methods. Boeing cited an instance when a multi-component module (MCM) used for military aircraft radar systems failed during performance testing due to water trapped underneath the MCM. However, these companies have also indicated that they continue to actively seek alternatives to their existing VOC solvent cleaners.

a) VOC Organic Solvents

The traditional method for cleaning parts is through the use of VOC organic solvents. Organic solvents commonly used today as degreasing agent are typically alcohols (isopropyl alcohol, ethanol, methanol, etc.) or blends of isopropyl alcohol with cyclohexane. Other VOC solvents used include normal methyl pyrrolidone (NMP), normal propyl bromide (NPB), hexane, and VOC-enhanced hydrochlorofluorocarbon (HCFC) 225, hydofluoroethers (HFEs), and hydrofluorocarbon (HFC) 43-10.

Alcohols are often used to dry parts after water-based cleaning due to their affinity for water molecules, and as cleaners in precision applications. They are commonly used in the removal of ionic particles such as electroplating salts and rosin activators used during the manufacture of military and aerospace circuit boards. The most widely used alcohol is isopropyl alcohol (IPA). IPA is also used to remove rosin flux on electrical components such as capacitors, and for removing pitch and polishing compounds in high precision optics manufacturing. Alcohols are also good rinsing agents for other hardware. In addition, alcohols remove light oils and fingerprints. Cyclohexane or other non-polar solvents are often added to IPA to boost its cleaning effectiveness. However, alcohols are not effective on non-polar soils such as waxes and heavy oils. IPA can be used in a vapor degreaser, but only with adequate fire suppression systems because of its flammability.

N-methyl pyrrolidone (NMP) and n-propyl bromide (NPB) are used in the high precision optics industry to remove pitch and wax off of mirrors, prisms, windows, and lenses. These parts undergo certain lapping and polishing procedures to obtain the desired shapes and improve optical characteristics. During this process, mounting blocks, wax and pitch are used in order to hold parts in place. The parts are then cleaned to remove the lapping, polishing, and blocking compounds. NPB, a VOC solvent with no flash point, is typically used in a vapor degreaser.

“Designer chemicals,” such as blends of AK-225 solvent, are used in some precision cleaning but mostly for electronics applications. In its pure form, the AK-225 chemical is a zero-VOC material since it contains mostly HCFC-225, a VOC-exempt compound. It has the highest KB value of all the new designer chemicals. Since the solvent is non-polar, some alcohol (e.g., ethanol) is added to remove the polar contaminants; thus, increasing the VOC content of the solvent blends up to 200 grams per liter. The solvent is mostly used in vapor degreasing rather than cold cleaning. However, the production of HCFC-225 is to be phased out in 2015 because of its ozone-depleting potential. Also, it has a 100-ppm exposure limit on an 8-hour time-weighted average. Low exposure limits are indicative of higher toxicity.

Other designer chemicals used in vapor degreasing are blends of HFEs (manufactured by 3M) and HFC 43-10 (sold under the trade name Vertrel and manufactured by Dupont). Similar to HCFC-225, HFE and HFC 43-10 are VOC-exempt solvents in their pure forms. These chemicals have low solvency as reflected by their KB values of 10 and 9, respectively. In order to increase the cleaning efficacy of these chemicals, VOC additives, such as trans-dichloroethylene, cyclohexane, cyclopentane and low molecular weight alcohols, are blended in; thereby increasing the VOC content of the mixture to as much as 650 grams per liter.

b) Alternative Cleaners

Many alternative cleaning solvents, such as VOC-exempt solvents, aqueous cleaners, and soy-based materials have been developed. Acetone, a highly volatile organic solvent, has gained wide acceptance as an alternative to VOC solvents. Acetone is used for cleaning in small batch-loaded cold cleaners particularly in optics manufacturing. The solvent used can be from low grade up to reagent grade acetone. Since acetone is a polar solvent, it effectively removes ionic contaminants and other oils, and is a de-blocking agent for waxes. It also has an affinity for water and, as such, is a good drying agent for wet parts. Blends of acetone are formulated with non-polar solvents so that both ionic and non-ionic contaminants can be removed. Recent data indicate that acetone is also used by industry in wipe-cleaning applications for cleaning electrical components and optics. Wipe-cleaning applications are covered under Rule 1171.

From an air quality standpoint, acetone is a VOC-exempt material and therefore is a preferred solvent. However, it is extremely flammable, with a flash point of 15°F (in an open cup). It can be diluted with water at various percentages to reduce its flammability and still display acceptable ionic cleanliness results. Like other flammable liquids, acetone should be used with extreme caution with proper safeguards in place for handling storage.

Other VOC-exempt solvents currently being used as alternative cleaners are pure HCFC-225, HFE, and HFC 43-10. These solvents are used mostly in cleaning certain electronics and electrical parts.

Water or aqueous systems (washing, rinsing, and drying) are employed in a wide variety of precision cleaning operations, e.g., certain electronic and electrical components, optics, and fluid systems. These aqueous systems replace beakers, buckets and trays of solvents. Aqueous solutions consist of three pH types: acidic, neutral and alkaline. Acid aqueous solutions are water-based mixtures with pH less than 7. Such aqueous solutions are used to remove scale, rust and oxides from metals. The cleaners may contain mineral acids (e.g., hydrofluoric, sulfuric), chromic acids or organic acids, detergents, and small amounts of water-miscible solvents. The choice of aqueous solutions and additives depends on the type of metal to be cleaned and the type of soil to be removed.

Alkaline aqueous cleaners are the most commonly used. They have a pH greater than 7, and can be used to remove a variety of soils and oils. Most alkaline aqueous cleaners range from pH 10 to 14. Alkaline cleaners contain additives such as surfactants/detergents, inhibitors, sequestering agents, emulsifiers, and/or saponifiers to aid in cleaning. Due to the level of specified cleanliness in precision cleaning applications, parts cleaned in water-based chemistries need to be completely rinsed in demineralized and/or deionized water to remove the products of the reaction with the contaminants, as well as any suspended particles. Drying of the component is also necessary to aid in the prevention of water spots, corrosion, and other residues. Water (neutral) can also be used to remove surface contamination typically through spray mechanisms or steam cleaning.

Soy-based cleaners, a relatively newcomer to the industry, are also being used to remove certain contaminants. Such cleaners, composed of methyl esters, are excellent, safe and cost-effective alternative solvents. The cleaner provides good solvency, has a very low VOC content and a high flash point, and is compatible with most surface materials and other organic solvents. Methyl esters are currently being used in optics manufacturing to remove pitch and wax. However, this solvent is not expected to be a viable replacement in high precision electronics cleaning because of its slow evaporation rate resulting in oily residue on the substrate being cleaned.

Low to No VOC Cleaning

The AQMD contracted the services of IRTA to evaluate low and non-VOC technologies and their application to AQMD cleaning rules. IRTA, a non-profit organization, has converted many companies from VOC and/or halogenated solvent degreasing into a variety of low and non-VOC technologies.

Two research studies completed by IRTA concluded that alternative cleaners are available for many solvent cleaning applications. Reports of the studies, which contain examples of companies that have converted to low and non-VOC cleaning systems, were submitted to the AQMD in September 1999 and August 2003. In addition, through several site visits, staff has identified more companies using low-VOC and no-VOC materials for cleaning purposes. Some of these companies were previously identified as using VOC solvents during the 2002 Technology Assessment, but have since converted to alternative cleaning solvents. Some of these conversions are discussed in the next section of this report.

Water-based cleaners, VOC-exempt compounds, soy-based products and other alternative cleaning techniques, such as CO_2 snow, plasma etch, and laser ablation, are examples of low to no VOC cleaning systems. Each of these options (as with any organic compounds or blends) should undergo a case-by-case study when evaluating potential conversion for a particular cleaning application.

There are a limited number of exempt compounds that are being used for cleaning. The VOC-exempt NESHAP chemicals such as 1,1,1-trichloroethane (TCA), methylene chloride (MeCl), perchloroethylene (Perc), and carbon tetrachloride are either toxic, global warming, or ozone depleting compounds. As a result, it becomes difficult to obtain air quality permits due to AQMD's 1400-series toxic rules, or the quantities are limited due to production banning. In addition, Rule 1122 now prohibits the use of NESHAP halogenated solvents for degreasing operations unless such cleaning operation is performed in an airless/air-tight cleaning system.

The most promising exempt compounds are acetone, HCFC-225, HFEs, and HFCs. Acetone has low toxicity, but is highly flammable and is aggressive to soft plastics and even on some hard plastics like PVC and acrylic. It is a polar material and will remove only polar species. The other three VOC-exempt compounds are very expensive and have relatively low KB values (low solvency) and may not be effective in cold cleaning applications. HCFC-225 has the highest KB value of 31. This solvent works best when combined with VOC polar solvents, such as ethanol. HCFC-225 is an ozone depleter and production will be banned in 2015. HFCs and HFEs are global warming compounds and may be regulated in the future.

Methyl acetate, another exempt material, has not shown great promise for use in most precision cleaning applications. Tertiary butyl acetate (TBAc) has been evaluated as a good solvent for cold cleaning applications. However, approval of this material by EPA as a VOC-exempt solvent is still pending. Low-VOC methyl esters (soy) have proven to be good substitutes for VOC solvents in high precision optics cleaning.

Staff has identified cleaning applications currently exempt under section (k)(1)(D) of Rule 1122 where aqueous or low-to-no-VOC cleaning materials have successfully replaced high-VOC solvents. These applications are discussed in the succeeding paragraphs.

Successful Conversions and Obstacles to Low and No VOC Cleaning Systems

A. Optics and Laser Hardware

For purposes of this discussion, high precision optics refers to electro-optical devices that include laser optics with hardware, infrared sensors or detectors used primarily for military and aerospace applications, and fiber optics.

Vapor degreasing with n-propyl bromide is the cleaning method widely used by the optical device manufacturing industry for removing wax and pitch from high precision optical devices. Semi-aqueous systems are also used for this type of cleaning application. The examples below depict cases where conversions to aqueous cleaning and frozen CO_2 have been successful. Generally, the removal of wax and pitch presents the biggest challenge to aqueous cleaning of optics. Anti-reflective coatings are applied after cleaning the glass components; thus, the level of cleanliness is very important with regard to the quality of the applied coating. In order to successfully clean with aqueous cleaners, it is generally recognized that bath temperatures of at least 180°F, combined with spray or other forms of agitation and hot water rinsing, must be used.[1] Carbon dioxide (CO_2) snow is being used to clean optics prior to coating. This process uses soft

[1] Elizabeth A. Bivens, Steven B. Hayes, Wax and Pitch Compound Removal: Refining the New, Revisiting the Old, December 1977

"snow flakes" of frozen CO_2 gas to clean surfaces. Supercritical carbon dioxide is being used on fiber optics.

Northrop Grumman Navigation Systems Division (formerly Litton Guidance and Control Systems) manufactures a variety of precision optical devices (e.g., laser guidance systems for commercial and military aerospace applications including spacecraft and aircraft missiles). Frames, as well as other fixturing devices, are used in the optics manufacturing processes. The high precision optic parts are lapped and polished and blocking materials are used to hold the parts in place during these operations. The parts are cleaned in several steps of the process to remove the lapping, polishing and blocking compounds.

Process changes have been made by Northrop Grumman to substitute other materials for wax and pitch, which act as blocking and holding media. Epoxy is now used to bond frames to holding fixtures and is subsequently debonded with hot air at a temperature of 200°F. The thermal differences between the glass frame, metal fixture, and epoxy cause the debonding. In the bonding operation, pitch has been replaced by thermoplastic to hold mirrors in place during polishing and lapping. Wax, which was used to plug the frame bores to prevent lapping compound from intruding, has been eliminated. Instead, O-rings are now being used to block the frame bores. Acetone and aqueous cleaners have replaced n-methyl pyrrolidone and terpene-based solvent in removing the thermoplastic.[2] Acetone is used for initial deblocking of the thermoplastic under a fire suppression fume hood.[3] However, a representative from Northrop Grumman recently informed AQMD staff that IPA is still being used as final rinse for the frames to remove water residues prior to assembly of the optical parts.

Northrop Grumman is not the only high precision optics company that has converted to aqueous and/or VOC-exempt solvent (acetone) cleaning. Pacific Coast Optics, formerly J.L. Wood Optical, specializes in the design, development, and manufacture of precision optical systems for use in military, scientific, and commercial applications. The company previously used methyl alcohol and dichloroethane for removing wax and pitch from the optical parts and fixtures (tooling), but switched to an alkaline aqueous cleaners and acetone in 2002. Recently, the company stopped using the alkaline aqueous cleaner because of water residue left on the optics and corrosion problems on the tooling used to hold the optics. Staff believes that the use of other aqueous cleaners with anti-corrosion agent and de-ionized water for rinsing optics may eliminate these problems. However, the company continues to use acetone for cleaning optics and tooling during the manufacturing process. In addition, the optic components are wipe-cleaned with acetone prior to the optical coating process. Such wipe-cleaning operation falls under Rule 1171.

Optical Components is another example of an optics manufacturer that successfully converted to alternative cleaners. The company is a supplier of precision optical components and finished assemblies (e.g., lasers and infrared sensors) mostly for military and defense applications. Optical Components previously used Perc in a vapor degreaser to clean optics. Since Rule 1122 prohibits the use of NESHAP halogenated solvents for degreasing operations after 2002, the company converted to a zero-VOC soy-based

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[2] Katy Wolf/Mike Morris, Evaluation of Low and Non-VOC Technologies: Application to SCAQMD Cleaning Rules, Sept. 1999

[3] Gary Augeri, Litton Guidance and Control Systems, Letter to Pyramid Optical, March 28, 2001

(methyl ester) cleaner for cleaning optics and tooling. The optic components are soaked in a bath containing methyl ester for about 20 minutes to remove pitch and polishing compound. The parts are then rinsed in hot water. According to a company representative, a small amount of dishwashing liquid soap is added to the (hot) water to ensure that no water stains are left on the optics after rinsing. If coating of the optic components is required, the parts (optics) are again cleaned in soapy water followed by an acetone rinse. Acetone removes any residual water left on the optic component.

Harold Johnson Optical Laboratories manufactures high-precision optics for commercial and military applications. During the 2002 Technology Assessment, AQMD staff reported that the company was using IPA to remove pitch and polishing compounds from optic components. Since then, the company switched to the same soy-based cleaner that Optical Components is using for cleaning optics. Warm soapy water is also used as rinsing agent. Acetone is used to wipe-clean the optics prior to coating.

Raytheon Co. develops highly sensitive electro-optical devices such as lasers and infrared sensors. According to Raytheon representatives, these devices fall under the category of high precision optics and cannot tolerate even very small levels of contamination. Raytheon indicated that if particles remain on the laser optics, the energy of the laser will burn the optic and cause less than optimal performance.

Raytheon uses VOC solvents and blends of exempt compounds, in conjunction with water-based cleaners, for cleaning laser optics and mechanical housing systems. Water is used as a first-step process. However, test results indicate that the level of cleanliness required is more than the aqueous system can attain. Subsequent cleaning is performed using a 50/50 blend of acetone and hexane to remove both polar and non-polar contaminants. Parts are then flushed with IPA and/or ethanol. Cleanliness verification testing is performed using a photospectrometer. According to Raytheon, the company has tested tertiary butyl acetate (TBAc), with very promising results, for wipe-cleaning applications. The company has also indicated that TBAc may be used in batch-loaded cleaners as well, as an alternative for the high-VOC solvents used in its optics cleaning process. This solvent is in the process of being de-listed as a VOC and approval of this material by EPA as a VOC-exempt solvent is still pending.

Despite Raytheon's claim that high-VOC solvents are necessary for high precision optics cleaning, staff believes that there is enough evidence to show that alternative cleaning technologies are available that could meet their cleanliness requirements for high precision optics and laser hardware. Low-VOC cleaning processes are currently being used by several companies for such applications. Some of these companies supply Raytheon with optical products.

B. Electronics

Hydro-Aire, an aerospace company that manufactures hydraulic braking systems for aircraft, switched from vapor degreasing using TCA to water-based cleaning in its printed circuit board defluxing operation. This company must adhere to a military specification that requires the use of rosin flux. Rosin flux is removed in a dishwasher-type water system (impingement cleaning) using an aqueous saponifier for flux residue removal.

The cleaning system operates on a 50-minute cycle that involves washing, rinsing and drying.[4]

Other companies are also using water to clean rosin flux from printed wiring electronic assemblies. These include Raytheon, formerly Hughes, and Boeing. Raytheon is using a water-based alternate technology in lieu of chlorofluorocarbon (CFC). The company developed a water-based cleaning system known as Reactive Aqueous Defluxing System (RADS) to remove flux of various types from electronic hardware. RADS is a three stage cleaning process (wash, rinse, and dry) that is identical to the conventional aqueous cleaning process and contains no VOCs. The first stage (reaction stage) involves the use of a chemistry called ECOSOLVE. This reaction phase chemistry is designed to emulsify and decompose rosin-based flux in an alkaline media, and is combined with a surface tension reducer for penetration of the fluid into small spaces and holes. Two rinse stages remove the alkaline carryover fluid from the reaction stage and subsequent ionic trace contaminants. A third rinse in deionized (DI) water completes the rinse stage. Finally, hot compressed air is used to remove and dry any residual moisture underneath the surface-mounted electronics, as well as any water remaining in and around through-hole components.[5]

RADS is an in-line cleaning process and takes about 15 minutes to complete the cleaning cycle. Raytheon's cleanliness data reflects that RADS attains higher levels of contaminant removal than the VOC-containing aqueous saponifiers. Boeing Satellite Systems also cleans some circuit boards with ECOSOLVE. Where automated assembly is occurring, hot DI water is used to clean water-soluble flux.

IPA is still used in small quantities by these companies for rework of electronic boards that are hand-soldered. The companies have stated that they rely on IPA primarily because of part sensitivity to water. Raytheon also has an automated vapor degreaser containing HCFC-225, blended with ethanol, which is used for the removal of both ionic and non-ionic contaminants.

Bench top defluxing using VOC-exempt solvents, such as acetone and methyl acetate, have been explored. Both solvents performed well at removing rosin, but not as well as IPA at removing residual ionics. Further testing was performed using these organic solvents diluted with DI water (at various dilution ratios) to determine its capability to solubilize ionic contaminants. Available data on ionic cleanliness shows that cleaning with 100% IPA has the least amount of ionic contamination.[6]

Boeing Satellite has tested cold batch cleaning of satellite components using different alternative cleaning solvents: linear volatile methyl siloxane (VMS); parachlorobenzotrifluoride (PCBTF); AK 225 blend; methyl acetate; 2-butoxyethanol (Yellow Magic); and 5% acetone/water mixture. Isopropyl alcohol was used as baseline during the testing. According to a Boeing representative, the VMS and PCBTF solvents

[4] Katy Wolf/Mike Morris, Evaluation of Low and Non-VOC Technologies: Application to SCAQMD Cleaning Rules, Sept. 1999

[5] Ronald E. Robbins, A Water-based Alternative to CFCs for Flux Removal from Electronic Hardware, Sept. 1994

[6] William Elias, Real Life Applications with Environmentally Compliant Solvent for Electronics Assembly, February 1999

left insoluble residue on the boards. In addition, Yellow Magic also produced a hydrolyzed white insoluble residue on the test boards. The AK 225 blend (25 g/l VOC) and 5% acetone/water mixture passed the ionic contamination test but both failed compatibility with conformal coat. Methyl acetate, an exempt solvent, did not perform well in removing residual ionics.

Cleaning to a lower level of contamination is essential for electronic components used in space and certain military applications. Companies have tested many alternative cleaning materials but have not found an acceptable substitute to existing high-VOC cleaning methods. However, research and testing by these companies continue in an effort to find suitable replacement solvents for cleaning high reliability electronic components.

C. Solar Cells

Northrop Grumman Space Technology (formerly TRW) uses a 50/50 mixture of IPA and methylene chloride, or a 50/50 mixture of HCFC-225 and methylene chloride (equal to zero VOCs since both are exempt compounds) for de-glassing of solar cells. Previously, de-glassing was identified as a cleaning operation and thus, covered under Rule 1122. However, AQMD staff further evaluated the process and concluded that de-glassing is not a cleaning operation but rather a stripping operation to remove cured adhesive from solar cells; therefore, de-glassing of solar cells is not part of Rule 1122.

In addition, Northrop Grumman uses an AQMD-permitted IPA spray cleaner to deflux solar cell circuits prior to bonding. Such cleaning operation falls under Rule 1171. Staff is not aware of any other facility that uses the (k)(1)(D) exemption for cleaning solar cells; therefore, there is no longer a need for this exemption.

D. Electrical Applications

Electrical applications include relay switches, transformers and capacitors. There is consensus among the aerospace companies that water cleaners should not be used for cleaning powered-up components. Leach Corporation designs and manufactures electrical switching and control devices (relay switches) for the aerospace industry. The company uses detergent during the cleaning process. Raytheon has cleaned small transformers with water, but has experienced difficulty in drying the parts. Without complete drying, "short outs" may occur when energized, which is the problem with water and polar solvent in general. However, other exempt solvents such as HCFC-225 in a vapor degreaser can be used in lieu of aqueous cleaning. Teledyne Electronic Technologies also manufactures relay switches, and currently uses pure AK-225 (HCFC-225) solvent for cleaning relays in a vapor degreaser.

Cables used to power circuit boards have also been cleaned with water. However, water causes wicking (capillary action) effects particularly on female connectors. Residual fluids remain inside the cables even after blowing air into the holes for drying. Testing also indicates corrosive effects associated with the use of water. Masking has been tried but was found not to be completely effective.

Cicoil manufactures flexible and cast cables that are used in aerospace and military applications. The company could not use water-based cleaners to remove flux from cables due to wicking effect which may cause failure. IRTA worked with the company to find an alternative cleaner. Today, Cicoil uses a 50/50 mixture of acetone and IPA (400 g/l VOC content) for flux removal in hand-wipe cleaning application. Hand-wipe cleaning falls under Rule 1171.

Johanson Dielectrics manufactures multi-layer ceramic capacitors (MLCC) for aerospace, military, medical, telecommunications, and other commercial applications. The company uses water-based chemistries for cleaning the capacitors, with centrifuge drying. No organic solvents are used for cleaning.

Novacap, a manufacturer of similar MLCC products and stacked capacitors, uses a heated aqueous cleaner in small (< 1 ft^2 open-top surface area) ultrasonic degreasing units to remove oils and rosin flux from capacitors. The company previously used Perc as cleaning solvent. Aqueous cleaning time is approximately 20 minutes. De-ionized water is used to rinse the capacitors, which are then placed in an oven for subsequent drying. For stacked capacitors, the company uses the same aqueous cleaning system to remove rosin flux from the leads and in spaces between stacked capacitors. As a result of the conversion to aqueous cleaner, the company realized savings in material and waste disposal costs.

Union Technology Corporation, another manufacturer of ceramic capacitors including stacked capacitors, has not converted to alternative cleaners at this time. The company currently uses ethyl acetate for flux removal and IPA for removing oils from capacitors. During a visit to the facility, AQMD staff informed Union Technology of other facilities with similar cleaning applications that have successfully converted to alternative cleaners (aqueous and acetone). A representative of Union Technology indicated that the company will convert after successful testing of the alternative cleaners.

The data obtained on electrical cleaning applications indicate that alternative cleaning technologies are available for such cleaning applications; therefore, the rule exemption for this specific application is no longer needed.

E. Fluid Systems

Astro Pak is a precision cleaning contractor specializing in the cleaning of high purity gas and fluid systems. It provides precision cleaning services and cleanliness certification for pipes, valves, tubing, components, tanks, hoses and fittings for a wide variety of industries including aerospace, military, pharmaceutical, microelectronics and semiconductor manufacturing. The facility converted their cleaning system from a vapor degreaser, using high-VOC organic solvents, to an ultrasonic water-based cleaning process. The water-based cleaning system, with a wash and two rinses, achieves lower NVR level than the previously used cleaning system (less than 0.700 milligrams per square foot[7]).

Kaiser Electroprecision manufactures high pressure, breathing oxygen valves for the aerospace industry. The company is also a manufacturer of missile casings for the

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[7] Katy Wolf/Mike Morris, Evaluation of Low and Non-VOC Technologies: Application to SCAQMD Cleaning Rules, Sept. 1999

military. For the oxygen valve cleaning process, the valves must achieve NVR levels below 3 milligrams per square foot by industry specification.[8] Valves cleaned with water-based cleaner failed the NVR test. At this time, the company has not found an acceptable substitute for TCA in (open-top) vapor degreasering. Degreasing operation using NESHAP halogenated solvents, such as TCA, is no longer allowed in Rule 1122 unless such operation is performed in a airless-airtight cleaning system. Recently, Kaiser has not manufactured oxygen valves but is actively pursuing different water chemistries for cleaning.[9] Kaiser considers Astro Pak's cleaning process to be cost-prohibitive.

In a recent article at Air Force Link[10], the Air Force Laboratory scientists and engineers at Wright-Patterson Air Force Base, Ohio recently teamed up with Aeronautical Systems Center experts to find a suitable replacement for Freon which was widely-used to clean liquid and gaseous oxygen systems in Air Force aircraft and ground service equipment. Freon has been banned because of its ozone depleting tendencies. According to the article, experts conducted tests on several potential solvent replacements to determine the solvents' ability to clean oxygen system components. The tests revealed that the solvent AK225G offers equivalent cleaning to Freon and has shown to be most effective among the cleaning solvents tested. The Material Safety Data Sheet for AK225G indicates that the solvent is composed of >99% HCFC-225cb, which is a Group I exempt compound under Rule 102. The AK225G is still an ozone depleting substance and its production is scheduled to be banned by 2015. The article indicates that AK225G offers an effective interim solution to existing cleaning solvents.

The information presented by staff indicates that aqueous cleaning and VOC-exempt solvents are effective substitute cleaning materials for cleaning fluid systems.

Alternative Emission Control Systems

While low-VOC content cleaning materials have been identified for most of the cleaning applications covered by the (k)(1)(D) exemption, some members of the Technical Panel indicated a preference for using an alternative emission control system, in conjunction with the use of small-sized degreasers identified in (k)(1)(D), as a compliance option in Rule 1122. The option would allow the flexibility of choosing the most suitable cleaning technology for a particular cleaning application, and at the same time, meet the emission reduction requirements of the rule. In spite of the many successful conversions to alternative cleaning methods, certain members of the panel remain reluctant of taking the risk of fully converting to them. In addition, many AQMD VOC rules provide the option of using alternative emission control systems in lieu of meeting the VOC limits of the rule.

Raytheon currently uses an emission control system (afterburner) to comply with AQMD's other VOC rules. Northrop Grumman Space Technology plans on using ductless fume hoods equipped with carbon filters to reduce emissions from the facility's

[8] Katy Wolf/Mike Morris, Evaluation of Low and Non-VOC Technologies: Application to SCAQMD Cleaning Rules, Sept. 1999

[9] Kieth Petis, Kaiser Electroprecision, Teleconference, April 2004

[10] http://www.af.mil/news/story.asp?storyID=123007186

solvent cleaning operations (Rule 1171). Permit applications for the carbon control systems have already been submitted to the AQMD.

Staff agrees that allowing the use of an emission control system in Rule 1122, for small degreasers identified in (k)(1)(D), would provide added flexibility to the affected facilities in choosing the most suitable cleaning chemistry and/or technology and still meet the requirements of the rule.

Limitations to Water and Exempt Solvent Cleaning

During the last several years, conversion to aqueous and other alternative cleaners (VOC-exempt and soy-based materials) has been successful in many cleaning applications. The number of vapor degreasers in the South Coast Air Basin has significantly decreased in the past five years, and the trend toward aqueous and other alternative cleaning methods is expected to continue. However, there are certain cleaning applications where near term use of solvent-based cleaners may still be needed due to limitations of water and/or exempt solvent cleaners. Examples of such limitations are provided as follows.

1) In high reliability military circuits boards, a high percentage of flux residues (≥50%) can remain under pad mounted surface components due to difficulty of the liquid (aqueous cleaner) to flow in spaces less than 3 mils.[11] Since residual flux is observed through microscopic inspection, a line of sight is necessary, and hidden contamination may go undetected.
2) The use of high-pressure spray and ultrasonic agitation to improve cleaning efficiency can damage wire bonds.
3) When high temperature solder techniques are used (esoteric alloy blends), rosin-based flux will char leaving a carbon-based residue that is difficult to remove. Charred flux requires soaking and scrubbing by hand in organic solvent in order to remove it effectively. Water and/or exempt solvents are not effective cleaners for this application.
4) Printed wiring boards may contain water-sensitive components such as plastic encapsulated microcircuits, tinned wire leads, gold plated wire leads, fine-pitch wire leads on hybrid circuits, and axial leaded passive components (capacitors, diodes, and resistors).[12]
5) Acetone may be too aggressive on soft plastics.
6) Ovens are used to drive residual moisture off when parts are cleaned in aqueous solutions. Thermally cycling electronic parts through an oven at 100 degrees Centigrade for two hours can reduce the overall life of the assembly.
7) Particles left in breathing oxygen apparatus can lead to explosions.

[11] William Elias, Interdepartmental Correspondence, Raytheon, August 1999
[12] Ray Shishido, Boeing Satellite Systems Materials, AQMD Correspondence, April 2001

Conclusions

Most of military and aerospace contractors utilize aqueous and/or exempt solvent cleaners as part of their cleaning process. Since the last amendment to Rule 1122 in 2002 that extended the (k)(1)(D) exemption until January 1, 2005, many of these companies have successfully converted to alternative solvents for cleaning applications involving high-precision optics, laser hardware, electrical applications, and fluid systems. Others remain reluctant to convert. For companies (identified in Table 1) that continue to use VOC solvents for these cleaning applications, staff believes that most of them can readily convert to alternative cleaners. Acetone, aqueous solutions, and soy-based cleaners are examples of these alternative cleaners. However, cleaning of high-reliable electronic components (space vehicle components) using low VOC cleaners has not been completely successful at this point. Companies engaged in such cleaning activities continue to use VOC solvents until acceptable replacements are found. The use of an emission control system, for degreasing operation utilizing small-sized degreasers identified in (k)(1)(D), may be a viable compliance option for these types of cleaning activities.

The emissions associated with the exempt applications are small (25 lbs/day or 0.0125 ton/day). About half of these emissions come from electronics cleaning applications. The remaining emissions come from optics and electrical components cleaning.

Recommendations

Staff recommends the following pertaining to the exemption in Rule 1122 (k)(1)(D):

1. Add language in the rule that allows for the continued use, beyond January 1, 2005, of degreasers with open-top surface areas less than one square foot, or with a capacity less than two gallons only for applications specified in (k)(1)(D), provided such degreasers are vented to a VOC emission control system capable of collecting at least 90%, by weight, of the emissions generated by the solvent degreaser and a destruction efficiency of at least 95% by weight.
2. Establish a permanent exemption for small-sized degreasers used for research and development programs, or laboratory tests in quality assurance laboratories. The VOC emission from cleaning activities associated with these operations is minimal (less than one pound per day).
3. Modify exemption language pertaining to section (k)(2) to include batch-loaded cold cleaners and vapor degreasers with open-top surface areas less than one square foot, or with a capacity of less than two gallons. This allows cleaning of electronic components that are designed to travel over 100 miles above the earth’s surface to continue using VOC solvents until an acceptable replacement solvent is found. All other conditions in section (k)(2) remain the same.