

**Bay Area Air Quality Management District
939 Ellis Street
San Francisco, CA 94109**

**Bay Area 2005 Ozone Strategy
Control Measure SS-4
BAAQMD Regulation 8, Rule 50:
Polyester Resin Operations**



**Workshop Report
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WORKSHOP REPORT

Proposed Amendments to Regulation 8, Rule 50

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I. INTRODUCTION

Bay Area Air Quality Management District (District) Regulation 8, Rule 50 limits the emissions of volatile organic compounds (VOC) from polyester resin operations during manufacturing and repair of composite products. For the purposes of this report, the term “polyester resin” specifically refers to unsaturated polyester resins, one of several resins categorized as thermosetting resins. Polyester resins and other composite materials are used to manufacture and repair recreational and commercial watercraft; recreational vehicle bodies; automotive vehicle bodies and interior parts; commercial and military aircraft parts; bathware products; architectural products; personal computer board parts; pipelines; and storage tanks for the sewage treatment industry and secondary containment for gasoline fuel dispensing components. The District is considering amendments to Regulation 8, Rule 50 to fulfill Bay Area 2005 Ozone Strategy Control Measure SS-4, which directed the District to examine potential further reduction of VOC from polyester resin operations. These operations also emit Hazardous Air Pollutants (HAP), which predominantly consist of styrene.

Currently, Bay Area polyester resin businesses that have permits to operate and are subject to Regulation 8, Rule 50 emit 0.8 tons per day (TPD) of VOC into the region’s atmosphere from the application of resins and gel coats in composite operations. The District estimates that HAP emissions from polyester resin operations are approximately 0.8 TPD also because styrene is the typical monomer used in polyester resin operations, according to industry. Styrene is both HAP and a VOC. An additional 0.5 TPD of VOC are emitted from the use of cleaning products associated with resin and gel coat operations. These VOC emissions are solely from permitted polyester resin facilities. They do not include emissions from other thermosetting resin operations which will be discussed later in this report.

Staff estimates that proposed amendments to the polyester resin rule will result in a reduction of VOC emissions of approximately 0.13 TPD from permitted polyester resin operations, and from vinyl ester resin operations. The estimated VOC emission reductions are attributable to changes in chemistry for resin and gel coat materials, and the use of nonatomizing application technologies. VOC emission reductions from the amendment of VOC limits for related cleaning and surface preparation operations appear negligible. Reductions in resin and gel coat monomer content will reduce VOC and HAP emissions. Furthermore, non-atomized applications enhance spray equipment transfer efficiencies, thus reducing VOC and HAP emissions and the amount of overspray waste. The amendments for the controls on polyester resins, gel coats, cleaning products and vinyl ester resin operations would take effect on October 1, 2010.

District staff recommends amendments to Regulation 8, Rule 50 that will add and clarify definitions, establish monomer limits for gel coats and align current polyester resin monomer limits to be consistent with existing limits at other California air districts, lower VOC limits for polyester resin cleaning products and impose VOC limits for vinyl ester resin cleaning products, clarify the permissible methods for applying polyester resins to open molds and impose the same requirements for applying vinyl ester resins to open molds, and allow only the use of nonatomizing spray guns when spray guns are used to apply polyester and vinyl ester resins to open molds.

Staff has identified the possibility that some Bay Area composite operations may use thermosetting resin and gel coat materials other than polyester resins, some of which also produce VOC and HAP emissions. Staff is considering a further study measure to establish an emissions inventory of other thermosetting resins and gel coats to determine if monomer limits should apply to such operations.

II. BACKGROUND

The District adopted Regulation 8, Rule 50 on December 5, 1990 and amended it three times thereafter. The most recent amendments in 1996 addressed the definition of a VOC, the method of analyzing polyester resin material samples, and the method of determining emissions from polyester resin operations.

Rule 50 limits emissions from polyester resin operations by setting limits on the amount of styrene monomer that an uncured resin can have, or requires that vapor suppressants that minimize emissions be used, or requires that a closed-mold system, that also minimizes emissions, be used. In addition, the rule sets application requirements to limit overspray and has a VOC content limit for gel coats, often applied as the surface of a polyester resin product.

There are approximately 64 permitted polyester resin operations in the Bay Area that range in size from single-person shops to shops with 10 or more employees. Approximately half of the polyester resin operations in the Bay Area specialize in gel coat operations. Touch up and repair operations are exempt from the rule.

Composite Products Overview

Polyester resin operations fabricate and repair composite products by applying gel coats and/or resins mixed with reinforcement and other materials to molds which provide the desired shape for finished products. Molds can be either open or closed. Monomers, catalyzing agents, binders, fillers, promoters, molding compounds, adhesives and fiber reinforcement materials are composite materials which are added to a polymer mix to contribute toward a specific appearance and/or performance standard of each cured product.

A. Open Mold Applications

Open mold production, the simplest polyester resin fabrication technique, has been the most prevalent composite operation methodology for decades. EPA data suggests that open mold fabrication accounts for approximately 80% of the 17,888 tons per year of styrene emissions nationally. Composite materials can be applied to open molds either manually or mechanically (spray technology).

The manual application method, often referred to as a “hand lay-up”, involves a multi-step process. The mold’s surface is treated with a mold release agent in the form of an alcohol or paste wax to facilitate the removal of the cured composite. Next, a catalyzed resin mix is applied over the mold release agent. After the resin cures, fiber-reinforced

materials are applied by hand. Additional resin, catalyst, and reinforced material may then be added. Hand rollers, brushes, or squeegees are used to saturate, to smooth out, and compact each layer of the matrix as it is applied. Figure 1 is an illustration of a hand lay-up resin application method. Figure 2 is a picture of resin application using a lay-up method for the fabrication of a canoe.

Figure 1

WET LAY-UP/HAND LAY-UP

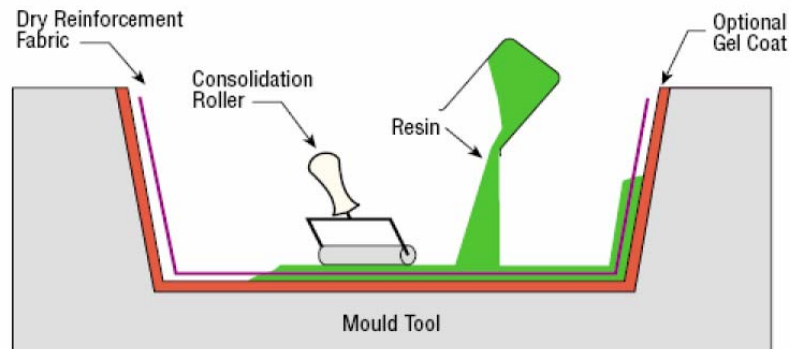


Image from Harveyscomposites.com

Figure 2

CANOE MANUFACTURING HAND LAY-UP



Image from Hemlockcanoe.com

B. Mass Production Open Mold Applications

In addition to the hand lay-up technique described above, composite material fabrication includes the following mass production open mold techniques:

- Continuous Lamination involves the fabrication of a glass/resin composite sandwiched between cellophane sheets which is pulled through a forming die into a curing oven.
- Pultrusion Operations continuously pull fiberglass material, which are in the form of strands or mats, through a tension device and immediately immerses them in a resin bath. As they exit the resin bath, the joint glass/resin composite strands are pulled first through a forming die and then through a heated die which cures the composite matrix into a shape.
- Filament Winding Operations are used to manufacture large pipes, storage tanks, and other hollow vessels that may be subject to elevated internal pressure. In this process, continuous fiberglass strands are pulled by a rotating mandrel through a strand-tensioning device into a resin bath. After emerging from the resin bath, uniformly-coated strands are wound onto a mandrel to the shape and pattern required for the finished product. The wound product is then cured in an oven or at room temperature.

C. Closed Mold Applications

Closed mold processing methods are those in which all or part of the fabrication takes place in a closed vessel or chamber, and are used to manufacture products with one or two smooth surfaces or complex shapes. Reinforced glass fibers, carbon fiber reinforced materials, and kevlar fiber reinforced polymers are manufactured in closed mold applications. In the closed mold process, continuous strands of fiber are applied by hand into a mold and catalyzed polyester resin is poured or injected into the mold cavity. Closed mold applications involve a variety of processes to create a resin/fiber matrix. These processes may force resin into a mold under pressure, draw it in with a vacuum, or may involve a combination of the two. Fiber and other reinforcement materials are impregnated with resin by various means, forming pressure and corrosion-resistant products.

These processes include:

- Rotational Molding,
- Resin Transfer Molding,
- Vacuum-assisted Resin Transfer Molding,
- Vacuum Bag Molding,
- Resin Film Infusion,
- Compression Molding,
- Reaction Injection Molding,
- Tube Rolling,
- Automated Fiber Placement,
- Automated Tape Laying, and,
- Centrifugal Casting.

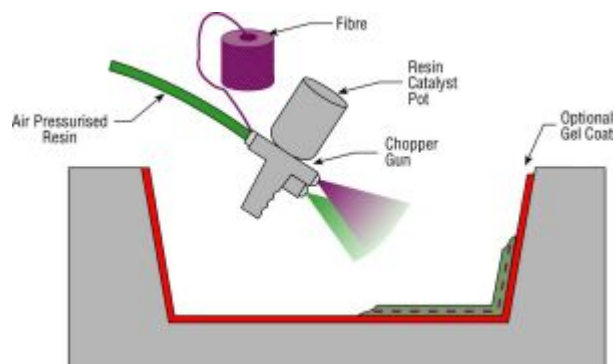
In both hand lay-up and spray-up operations, gel coat is applied to the closed mold prior to the application of a resin matrix. It is a customary practice to combine hand lay-up and spray-up operations.

D. Spray Technologies

Similar to the lay-up method, spray-up methods also begin by treating an open mold's surface with a release agent. After the release agent sets up, reinforced material and a predetermined amount of resin and catalyst are applied to the mold's surface with an atomizing spray gun. Industry representatives state that spray-up methods have several advantages over hand lay-up techniques, including increased production rates, increased uniformity of products, the utilization of a greater variety of molds, and a process which requires less man-hours. Atomization spray technologies separate resin and gel coat liquids into a fine mist by forcing the liquid under high pressure through an elliptical orifice, by bombarding a liquid stream with air jets, or by a combination of each technique. The net result is some overspray that reduces the transfer efficiency (percent of material sprayed that adheres to the intended surface) of the material sprayed onto molds, resulting in emissions of VOCs and HAPs to the atmosphere. Figure 3 is an illustration of a spray-up method.

Figure 3

Illustration of a Spray-up Method



Currently, Regulation, Rule 50 allows four types of spray gun technologies for the application of composite resins and gel coats.

- Airless Spray, which includes a pump to deliver the resin to the fluid tip at high pressure. As the high-pressure resin stream exits the small fluid tip (orifice), the stream's flow is reduced and the sudden reduction in pressure causes the fluid to atomize into a spray pattern.
- Air-assisted Airless Spray, which is a hybrid of airless and air-atomized spray gun technologies, uses a pump to deliver the resin to the fluid tip (orifice) with much less pressure than an airless gun. Low pressure air improves the resin spray pattern exiting the gun's tip.

- Electrostatic Spray, where an electric charge is imparted to the mold surface and an opposite charge is imparted to the spray droplets, which are attracted to the mold.
- High-volume, Low-pressure Spray, is similar to air-assisted guns. They operate with air atomizing pressures of 10 psi or less. High pressure air typical of an air spray gun is replaced by a high volume of low pressure air.

The type of spray gun selected for a given application is based on four primary considerations:

- How the material is delivered to the gun,
- How the catalyst is added,
- How the resin or gel coat is atomized; and,
- The type of mold which is receiving the resin or gel coat.

According to industry, for approximately five years, nonatomizing spray techniques have been used effectively in other air districts for the application of resins, and to a lesser extent, for the application of gel coats. The net results are enhanced transfer efficiencies and reduced emissions. Details of nonatomizing application techniques are discussed in the Technical Review Section (Section III) of this document.

E. Materials Used in Composite Operations

Resins

Resins are the backbone of a composite product. Resins bind fibers and other materials in a composite product together by polymerization, thus allowing the product to tolerate more stress and other forms of tension. Resins also provide a barrier to weather, water or chemicals. Thermosetting resins are resins that are usually in a liquid state at room temperature and are shaped by a heating process which causes the resin molecules to polymerize or “cross-link” and thus become fixed. Thermosetting resins cannot be reheated and re-shaped due to the molecular cross-linking process that has occurred, unlike thermoplastic resins that can be reheated and reshaped.

Some thermosetting resins emit VOCs and HAPs while others do not. Emissions depend on the type of monomer the resin is based on. Polyester resins have the greatest emissions of all thermosetting resins because they are the most widely used and because emissions from polyester resins are the greatest per amount of resin used. Polyester resins are thermosetting resins. However, they are not the only thermosetting resins used to manufacture products in the composite industry. The following are types of thermosetting resins.

1. Polyester Resins – Polyester resins are the primary resins used in the composite industry. According to industry representatives and suppliers, polyester resins are the most affordable and the most versatile of thermosetting resins. They have the widest application in the industry and are used to fabricate products in the automotive, leisure craft, boating, aerospace, bathware, residential, commercial, construction and other industries.

Polyester resins are polymers of ester molecules that are chained together in a particular order called ester linkages. Ester monomers are formulated by the reaction of acid and alcohol molecules. For example, polyethylene terephthalate (PET) resin is formulated by the reaction of ethylene glycol and terephthalic acid. Polyester resins include phthalic resins, halogenated/clorendic resins, bisphenol-A resins, and furan resins.

2. Epoxy Resins – Resins which show extremely high three-dimensional crosslink density, resulting in the best mechanical performance characteristics of all the thermosetting resins. The most demanding strength/weight applications use epoxy resins. Epoxy resins are typically used to fabricate marine craft parts, automotive parts, electrical composites, appliance parts, and aircraft components. They do not emit significant VOC.
3. Phenolic Resins – Resins with properties such as low heat transfer, high thermal stability, high electrical resistance, excellent adhesion, and resistance to chlorinated solvents and moisture. Phenolic resins are used primarily to fabricate products that can meet fire-resistant standards mandated by the public transportation and aviation industries. They are also used to fabricate electrical switches, junction boxes, automotive parts, consumer appliance parts, handles for pots and pans, and billiard balls.
4. Polyurethane Resins – Resins which are used to fabricate composite products requiring superior strength, stiffness, heat resistance, thermal insulation, and dimensional stability. Polyurethane resin products are also resistant to weathering and aging. Polyurethane resins are used to manufacture products for the home-building industry, the ballistics industry, the sporting goods industry, the automotive industry, as well as the fabrication of highway products and many other products. Typical polyurethane resin products include hockey sticks, bowling balls, automotive body and seat parts, laboratory equipment parts, highway sign posts, trusses, guardrails and light poles. Polyurethane resins emit little or no VOC.
5. Vinyl Ester Resins – Resins which are used for products requiring superior physical strength, impact strength, exceptional mechanical properties, or resistance to organic solvents or water corrosion. Vinyl ester resins are used for U.S. Department of Defense applications; to manufacture products such as pipes and tanks for the chemical industry, hull and deck laminates for the marine industry, skin coats for fiberglass mold making, scrubbing towers for air pollution control equipment, protective housing for equipment such as motorcycle frames, and protective clothing made of carbon fiber and kevlar. Vinyl ester resins are also preferred for filament winding applications and machine-made piping. Vinyl ester resins emit VOC and HAP, but because they can be formulated with less styrene content, emit less than polyester resins.
6. Acrylic Resins – Resins which are used to fabricate composite products requiring superior clarity and optical properties. Acrylic resins are typically used to fabricate lighting fixtures because they are slow-burning and do not produce harmful smoke or gases in the presence of flame. Acrylic resins are

also used as tooling resins for because they can stand up to the high stress and heat molds are exposed to. Acrylic resins do not emit significant VOC.

Gel Coats

Similar to thermosetting resins, different gel coats emit VOCs and HAPs to varying degrees, depending on the type of monomer the gel coat resin is based on. Gel coats are modified polyester, vinyl ester, phenolic or epoxy resins. They are applied to the interior of a mold to replicate its surface. Gel coats have both decorative and protective features. A gel coat's surface is exposed to a variety of environments, so it must be able to resist UV light, chemicals, heat, discoloration, pock marks, and cracking. Ordinarily, gel coats are applied to molds in multiple applications via spray technology with a preferred thickness between 0.010 to 0.020 of an inch. Gel coats applied too thinly will under-cure, while those applied too thickly will crack when exposed to flexing forces. Occasionally, gel coats are hand-applied to surfaces with a brush.

Specialized gel coats with high levels of durability are sometimes used to manufacture molds which in turn are used to fabricate composite products. Such gel coats must resist mechanical and thermal stresses encountered during the curing and de-molding processes. A primer gel coat is a specialized gel coat designed to protect the exterior of a composite product and is painted after the product is removed from the mold.

Monomers

Monomers are small molecules that partially combine with themselves and/or molecules from a catalyzing agent to form the basic repeating unit of a polymer (resin). Monomers have two primary roles in a resin: 1) they reduce the resin's viscosity, which makes the resin flow more readily during the fabrication process; and 2) they are crucial to the curing reaction which enables the resin to transform from a liquid to a solid.

Styrene is by far the most commonly used monomer in composite manufacturing, although many specialty resins and gel coats contain other monomers, such as vinyl toluene or methyl methacrylate. Styrene and other monomers are emitted into the air when resins are applied to molds, when air bubbles are rolled out of the composite materials, and during the curing phase. Styrene is a HAP, so exposure to styrene emissions is an air quality concern.

Suppressants

Suppressants are compounds that migrate to the surface resin to form a layer during the polymerization process, thus decreasing monomer emissions into the ambient air. Consequently, suppressants are one method of HAP and VOC control. In some cases, surface wax prevents optimal bonding between composite layers. Usually, suppressants are wax compounds.

Reinforcement Materials

Fiber reinforcement materials (FRM) are used in the manufacturing of composite products to enhance a variety of desirable properties that are of a mechanical and/or

structural nature. The desirable properties include tensile strength, tensile modulus, flexural strength, flexural modulus, compressive strength, stiffness, fatigue endurance, and elasticity. FRM enhances thermal, protective, and other capabilities. FRM does not react with resins; however, they are an integral part of the composite matrix.

FRM include multi-filaments of glass or other fibrous materials such as carbon, graphite, aramid, boron, metal, silicon carbide, kevlar, and natural fibers. Due to its low price and excellent performance, fiberglass is the most commonly used FRM in the industry, available industrially either as mats of woven cloth or as filaments.

Fillers

Fillers are solid, finely divided materials, such as carbon black, titanium dioxide, limestone, talc, mica, silica, clay, and calcium carbonate, as well as short fibers of a variety of materials. They are sometimes added to a polymer matrix to reduce the overall cost of the product. Fillers are also added to provide or enhance specific mechanical properties of a product. Desirable mechanical properties for composite products include flame retardation, heat resistance, optical clarity, color, thermal, magnetic or electrical properties, and lubricity.

Catalyzing Agents, Promoters and Inhibitors

Catalyzing agents, often called initiators in the composite industry, supply free radicals, which are required to initiate monomer cross-linking reactions. Methyl ethyl ketone peroxide and benzoyl peroxide (BPO) are the most commonly used catalyzing agents. BPO is used with aniline promoters when heat is used to cure the resin.

Catalyzing agents used with unsaturated polyester and vinyl ester resins do not supply an adequate amount of free-radicals to initiate cross-linking reactions. In those circumstances, operators may heat the catalyst or resins or add chemicals called promoters (sometimes referred to as “accelerators”). Other considerations that factor into the choice of promoters include color requirements, odor, and variations in reactivity with specific catalyzing agents. In the presence of a promoter, catalyzing agents are typically added separately, immediately prior to use.

Inhibitors are used to prolong the shelf life of molding compounds, to enhance resin stability for long-term storage, and to adjust the cure rate of thermosetting resins to prevent cracking of thickly layered sections. Inhibitors prevent spontaneous cross-linking.

Cleaning Products

Cleaning products are materials used to clean equipment and parts associated with composite operations including operators’ hands, tools, rollers, brushes, molds, work area, chopper guns, laminating equipment and other process-related equipment.

Composite industry representatives have reported that acetone is their preferred cleaning product because it is the most effective product for cleaning cured resins and gel coats from application equipment.

Cleaning products other than acetone, such as low-VOC and low vapor pressure materials, are available and can be used on a limited basis to clean non-cured composite materials.

Some Bay Area fabricators have experimented with aqueous cleaners, such as dibasic ester (DBE), with mixed results. Aqueous cleaners rely on mechanical action (such as brushing) to clean resin from contaminated applicators while acetone and other solvents clean by dissolving the resin. The resin droplets are wetted by the aqueous cleaner and settle to the bottom of a cleaning tank. Although aqueous cleaners contain few VOCs, they create waste materials such as the spent liquid solution and under-cured resins.

An emerging cleaning technology is being developed with soy-based cleaners. They can be used to remove cured and uncured resins via an immersion process.

III. TECHNICAL REVIEW

Staff has identified a number of technical matters for consideration.

A. Emissions Inventory

Total VOC emissions from permitted Bay Area polyester resin operations are estimated at 1.3 TPD. This figure is derived from the 2005 Base Year inventory, adjusted downward to account for the recent closings of the Hubbel-Lenoir Company and the Isola Corporation, the largest sources of polyester resin emissions in the Bay Area. VOC emissions from polyester resin application operations are estimated at 0.8 TPD while the VOC emissions from the use of cleaning products for such operations are estimated at 0.5 TPD. HAP emissions from polyester resin application operations are also estimated to be 0.8 TPD because styrene, the monomer which according to industry is typically emitted from polyester resin operations, is both a HAP and a VOC.

An undetermined number of Bay Area operations use vinyl ester resins and other thermosetting resins when they manufacture composite products. Thus, the VOC and HAP emissions from these resins are currently unknown.

B. Controlling VOC Emissions

Control of open molding VOC and HAP emissions can be achieved by pollution prevention and/or capture and control technologies. Pollution prevention involves modifications to the chemistry of the materials and to the application methods to minimize the release of VOCs and HAPs at the source. Capture and control reduces emissions through the use of abatement equipment such as carbon adsorption or incineration. Additionally, operator training and good operating practices can contribute toward significant emissions reductions.

Pollution prevention includes use of the following technologies:

- Nonatomizing Application Technologies
- Low Monomer and Zero Emission Resins
- Vapor Suppressants
- Fillers

Nonatomizing Application Technologies

Advancements in resin application technologies allow significant reductions in VOC and HAP emissions. For example, the replacement of atomized spray applications of gel coats and resins with non-atomized applications improves transfer efficiencies and reduces VOC and HAP emission significantly. Nonatomizing applications reduce the over-spray because of greater transfer efficiency, minimize the amount of waste, and control styrene and other monomer emissions in the working area.

The following nonatomizing application technologies can offer significant emission reductions when compared with conventional atomizing application technologies:

- Nonatomizing spray applicators
- Flow Coaters
- Pressure-Fed Rollers
- Resin Impregnators
- Hand lay-up

U.S. EPA (through its Research Triangle Institute and Comtech, Inc) conducted studies of nonatomizing application technologies and reduced styrene content to prevent pollution. U.S. EPA measured the average styrene emissions concentration (ppm) and percent emissions reduction during the application stage from airless air assist spray guns, flow coaters, and fluid impingement technology (FIT) systems. Table 1 summarizes the results.

Table 1
Styrene Emission Comparison During Application Stage

Resin Application	Average Styrene Emission (ppm)	% Emissions Reduced
Airless Air Assist Gun	87	--
Flow Coater	34	61
FIT System	19	78

According to the 2008 EPA Control Technique Guidelines for fiberglass boat manufacturing materials, changing both the application method and reducing the monomer content of a resin can significantly reduce monomer VOC emissions. For example, changing from an atomized application of resin with a monomer content with 40% styrene to a resin with 35% styrene content that is applied with nonatomizing technology may achieve a 58% emission reduction.

Low Monomer, Near-Zero and Zero Emissions Resins

One way to minimize the loss of monomer from composite operations is to use resins formulated with less monomer. Low monomer resins can be formulated using non-styrene monomers such as vinyl toluene, p-methyl styrene, or other monomers, which are less volatile when exposed to air. However, reducing the monomer content (such as styrene) of the resin presents challenges. Lowering the styrene monomer content typically tends to reduce viscosity, which may adversely impact the resin application. Lowering the molecular weight of the resin to reduce its viscosity may also compromise its ability to resist corrosion.

Ultraviolet curing resins derive their benefits from a photo-sensitive curing mechanism where UV light serves as the catalyst. This curing agent or initiator can be used in either vinyl ester or polyester resins. The curing process involves the decomposition of a photo-initiator by exposure to a particular wavelength of light. Once exposed, the decomposition produces free radicals, which trigger the polymerization reaction of the resin.

In electron beam (EB) technology, the electron beam translates energy to the resin molecules, breaking the carbon-hydrogen links, thus initiating polymerization. To assess the feasibility of EB technology in curing composite materials, District staff contacted RadTech, the association for the EB and UV industry. A RadTech representative verified that EB technology has evolved and is now used to cure composite materials. Therefore, the use of EB curing technology in the composite industry appears to be a promising technology for certain composite applications. Both UV and EB curing technologies emit almost no VOC.

Vapor Suppressants

Another way of reducing emissions is through the use of vapor suppressants, which are typically waxes. VOC emissions occur during three separate phases of a composite open molding process; the application phase, the rollout phase, and the curing phase. During the curing process of a resin, a vapor suppressant forms a layer on the surface of the resin and minimizes the outward diffusion of monomers into the atmosphere. Vapor suppressants may be blended into resin products at the resin-manufacturing site before packaging or shipment to the fabricators, or may be added just prior to fabrication.

Generally, vapor suppressants work best when the resin is relatively undisturbed, so that the layer of wax can be formed on the surface. In 1998, the Research Triangle Park Institute conducted a study to determine the effectiveness of vapor suppressants on reducing styrene emissions from the composite operations. They found that the effectiveness of the vapor suppressant in reducing styrene emissions varied with different resins. Furthermore, the effectiveness of vapor suppressants appeared to decrease for the same type of resin containing higher styrene monomer content. Vapor suppressants have little to no reduction of emissions during the application phase but they have virtually a complete reduction of emissions during the rollout and the cure emission phases, which represent 50% and 45% of the total emissions of the manual and mechanical applications, respectively.

Fillers

Fillers are finely divided materials, which are added to the resins to enhance the mechanical properties, extend the volume and lower the cost of plastic products. When fillers are used, less resin and monomer are used for any given product, reducing emissions. Cultured marble and cultured granite are cast polymer products comprised of approximately 25% polyester resin and 75% crushed stone, natural marble or granite as filler. These marble or granite fillers chemically bond with resins that allow them to be molded into an infinite number of shapes and sizes. Marble and granite fillers are often used for the production of countertops, sinks, tubs, and showers.

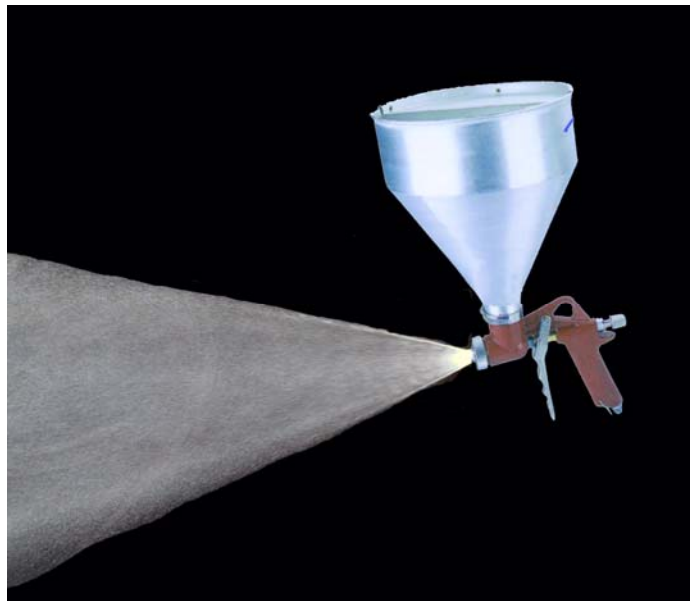
Capture and Control Technology

Composite operations have the option of using abatement equipment (add-on controls) to control VOC emissions in lieu of using resin, gel coat and cleaning products which comply with specified VOC and monomer limits. The majority of VOC emissions from resins and gel coats occur in open molding processes which take place in an open shop environment. Some emissions occur in spray booths where gel coat spraying for smaller parts may be done. The volume of air exhausted from an open shop or from spray booths is typically high, and the VOC concentration is typically low. Therefore, due to the large volume of air that must be processed to control a small amount of VOC, it is rarely cost-effective to use add-on controls to reduce VOC emissions. Catalytic and thermal oxidizers, which are the typical abatement equipment utilized in this industry, are particularly expensive to install, operate and maintain. Because of the wide availability and lower cost of low-monomer VOC content materials and alternative application methods, these materials and methods are used to reduce monomer VOC emissions from manufacturing facilities.

C. Hopper Guns

One Bay Area composite product manufacturer fabricates architectural products for buildings. It uses a hopper gun because of the large amount of crushed rock in the composite mix. A hopper gun is a gun-like nozzle and trigger connected to a large upright gravity-fed hopper. The underside of the gun's nozzle is connected to a specialized hose which is connected to an air compressor. When the gun's trigger is pressed, the hopper gun expels the contents of the hopper out of the nozzle in a steady stream or spray. Hopper guns are typically used to apply thick, viscous materials for drywall textures, plaster, concrete floors, cinder block walls and stucco ceilings. The hopper gun uses high air pressure (30 psi – 40 psi) to expel a thick, viscous mixture of catalyzed resin (or gel coat) and rock crushed to the consistency of sand through a spray line. Because the product is not atomized, the monomer emissions are minimal compared to other spray guns using air pressure. Figure 4 is a picture of a hopper gun.

Figure 4
Hopper Gun



D. Acetone Cleaning

Currently, acetone is only allowed by the local composite manufacturing industry on a wipe-cleaning basis. Bay Area fabricators have commented that while acetone wipe-cleaning is an effective way to clean some parts and equipment used in composite fabrication processes, it is not an efficient method of cleaning larger pieces of equipment, and equipment with inaccessible components or narrow crevices. Industry has requested the District consider amending Regulation 8, Rule 50 to allow the use of acetone in small cold cleaners (sink-on-a-drum) to clean larger tools and other processing equipment that contain cured resins and gel coats from composite fabrication and other manufacturing processes. Wipe cleaning in composite manufacturing is regulated by provisions in Regulation 8, Rule 50. Wipe cleaning in a container (including cold cleaners, solvent washers, etc.) is subject to the provisions of Regulation 8, Rule 16: Solvent Cleaning Operations, which does not exempt acetone. Acetone has a low reactivity but a high evaporation rate. The uncontrolled and unlimited use of acetone in a container would cause more ozone formation than low volatility materials such as mineral spirits.

E. Gel Coat Porosity

Gel coat manufacturers have informed District staff that tiny air bubbles are entrapped in gel coats, a chemical process known as porosity, when gel coats are applied to a mold in cold environments. Porosity occurs when a cold gel coat is applied to a mold or when a warm gel coat is applied to a cold mold. Porosity damages the appearance of the composite product because of a fogging or bubbling effect when a gel coat cures. Technology does exist to warm gel coats as they exit spray guns. However, heating gel coats isn't enough to prevent porosity if the molds aren't sufficiently warm as well. According to the Bay Area composite industry, when ambient shop temperatures are cool,

the only way to prevent porosity on gel coat surfaces is to warm both the gel coat and the molds to which they are applied. Molds can be kept warm by warming the rooms where the composite fabrication takes place. To do so is an extra cost to industry and it also requires the burning of more fossil fuel.

F. Green House Gas Emissions

In June, 2005, the District's Board of Directors adopted a resolution that recognizes the link between global climate change and localized air pollution impacts. Climate change, or global warming, is the process whereby emissions of anthropogenic pollutants, together with other naturally-occurring gases, absorb infrared radiation in the atmosphere, leading to increases in the overall average global temperature.

While carbon dioxide (CO₂) is the largest contributor to global warming, methane, halogenated carbon compounds, nitrous oxide, and other greenhouse gas (GHG) species also contribute to climate change. Gases in the atmosphere can contribute to the greenhouse effect both directly and indirectly. Direct effects occur when the gas itself is a GHG. While there is relative agreement on how to account for these direct effects of GHG emissions, accounting for indirect effects is more problematic. Indirect effects occur when chemical transformations of the original compound produce other GHGs, when a gas influences the atmospheric lifetimes of methane, and/or when a gas affects atmospheric processes that alter the radiative balance of the Earth (e.g., affect cloud formation).

VOCs have some direct global warming effects; however, they may also be considered greenhouse gases due to their indirect effects. VOCs react chemically in the atmosphere to increase concentrations of ozone and may prolong the life of methane. The magnitude of the indirect effect of VOCs is poorly quantified and depends on local air quality. Global warming not only exacerbates ozone formation, but ozone formation exacerbates global warming because ozone absorbs infrared radiation. Consequently, reducing VOCs to make progress towards meeting California air quality standards for ozone will help reduce global warming.

Adoption and implementation of the proposed amendments to Rule 8-50 should not result in any adverse impact on the emissions of greenhouse gases. The proposed methods of control include the reduction of monomer content for various polyester resins and establishing monomer content limits for gel coats; lowering the VOC limits for products which clean equipment used in polyester resin and gel coat operations, and vinyl ester resin operations; and resin application and operational controls.

Abatement equipment can be used to control emissions; however, staff is not aware of any operations in the Bay Area which utilize abatement equipment. Consequently, there would be no increase in energy demand to implement these amendments and, therefore, the proposal is neutral in regards to greenhouse gas generation.

IV. RULE AMENDMENTS

VOC and Monomer Limit Requirements

Currently, Regulation 8, Rule 50 requires that Bay Area composite operations use gel coats with VOC content no greater than 250 grams per liter. Composite operations must use polyester resin materials with a monomer content no greater than 35% by weight. Gel coats are a specialized class of resin and amendments to polyester resin rules at various California air pollution control districts now limit VOC emissions from composite operations by specifying a maximum monomer content for both polyester resins and gel coats. Staff has identified studies and field testing which have established maximum monomer content for polyester resins and gel coats that enable them to work effectively while reducing VOC and HAP emissions. Staff proposes that monomer limits, rather than VOC content limits, apply to gel coats used in Bay Area composite operations. The amendments for Regulation 8, Rule 50 are proposed to become effective on October 1, 2010.

Table 2 lists proposed limits for resin and gel coat materials.

Table 2
Proposed Monomer Limits for Resin and Gel Coat Materials

Gel Coats and Resin Materials	Monomer Percentage by Weight as Applied
Gel Coat Materials	
Clear Gel Coats	
Marble Resin	40%
Boat Manufacturing Resins	48%
Other Resins (all other "clear gel coat" resins)	44%
Pigmented Gel Coats	
White and Off-White Gel Coats	30%
Non-White Boat Manufacturing Gel Coats	33%
Other Non-White Gel Coats	37%
Primer Gel Coats	28%
Specialty Gel Coats	48%
Resin Materials	
Marble Resins	10% or 32% as supplied* -- (no fillers)
Solid Surface Resins	17%
Tub/Shower Resins	24% or 35% as supplied* -- (no fillers)
Boat Manufacturing (atomized)	28%
Boat Manufacturing (non-atomized)	35%
Lamination Resins	31% or 35% as supplied* -- (no fillers)
Fire Retardant Resins	38%
Corrosion Resistant and/or High Strength Resins	
Mechanical (nonatomizing)	46%
Filament application	42%
Manual application	40%
Other Resins (non "clear gel coat" resins)	35%

*As supplied by manufacturers

Spray Technology Requirements

Nonatomizing (fluid impingement) spray guns that effectively apply composite resins have been available for several years. This spray technology provides the greatest transfer efficiency. Staff recommends requiring nonatomizing spray guns as the only type of spray application technique allowed for the application of polyester resins to open molds. This requirement will also apply to vinyl ester resin operations.

Staff also recommends re-naming Section 8-50-302, currently entitled “Spray Operations” to “Application Requirements.” This section will specify the allowable application technologies for resins and gel coats which are nonatomizing methods in addition to nonatomizing spray guns. The section will allow the use of air spray hopper guns only for the application of viscous blends of resin or gel coat mixed with solid, particulate material to open molds. The particulate material may be in the form of quartz, mineral, silica, or crushed stone, such as granite, marble or limestone. Additional language will be added to this section to clarify that hand-held spray guns can be used when composite products are repaired.

The application of gel coats to open molds will not require nonatomizing spray guns. A study has shown that there are no significant differences between the VOC emission rates between air-assisted airless and nonatomizing applications when the nonatomizing spray gun is used at a pressure high enough to achieve an acceptable surface quality. Due to the results of that study, other California air districts that had previously required nonatomizing spray application techniques for gel coats have deleted the requirement.

Cleaning Product Requirements

Currently, the VOC limit for cleaning products used in Bay Area composite operations is 200 grams per liter. Cleaning products which comply with a VOC limit of 25 grams per liter have been required in other California air districts for several years. Such cleaning products are effective for certain applications. Other air districts have confirmed that, to date, they have not received complaints from the composite industry regarding their limited ability to use low-VOC cleaning products because they rely on acetone for the majority of their application equipment cleaning needs. Staff recommends lowering the VOC limit for cleaning products used in Bay Area composite operations from 200 grams per liter to 25 grams per liter. Staff also recommends that vinyl ester resin operations comply with these requirements.

Emissions Reductions

VOC emissions for currently District-permitted polyester resin and gel coat operations are approximately 0.8 TPD. Roughly half of the VOC emissions are from resin application while the other half are from gel coat application. After the new monomer content limits are implemented, the VOC and HAP emissions from resin and gel coat monomers will be approximately 0.73 TPD.

The additional VOC emission reductions from resin application operations that must switch to non-atomization spray application equipment is difficult to quantify because the number of facilities that must make the switch, and the number of systems needed at each facility, is unknown currently. Assuming one nonatomizing spray system is purchased

per facility that applies resin with a spray applicator, staff conservatively estimates an additional 0.04 TPD in VOC emission reductions. Staff also conservatively estimates that subjecting vinyl ester resin operations to the Application Requirements, Surface Preparation Requirements, and the Equipment Requirements in Regulation 8, Rule 50 will further reduce VOC emissions by 0.02 TPD. When fully implemented, the amendments to Regulation, Rule 50 will result in a total VOC emission reduction of 0.13 TPD and a HAP emission reduction of 0.12 TPD.

From the District's Base Year 2005 emissions inventory for cleaning product (solvents) usage, it is estimated that less than 25 pounds per day of VOCs are emitted into the atmosphere from permitted Bay Area polyester resin operations that currently use cleaning products. The VOC limit for cleaning products is 200 grams per liter. Cleaning products with a maximum VOC content of 25 grams per liter have been available for several years largely based on acetone, the composite operator's solvent of choice. Staff proposes to reduce the VOC limit to 25 grams per liter, which is an 87.5% reduction in VOC content.

Costs

According to several composite product distributors who do business in the Bay Area, the cost to operators to purchase gel coats and resins that have been reformulated with less monomer content will increase by approximately 25 cents per pound of material. Table 3 illustrates the increase in cost for each regulated class of gel coat and monomer.

Table 3 - Prices for Gel Coats and Resins, Current and Future

	Current List Pricing	Estimated Pricing
<u>Clear Gel Coats</u>		
<u>Marble Resin</u>	<u>\$2.58/lb</u>	<u>\$2.83/lb</u>
<u>Other Resin</u>	<u>\$4.30/lb</u>	<u>\$4.55/lb</u>
<u>Boat Manufacturing</u>	<u>\$4.30/lb</u>	<u>\$4.55/lb</u>
<u>Pigmented Gel Coats</u>		
<u>White and Off-White</u>	<u>\$3.84/lb</u>	<u>\$4.09/lb</u>
<u>Non-White Boat Manufacturing</u>	<u>\$4.30/lb</u>	<u>\$4.55/lb</u>
<u>Other Non-White</u>	<u>\$7.03/lb</u>	<u>\$7.28/lb</u>
<u>Primer</u>	<u>\$3.95/lb</u>	<u>\$4.20/lb</u>
<u>Specialty Gel Coats</u>	<u>\$4.55/lb</u>	<u>\$4.80/lb</u>
<u>Resin Materials</u>		
<u>Marble Resins</u>	<u>\$2.53/lb</u>	<u>\$2.78/lb</u>
<u>Solid Surface Resins</u>	<u>\$2.55/lb</u>	<u>\$2.80/lb</u>
<u>Tub/Shower Resins</u>	<u>\$2.55/lb</u>	<u>\$2.80/lb</u>
<u>Boat Manufacturing (atomized)</u>	<u>\$2.29/lb</u>	<u>\$2.54/lb</u>
<u>Boat Manufacturing (non-atomized)</u>	<u>\$2.29/lb</u>	<u>\$2.54/lb</u>
<u>Lamination Resins</u>	<u>\$2.29/lb</u>	<u>\$2.54/lb</u>
<u>Fire Retardant Resins</u>	<u>\$2.74/lb</u>	<u>\$2.99/lb</u>
<u>Corrosion Resistant and/or High Strength Resins</u>		
<u>Mechanical (nonatomizing)</u>	<u>\$3.77/lb</u>	<u>\$4.02/lb</u>
<u>Filament Winding Application</u>	<u>\$3.77/lb</u>	<u>\$4.02/lb</u>
<u>Manual Lay-up Application</u>	<u>\$3.77/lb</u>	<u>\$4.02/lb</u>
<u>Other Resins</u>	<u>\$3.60/lb</u>	<u>\$3.85/lb</u>

According to industry sources and equipment distributors, the cost for a new, basic nonatomizing (FIT) spray system ranges from \$9,000.00 to \$11,000.00 per system. It includes a spray gun, pump, hoses, and a cart. State-of-the-art, computerized FIT spray systems can cost up to \$30,000.00. Some shops may need more than one system. The cost estimates include the costs for new equipment and the installation costs.

The costs for low-VOC cleaning products which will comply with the recommended VOC limit of 25 grams per liter are negligible because the technology isn't new. In some cases, the cost for petroleum-based cleaning products meeting the current VOC limit of 200 grams per liter will be higher than the cost for low-VOC cleaning products.

V. RULE DEVELOPMENT / PUBLIC CONSULTATION PROCESS

Publication of this Workshop Report and conducting the public workshop are the latest steps in the District's consultation process with stakeholders as the District considers amendments to Regulation 8, Rule 50: Polyester Resin Operations. District staff has consulted with representatives from other air districts, the EPA Region 9 Office, composite industry representatives, composite manufacturing operators, and composite product distributors to discuss technological issues, monomer limits, VOC limits, costs, health effects, and future trends in the thermosetting resin and composite industry.

The purpose of the public workshop is to solicit comments from the public on the proposed amendments to Regulation 8, Rule 50. During the workshop, District staff will seek comments on material presented in this Workshop Report and will respond to questions about information set forth in this Workshop Report. Staff will review and consider all comments received during the public workshop and revise the proposal as appropriate.

Staff will complete its CEQA analysis and prepare a final proposal for Rule amendments that will be available for public comment prior to a public hearing of the District's Board of Directors.

VI. REFERENCES

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