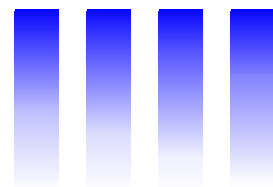




Re-Certification Workbook

for renewal of CCT-CP credentials
Version 1.0 - 2007



CCT-CP Re-Certification

Certified Composites Technicians must re-certify their credentials on a three-year cycle. The CCT-Cast Polymer Re-Certification Workbook is a self-study course designed to facilitate the revalidation of your CCT-CP credentials and help you to keep abreast of developments in the composites industry. The articles presented in the workbook include a review of selected CCT information, an introduction to composites processing technologies not discussed in the original study guide, and information on selected plant safety issues. Successful completion of the workbook test is the basis for renewal of your CCT-CP credentials.

The Re-Certification Process

- Step 1** – Read the Re-Certification Workbook.
- Step 2** – Complete the re-certification application.
- Step 3** – Complete the section tests.
- Step 4** – Send the completed test booklet and renewal fee to ACMA.
(Please note: Your credentials cannot be processed without the fee.)
- Step 5** – Upon completion of the test with an 85% score or higher, your credentials will be revalidated.

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Defining Composites: *What are thermoset composites?*

What are composites? As elementary as the question may seem to those in the composites industry, the exact definition of composites is somewhat elusive.

The term 'composite' is used in a number of contexts within the English language. For example, there is the field of *composite photography*, where two or more photographs are joined to form a single image. The Air Force operates *composite wings*, which are units made up of various types of aircraft. Mathematicians define a *composite number* as an integer exactly divisible by at least one number other than itself. And then of course there are *composite materials*.

The term composite is derived from the Latin *compositus*, stemming from the root word *componere*, to bring together.¹ This accurately describes our industry's practices in putting together materials to form a composite.

Defining composites as an engineering material requires a progressive definition, which begins with the general and moves to the specific. The broad general definition of a composite is: "*Two or more dissimilar materials which when combined are stronger than the individual materials.*"²

This definition draws attention to the positive effects of combining materials that have different properties to create a new material with superior properties. This definition applies both to natural and synthetic (manmade) composites. Wood, a

combination of cellulose fiber and lignin, is an example of a natural composite that falls into the broadest definition of composites. The cellulose fiber provides strength and the lignin is the 'glue' that bonds and stabilizes the fiber.

Manmade composites can be constructed using natural materials. Adobe bricks are a perfect example of a composite material; the combination of mud and straw forms a material that is stronger than either the mud or the straw.

There are many forms of synthetic composites. Steel and concrete combine to create structures that are strong and rigid. In this case the high stiffness and compression strength of the concrete combine with the high tensile strength of steel, creating a structure that is strong and stiff. A very different composite is an automobile tire. A steel belted radial tire uses rubber as a strong but flexible matrix to encapsulate steel strands which have high tensile strength.

This broad definition, however, is too general to describe the specialized form of materials from which the composites industry takes its name. We require a definition that adequately segregates these structural materials from other engineering materials. Brent Strong uses this definition for composites in his book, Fundamentals of Composites Manufacturing:

The combination of a reinforcement material (such as a particle or fiber) in a matrix or binder material.³

Dr. Strong points out,

The term composite also implies that the materials are macroscopically identifiable, that is, the materials are not merely different at the molecular level but have distinctive component properties and they are generally mechanically separable. This definition excludes many materials which might have been included in the broader definition such as: metal alloys, plastic copolymers, minerals, glasses, and wood.

For our purposes, we must develop the definition still further by examining the engineering properties of the component materials that form a composite. Considering that a composite is a combination of reinforcement in a matrix, it becomes necessary to define the terms *reinforcements* and *matrix*.

In engineering terms, one of the functions of reinforcements in a composite is to take up the load strain transferred through the matrix. The load must then be distributed throughout the matrix and reinforcements.

Fibers are reinforcements having one long axis and one short axis: a high aspect ratio (a comparison of length to width). In the matrix, fibers overlap to a degree that strain within the matrix is transferred to a series of fibers. Where fibers overlap, the load is distributed to adjacent reinforcements, with the matrix holding the fibers in place and

Defining Thermoset Composites

General Definition:

“Two or more dissimilar materials which when combined are stronger than the individual materials.”

This definition includes a wide range of material combinations, such as wood, adobe bricks, steel and concrete, rubber and steel (tires), concrete, and (of course) the combination of polymer resins and fibers.

Intermediate Definition:

“The combination of a reinforcement material in a matrix or binder material.”

This more focused definition narrows the range of materials to a reinforcement and a matrix. In this case reinforcements could include fibers or particles, and the matrix may be a polymer resin, ceramic, or metal. Examples include: metal and ceramic matrix materials, reinforced thermoplastics, and reinforced thermoset polymer resins.

Precise Definition:

“Composites are a combination of a reinforcement fiber in a thermoset polymer resin matrix, where the reinforcement has an aspect ratio that enables the transfer of loads between fibers, and the fibers are chemically bonded to the resin matrix.”

The precise definition of thermoset composites as an engineering material is based on the physical property characteristics of these materials. The synergy created by load transfer between fibers, and the chemical bonding of the reinforcement to the matrix, are the defining terms of this description.

transferring the strain from fiber to fiber. Fibers may be oriented in a specific direction and have the capability to produce a material with anisotropic properties: a material that is stronger in one direction than the other. Fibers can be used to produce a non-homogeneous structure, which has different properties throughout. This is a distinct advantage in an engineering material.

On the other hand, particles generally have a low aspect ratio and are roughly spherical in shape. Generally referred to as *fillers*, particles consist of both organic and inorganic materials. The most common particles found in plastic materials are calcium carbonate (limestone), calcium sulfate, and alumina trihydrate. Additionally, hollow or solid spheres of glass or other materials may be used as fillers.

Particles in a matrix (such as a resin) produce isotropic properties, meaning that the material will have the same tensile, compression and elongation properties in the X, Y and Z-axes. In other words, a particle-filled matrix will be homogeneous (the same throughout), as are metals. Particles, however, are *not* effective as reinforcements. By virtue of having low aspect geometry (rough spherical shapes), they do not effectively transfer loads from particle to particle, and they produce a homogenous structure. *Therefore, particles are not*

considered, or referred to, as reinforcements in composites materials.

The function of the matrix in a composite is to provide a relatively rigid media that is capable of transferring loads to the fiber components of the material. The matrix encapsulates the reinforcement, creating the physical properties synergy between the two materials. In scientific terms, synergy is the phenomenon in which two or more separate things, acting together, create an effect greater than that predicted by knowing only the separate effects of the individual things. In forming composites, one critical aspect in combining the matrix and the reinforcement is that a chemical bond is formed between the matrix and the reinforcement.

To explore this concept further, consider the combination of a thermoplastic resin (such as polypropylene) and glass fiber. In this case, the reinforcement fiber is merely encapsulated by the resin matrix but not molecularly bonded to the resin. However, the combination of glass fiber and a thermoset polyester resin produces chemical bonds at the interface of the fiber and the resin. Therefore, we arrive at one of the distinctive characteristics of a composite engineering material – the reinforcement is not merely encapsulated by the matrix, but is actually molecularly bonded to the matrix. This bonding of reinforcement and matrix produces the superior physical properties, chemical resistance, and fatigue endurance that characterize composite materials.

Now, with the technical aspects of composites characterization in hand, the definition of these materials can move to the final step of refinement:

Composites are a combination of a reinforcement fiber in a polymer resin matrix, where the reinforcement has an aspect ratio that enables the transfer of loads between fibers, and the

fibers are chemically bonded to the resin matrix.⁴

This precise definition accounts for the attributes of thermoset composites as engineering materials, and differentiates them from a host of *combined* materials having lesser degrees of synergy between the individual components.

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Understanding Polyester Resin Curing: *Effective handling of resin in the shop*

The chemical reaction of cross-linking is the fundamental process of producing composites products. The work of converting a liquid polyester or vinyl ester resin into a solid is termed curing, and the mechanism by which curing occurs is cross-linking, or addition polymerization. Understanding the cross-linking reaction for polyester resins can make a significant difference in procedures used in laminating or gel coating, and in the products' quality.

Polyester resins consist of a polymer (a long chain molecule) and a cross-linking agent, usually styrene. Styrene not only works in the cross-linking role, but also lowers the viscosity of the polyester polymer to provide a workable product. Picture a series of tennis balls connected in a string. The molecular chains are independent and possibly mechanically intertwined but otherwise unconnected; this is resin in the liquid state.

The cross-linking reaction begins with the addition of a curing agent known as an initiator. The common initiators used in open molding are sometimes erroneously called catalysts. However, technically a catalyst starts a reaction but is not consumed in the process. An initiator enters into the reaction and is consumed; *therefore MEKP and BPO are actually initiators and not catalysts as commonly termed.*

The initiator (an organic peroxide) produces free radical molecules. These free radicals open the bonding sites on the polyester chain molecule. Imagine the tennis balls on a string as molecules. The initiator causes a tennis ball in the molecular chain to be

covered with Velcro of the loop variety. The bonding sites on the styrene molecules are also opened, so we also have a styrene 'tennis ball' covered with Velcro of the hook variety. The bridging step in the reaction takes place when the Velcro tennis balls touch to form a bond. The bond between the polyester molecule and the styrene molecule actually produces a new free radical molecule (another Velcro covered tennis ball) that is available to open a new bonding site and keep the reaction going.

The result of the molecular bridging or bonding is a network of interconnected polyester polymers with the styrene molecules serving as the links between the chains. Resin converting from a liquid to a solid is the result of this *cross-linking* or addition polymerization.

The cross-linking reaction is at maximum activity from the time the initiator is introduced to the resin to the time of peak exotherm. As the molecular matrix proceeds to interconnect, the cross-linking activity slows down as the conversion proceeds to a solid. In the beginning of the reaction there are many molecules available for bonding and they are very mobile in the liquid state. However, as the reaction progresses, and the cross-linking density increases, there are fewer available bonding sites and the molecules are less mobile.

How does this affect the practical aspects of curing a resin or gel coat in a production setting? A vast majority of cross-linking takes place in the early stages of the curing process from the addition of the initiator to

peak exotherm. As the cure progresses, a smaller number of reactions take place. The molecular chains are bound in the increasingly solid matrix and there are fewer opportunities for contact with a free radical molecule. By the time peak exotherm occurs, only a small number of bonding sites are available and the reaction declines rapidly.

On the practical level, it is important to get a good cross-linking reaction upfront during the early stages of the curing process; that is from the time of the addition of initiator to the time of resin peak exotherm. If an inefficient reaction occurs in the initial stages of cure, it is difficult to remedy the problem later.

What causes a poor initial cross-linking reaction? Low initiator levels are always suspected; improper amounts of promoter or inhibitor in the resin; and low shop temperature all contribute to poor cure. Assuming the proper initiator is being used, all resins and gel coats have a minimum specified level of initiator. Any amounts less will not provide a sufficient quantity of free radicals to fully cross-link the resin. If the levels of promoter or inhibitor additives in the resin are out of balance a sluggish cure may result. Low ambient air temperature is one of the most common and overlooked problems associated with poor cure. Because the cross-linking reaction is very dependent on temperature, conditions below 60°F present a potential curing problem. A thin laminate or gel coat film may also contribute to a sluggish cure. Other problems such as poor initiator mixing or water in the plant air system will contribute to improper curing.

In many cases, fabricators attempt to compensate for a poor upfront cure with questionable methods. One is the mistaken idea that given enough time laminates will fully cure. This has bred the fiberglass folklore that laminates never stop curing, or that it takes two months (or two years) to get

a complete cure. This is incorrect. Very little cross-linking takes place in a solid resin matrix. What is sometimes perceived as a continuing cure over a period of time is usually un-reacted styrene being released from the resin matrix. Eliminating these 'loose' styrene molecules may cause some shrinkage in the laminate and sometimes can be identified by styrene odor if the laminate is in a confined area. However, additional cross-linking is not taking place.

The same holds true for post-curing at elevated temperatures. If two un-reacted bonding sites are in intimate contact, a cross-link may occur if the temperature is elevated. However, for the most part, 'post-curing' does not cause further curing, but rather eliminates unreacted styrene from the resin matrix.

Understand that getting a high cross-linking density in the initial stages of curing will contribute to quality laminates. Make free radicals work for you. The molecule you cross-link today will be one less molecular delinquent to deal with tomorrow.

It is important to get the proper cure *upfront*, and it is ineffective to attempt to compensate for a poor cure with remedial action. Allowing the laminate to dwell longer in the mold, or post-curing at elevated temperature, does not compensate for the initial problem. Many composite quality problems are a direct result of a faulty cure. These problems are best addressed by implementing proper production procedures. For example, use the proper initiator in the proper ratio; maintain shop temperatures above 60°F at all times; pay attention to

details such as initiator mixture, compressed air quality, and application techniques.

In warm weather, do not drop initiator levels below the minimum specified percentage. If gel times are too fast at the minimum initiator level, the solution is to extend the resin gel time with the help of the resin supplier. Do not use 'half-strength' or 'summer' initiator without increasing its percentage to correspond to the minimum level; using these products can result in permanent undercure even in the hottest weather.

Composites Manufacturing Processes: *A review of manufacturing techniques*

There are two general divisions of composites manufacturing processes: open molding (sometimes called contact molding) and closed molding. With open molding, the gel coat and laminate are exposed to the atmosphere during the fabrication process. In closed molding, the composite is processed in a two-sided mold set or within a vacuum bag. Both manufacturing processes require reinforcements, usually glass fibers.

Cast polymer molding is a process for the manufacture of flat or shaped goods using either filled or unfilled resin systems, usually without fiberglass reinforcement.

Typical products manufactured using cast polymer molding include bathware (vanities and tubs), kitchen countertops, and ornamental castings. The casting process involves mixing resin, initiator, and filler, then pouring the matrix into an open or closed cavity mold. The type of filler used determines the look and properties of the casting. A high loading of filler in the resin creates the casting matrix. Cast polymers can be molded in a wide variety of tooling, ranging from low-cost composite molds to state-of-the-art metal tooling. This process can be automated and is capable of producing rapid cycle times. A vacuum can be used to remove entrapped air in the matrix, such as in cast solid surface.

Cast products, including cultured stone

and solid surface, are considered unreinforced composite products. Reinforced composites consist of a laminate using fiber reinforcement, such as glass fiber. The molds used to process cast polymer products are often reinforced composites composed of polyester resin and glass fiber.

Cast polymer molding may use either hard or soft tooling, depending upon the product and production requirements. Hard tooling may consist of FRP composite polyester or epoxy molds, cast or machined aluminum, electroformed nickel shell, or machined steel or even glass molds. Soft tooling may be constructed of various flexible compounds, such as RTV silicone, polysulfide, or polyurethane molding compounds.

This open-molding process can produce parts of any shape or size. A wide range of tooling can accommodate high- and low-production volumes. It is possible to make complex and detailed parts with sharp undercuts or two-sided finishes. Fast production-cycle times are possible and the process equipment ranges from basic manual tools to highly automated equipment.

In gel-coated cultured marble molding, a gel coat film (usually clear) is sprayed on the mold surface. Once the gel coat is sufficiently cured, a polyester resin matrix is blended by adding various types of

fillers to the mixture. Pigments both for solid background color and the look of veins found in natural stone can be added. The resin matrix is then transferred to the mold, where vibration is applied to level and compact the matrix. Following the cure, the part is removed from the mold. The types of fillers used and the application of colorants to the matrix determine the appearance of the cultured stone product.

For cultured marble, formulating a matrix using calcium carbonate filler reproduces the natural marble look. (In some cases, other fillers or combinations of fillers may be used.) Resin, initiator, filler, and pigment are mixed to form a solid-color matrix. The marble veining effect is created by adding a second pigment to the matrix and partially mixing it to produce the desired look.

The process of manufacturing cultured onyx is similar to that of cultured marble, except alumina trihydrate (ATH) filler is used. The cultured onyx matrix generally has a higher resin content compared with cultured marble, and its combination of materials creates a translucent appearance. Background and veining pigments are added to the matrix to produce an onyx stone look.

Blending colored chips into the resin matrix creates the cultured granite appearance. These chips can be made from cultured marble castings, thermoplastics, or even actual stone that has been ground into particles. The cultured granite matrix usually consists of polyester resin, initiator, colored chips, and ATH filler.

Solid surface products (also known as densified products) consist of a cast matrix without a gel-coated surface. Solid surface is a void-free casting made from a blend of acrylic or polyester resin, initiator, Alumina Trihydrate (ATH), color

chips, and pigment and is used to manufacture products such as kitchen countertops. Solid surface can be formulated to achieve a wide variety of looks and cosmetic effects, such as simulating natural granite. In contrast to the gel-coated surface of cultured marble, solid surface parts are homogeneous throughout, which makes it possible to join fabricated pieces with inconspicuous seams and to repair and refinish the surface to its original condition.

Densified castings are made using vacuum-mixing techniques to produce a matrix that is void-free, presenting a uniform surface when it is cut, sanded, or bonded. Solid surface castings are cured at elevated temperatures (in the range of 200 degrees Fahrenheit) to enhance the physical properties of the matrix and produce a stable product.

Solid surface can be compression molded, which is a high-pressure closed-molding process suitable for molding high volumes of complex solid surface parts. The compression molding process uses matched metal-heated molds mounted in large hydraulic presses. Compression molding produces fast molding cycles and high part uniformity but requires a high capital investment in tooling and equipment. Features such as inserts, ribs, bosses, or attachments can be molded in, and good surface finishes contribute to lower part-finishing cost. Subsequent trimming and machining operations are minimized in compression molding. This process is very capital-intensive and but is labor-efficient. Labor costs are low due to the fast cycle times and reduced post-mold-finishing, while capital costs are high for heated-metal tooling and molding presses. Compression molding can be attractive for large production volumes of uniform parts.

Engineered stone refers to cast products

that combine natural stone materials with polymer casting resins. Features include high heat resistance, low thermal expansion, and good stain or scratch resistance. The engineered stone matrix bonds relatively large-sized particles (compared with fillers) of natural stone with a thermoset resin. Typically a small amount of resin (8 to 15 percent by weight) is combined with the stone particles and poured into an open-cavity mold, or a vacuum-assisted press technique can be used to extract air from the matrix and compress it into a low-porosity casting. These products, by virtue of the actual stone in the matrix, are the hardest and most durable product of all consumer-grade cast polymer products.

Cast Polymer Materials: *a review of fundamental material concepts*

Cast polymers are unique in the composites industry. Cast polymer products, typically with no fiber reinforcement are designed to meet specific strength requirements of an application. They are often stronger than real stone or cement, the products they commonly replace. Cast polymers offer a number of advantages over traditional engineering materials.

Cast polymers differ from other homogeneous materials like metal due to the variety of combinations of resins and fillers that can be formulated for use in producing the finished product. There is no 'engineering handbook' to design. Performance characteristics can be achieved by the proper selection of resin, fillers, and (at times) reinforcements.

Polyester resins are the most common resin systems used in cast polymer manufacturing because their low cost and their cured physical properties meet many of the needs in the cast polymer industry. Vinyl ester resins offer superior corrosion resistance and mechanical properties at a higher cost.

The polymer backbone refers to the specific type of molecule that is the basic building block of the resin system. The chemical designation of the polymer backbone is typically used to describe resin formulations.

Resin System

The categories of resins used in cast polymers are:

Orthophthalic acid-based resins (ortho) are sometimes called general purpose or GP resins. They are generally the lowest-cost polyester resins and are commonly used in applications where high mechanical properties, elevated service temperature, and superior corrosion resistance are not required.

Isophthalic acid-based resins (iso) have greater mechanical and corrosion-resistant properties than ortho resins because they generally have higher molecular weights. When increased strength, corrosion resistance, or elevated-temperature performance is required, iso resins are used.

Dicyclopentadiene-based resins (DCPD) are generally used where cosmetic finishes are critical. DCPDs have a low-volumetric shrinkage when curing and produce minimal surface profiling. DCPD-blend resins are used today. DCPDs are blended with ortho, iso or vinyl ester resins to either enhance the properties of the DCPD resin or to reduce the cost of a premium resin.

Vinyl ester resins are used where either superior corrosion resistance and/or toughness are required properties. Vinyl esters are formulated by reacting epoxy resin with acrylic acid, forming a polymer that has characteristics like both polyester and epoxy. Vinyl ester resins are cured and handled very similarly to polyester resins.

Gel coat is a specialized polyester resin that is formulated to provide a cosmetic outer surface on a composite product, and to provide weather-ability for outdoor products. Gel coat is not paint. Paint contains solvents that must evaporate for the paint to dry. The 'solvent' in gel coat is styrene monomer and/or methylmethacrylate (acrylic), which cross-links during curing. The monomer does not have to leave the system for the gel coat to cure; in fact, it is beneficial to reduce monomer loss. Gel coat consists of a base resin and additives.

Fillers influence the cast polymer matrix's physical characteristics, chemical reactivity and appearance. The word filler implies something that takes up space. While fillers do take up space in the volume of resin matrix, they also provide functional attributes to the system. The term 'functional filler' describes a filler with properties that affect a polymer matrix. The role of fillers in the polymer matrix system is complex and multifaceted.

Filler Functions

Understanding how fillers function in a resin casting system is an important aspect of controlling the manufacturing process. Fillers are combined with polyester resin and wet-out by the resin. The term wet-out is used to describe the surface saturation of individual particles. It is the styrene monomer component of the polyester resin that acts as the wetting agent with the filler. As more

styrene is used to wet-out the filler, the viscosity of the homogeneous matrix increases and flow decreases, resulting in a thicker matrix. As the matrix thickens it becomes more difficult to blend additional filler into the batch. The surface area of the particulate is one of the controlling factors in determining how fast the viscosity builds up when filler is added to the resin.

Fillers generally slow the gel time and cure of the resin in the matrix. This retardation effect will vary with the type and amount of filler used. Factors that affect the cure properties are the type of filler, particle size, and moisture content. ATH contains sodium hydroxide. The level of sodium hydroxide may vary due to the method by which the filler is manufactured; this in turn may affect resin gel time, cure, and the color of the matrix.

Polyester resin shrinks as it cures and filler does not shrink; therefore, the more filler loaded into a matrix, the less volumetric shrinkage will occur. The control of shrinkage using fillers is a key function of a matrix formulation. While a small amount of shrinkage is acceptable in cast polymer parts, too much shrinkage may cause the formation of internal stresses that lead to cracking.

Particle Packing

Because fillers are a major component of a cast polymer matrix, the behavior of particles in the mixture is an important issue. In a matrix formulation, the amount of resin required, the viscosity, flow characteristics, and density are all related to how the filler acts in the mixture. How much filler can be used in a matrix formulation is related to the shape of the particles and how the individual particles nest with one another. This nesting is a property known as particle packing.

The science of particle packing is

complex and the discussion can quickly progress into mathematical calculations on the theoretical level. There are however, fundamental aspects of particle packing that are relevant to the filled resin systems used in cast polymer production. The first point of discussion in understanding particle packing is to look at the void content of uniform spheres in an unpacked and packed configuration.

Stacking these theoretically perfect spheres produces spaces between the particles due to their geometry. These spaces represent a void content of about 36 percent between the particles. Note that the perfect alignment is only possible because the spheres are contained within walls.

When the walls are removed, allowing the spheres to nest within one another, the particles are said to be packed. The void content is significantly reduced (to about 26 percent) by packing the spheres in a non-uniform alignment.

A second particle size is then introduced. Smaller spheres fit into the voids between the large spheres. Combining particles of different sizes (or shapes) further enhances packing by placing particles in the gaps.

Calcium carbonate and dolomite fillers are usually formulated to make up 75 percent or more of the weight of the matrix. Pigment may be used for the background color of cultured marble castings. If a solid color gel coat is used, the color of the filler itself is less of an issue than with a clear gel coated surface.

Ideally the filler should be added after the resin is initiated. By thoroughly mixing the initiator with the resin prior to adding filler, the safety hazard of direct contact between the initiator and dry filler is avoided. **Organic peroxide initiators, such as MEKP, should never be**

allowed to come into (direct) contact with dry fillers.

Common Fillers

Fillers come in a variety of materials. Many of the fillers used in the composites industry are mineral substances. Mineral fillers have distinctive shapes that relate to their chemical structure. They can be sphere-like, irregular with a low aspect ratio, or have a high aspect ratio similar to the glass fibers used in reinforced composites. In general, high aspect ratio filler will provide an increase of strength of the composite. The particle surface area is also an important characteristic of filler. Surface area is described as the external area of a filler particle. The higher the surface area, the more resin it will take to coat the surface of the particle. High surface-area particles will increase the viscosity of a resin matrix.

Spherical particulate is characteristic of most ground fillers. A sphere is a geometric shape that provides the largest internal volume for the smallest exterior surface area. Granule fillers are usually considered 'spherical' in shape even though they have many uneven surfaces. The smoother the surface, the lower the surface area of the particles, which produces a lower matrix viscosity. Examples of spherical particulate include alumina trihydrate (ATH), calcium carbonate, calcium sulphate, and dolomite.

Other Fillers

Microspheres are hollow spheres made of either glass or plastic materials. These lightweight, high-volume fillers are sometimes used to reduce the density of a casting matrix. Microspheres have a very smooth spherical surface and are generally used in applications where weight is an issue. Because

microspheres are high volume/low-mass fillers, they have a significant effect on the viscosity of the matrix. Porosity is not desired in solid surface products; therefore microspheres and other lightweight materials are not used in these applications.

Some fillers have a high aspect ratio giving them fiber-like properties. These fillers, including Franklin fiber, Wollastanite, and acicular mica, provide reinforcement to the matrix and can increase the mechanical properties of a casting. Generally, these products are not used in cast polymer products.

Fiber reinforcements, possibly in the form of short length milled fibers, are used in some casting applications where additional part strength is desired, such as cast bathtubs. Although added as a low percentage of the matrix, reinforcing properties of the fiber can improve thermal-shock resistance.

Long fibers, such as glass fiber, are considered reinforcements rather than fillers and are generally used in laminated composites. The primary attributes of a reinforcement fiber are a high aspect ratio and the ability to transfer loads from fiber to fiber within the cured resin matrix. Fiberglass reinforcements are commonly used in the construction of molds, and occasionally short fibers or milled fiberglass are used for reinforcements in cast polymer products.

Fillers in Specific Applications

Cultured Marble

The filler most often used in cultured marble manufacturing is calcium carbonate. Because it is a mined mineral, it is never chemically pure from batch to batch; calcium carbonate may be a slightly different color and vary in levels

of contaminants or specific gravity.

A second type of mineral used to manufacture cultured marble is dolomite. Dolomite is a mixture of calcium and magnesium carbonates. As the magnesium carbonate proportion increases, the specific gravity of the mix increases. While calcium carbonate fillers have a specific gravity of about 2.72, dolomite can have a specific gravity of 2.9. This difference in specific gravity is enough to change the resin-to-filler ratio needed to achieve the same mix viscosity.

Cultured Onyx

Cultured onyx presents a semi-translucent effect in a veined cast polymer product. This aesthetic effect is usually achieved by using white ATH, a granular filler. The ATH matrix can range from bright white to a champagne color. ATH is not a natural mineral but rather a product made from the mineral Bauxite. In addition providing a visual effect, ATH acts as a flame retardant. At a temperature of about 410 degrees Fahrenheit, ATH releases water that is chemically attached to the particles. The effect is a reduction in the burning temperature to the point where the flame may be extinguished. Additionally, smoke generation is reduced. ATH usually makes up 65 percent or more of the weight of the matrix when producing cultured onyx, and the higher resin content contributes to the translucency of the matrix. Onyx matrixes require a higher percent of resin due to the particle-packing configuration and specific gravity of ATH.

Cultured Granite

Cultured granite filler systems have been made with a variety of materials. The particulate that provides the texture can be thermoplastic granules, natural stone granules, or polyester resin granules.

The granules are sometimes mixed with either calcium carbonate or ATH. Calcium carbonate can be used when the matrix is cast behind a gel coat while ATH is used with non-gel coated product. The entire matrix may be cast with the granite filler or a spray granite layer can be applied as a surface coat (gel coat) with a cast marble backing. A wide variety of options are available with granite-filler systems, featuring various sized granules or chips and many color variations.

Colored-chip or granule fillers are used to produce the granite-look products. The granite effect is produced using particles having a variety of sizes and colors. These larger colored particulates produce the unique coloration and texture associated with granite. Colored granules may be coarse ground minerals or synthetic granules made from pigmented resins. Synthetic granules provide the wide variety of colors and textures demanded by the consumer.

Filler Challenges

An inherent problem with fillers is their hygroscopic nature, resulting in moisture adsorption. If fillers are improperly stored or handled, moisture can be introduced into the matrix mix. This may inhibit the resin cure and result in a poor bond between the resin and filler. Quality problems can result, including poor mechanical properties or long-term blushing. A shop floor quality-assurance test can be easily performed on filler to determine the moisture content: If the filler can be squeezed in your hand forming a ball that does not break down easily, the filler may have high moisture content.

Cast Polymer Processing: *limiting emissions*

As fluid tip technology improved, it became apparent that the application of gel coat using a low-pressure fluid stream was possible.

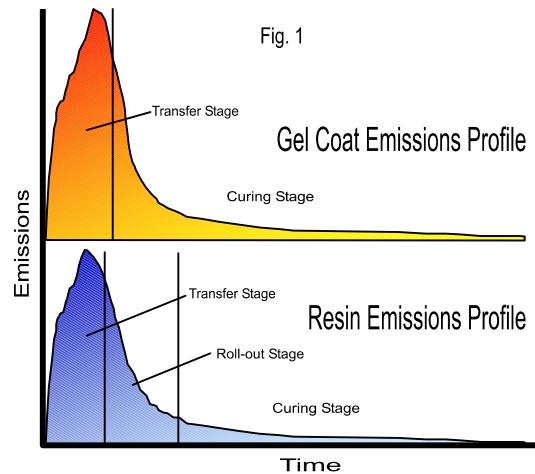
Phases of Emissions Generation

There are distinct characteristics of the emissions profile for gel coat and resin application. This includes two phases during the gel coat sequence: transfer and curing. There are three phases for resin: mixing, transfer and curing. During the transfer (spraying) phase, a high concentration of emissions is produced in a relatively short time. In the curing phase, lower concentrations are emitted for a longer period.

Although short in duration, the transfer stage is a major contributor to overall emissions. Where curing stage emissions are inherent to the volatile content of the material and ambient conditions, transfer stage emissions can be greatly reduced by adjusting the level of atomization of the spray gun. The type of spray gun and its operational fluid pressure are major variables in the overall influence on emissions.

The Emissions Mechanism

Two concepts must be understood about emissions: transfer efficiency and surface area. Transfer efficiency describes how much of the material that



exits the spray gun is deposited on the mold surface. Transfer losses are both evaporative loss and overspray loss.

During resin and gel coat application, a certain amount of volatile component (i.e., styrene and/or methylmethacrylate - MMA) will be lost in the 'tip to target' transport of the fluid. This evaporation is governed by a complex set of interactions involving the level of fluid stream atomization, material vapor pressure, temperature, rheology and other surface effects. The evaporative loss is greatly influenced by the percentage of monomer (styrene or MMA) available.

Overspray is a by-product of inefficient transfer and is controlled by spray gun pressure, the level of spray gun atomization and operator spraying technique. Overspray is material that leaves the fluid tip and is deposited *off-mold*, e.g. on the floor, walls, or spray booth filters. Evaporative loss is

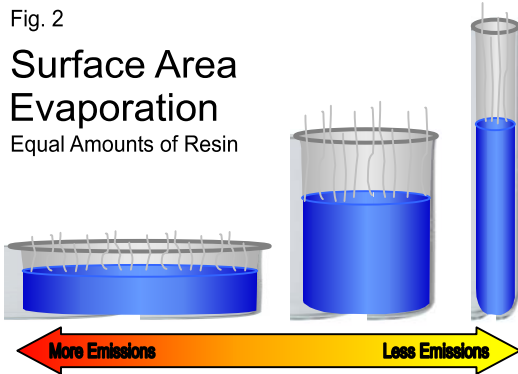
automatic and based on the sum of the influencing factors on the material.

Emissions from the open molding process are a function of the wet surface area of resin or gel coat. To illustrate this point, the same quantity of resin is placed in three different containers; these containers present a variable surface area (see Figure 2).

Fig. 2

Surface Area Evaporation

Equal Amounts of Resin



Evaporative emissions are not a function of the volume of resin, but rather of the exposed surface area. In the static (undisturbed) state, a thick matrix or gel-coat film will produce the same emissions as a thin matrix or film assuming equal cure times. **The emissions are not a function of the thickness but the surface area.** Even in the case of a thick matrix that produces measurable exotherm, as the cure advances emissions will follow a curve similar to a thin matrix of the same surface area.

With the understanding that emissions are a function of surface area, the effect of overspray is to dramatically increase wet surface area. Figure 3 illustrates the impact of overspray on emissions. In this example, a particular combination of gel coat and conditions produces 0.0177 lb/ft² of emissions per wet surface area. This does not include transfer stage emissions. As shown, there is a direct relationship between the increase in wet surface area and emissions from relatively small volumes of overspray

Fig. 3

Mold Size - 4' x 4'
Surface Area Emissions = .0177 lb/ft²

Wet Surface Area = 16 ft²
16 ft² x .0177 lb/ft² = .28 lb Emissions

Controlled Spray Application

Wet Surface Area = 32 ft²
32 ft² x .0177 lb/ft² = .64 lb Emissions

12" Over-Spray Application

Wet Surface Area = 64 ft²
64 ft² x .0177 lb/ft² = 1.13 lb Emissions

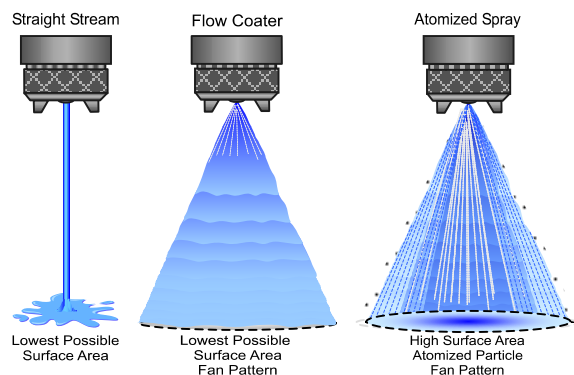
24" Over-Spray Application

spread over a large area. This emphasizes the importance of controlled spraying techniques, and in the larger view illustrates the function of surface area effects on spray patterns during the transfer stage.

Surface Area and Spray Patterns

The concept that surface area is a major determinant of emissions extends to spray gun fluid delivery. Figure 4 illustrates three modes of fluid flow.

Fig. 4



The straight stream represents the lowest possible surface area for delivery of a given flow rate of material. However, delivery in this form is not practical or useful for application to a

mold. A low-emissions spray gun presents the lowest achievable surface area spray pattern by using a coherent flow stream. And finally, the atomized fan pattern produces a large increase in surface area due to reduced particle size and the footprint created by associated overspray.

The purpose of a low-emissions fluid tip is to modify a flow stream into a shape that is useful to distribute material across a mold. This is accomplished in several different ways. Impingement designs use two intersecting fluid streams to form a flat pattern. Mono-orifice designs direct the flow within the orifice to spread the stream into a fan shaped pattern. The older multiple orifice equipment produces a series of straight streams that are aimed into a fan shaped array.

A hypothetically perfect fluid nozzle would produce a coherent flow stream of the appropriate shape and width for efficient material coverage on a mold. This flow stream would represent the lowest surface area for a workable spray pattern. In reality, a perfectly coherent flow stream is not achievable in the shape of a fan pattern. In practical terms, an effective low-emissions spray gun produces a coherent flow stream for a distance from the orifice; this flow stream transitions into ligaments and further into large droplets. In actual operation this form of fluid flow results in the lowest *achievable* surface area and produces emissions equal to or less than the UEF emissions factors. Because the coherent stream of a low-emissions spray gun degenerates into ligaments and droplets, the particle size distribution within the spray pattern is of great interest when considering the lowest achievable surface area.

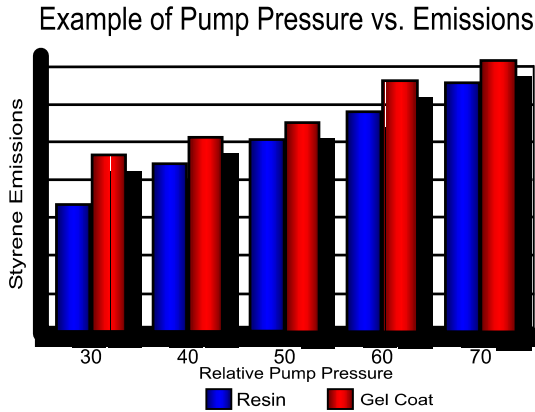
At some point on the fluid pressure curve, a coherent flow stream with ligaments and large droplets will be converted into a flow that is populated with small particles – this is the point of atomization. The affect of reducing large droplets into smaller particles is to significantly increase the effective surface area of the flow stream. Figure 5 illustrates the relationship between the size of fluid droplets and surface area. A single large droplet 100 microns in diameter has a volume of 52,360 microns³ and a surface area of 3,141 microns². If that same droplet is broken into one hundred particles with a 10-micron diameter and the same overall volume is maintained; then the surface area is now 31,416 microns², or a 10x increase in surface area. The result of this particle size reduction is a large increase in emissions during the short duration tip to target transport phase.

The Relationship between Fluid Pressure and Emissions

Non-Newtonian fluids, such as resin or gel coat, are responsive to the abrupt pressure gradient as a fluid stream exits a spray tip orifice. As increasing fluid pressure imparts more 'push' to the flow, the differential pressure causes a more energetic distribution of the flow across the spray pattern. This energy is manifested in a correlation between pressure and particle size distribution. Higher pressures produce a more energetic break-up of the fluid stream with smaller particles spread over a larger area.

With resin and gel coat application there is a direct correlation between tip pressure and emissions. Figure 6 shows a nearly linear relationship between pump pressure and emissions.

Fig. 6



In the case of atomized equipment, it appears the linearity of the pressure /emissions curve is very predictable. With 'non-atomized' fluid delivery the emissions curve may not be as linear or predictable. It appears that low-emissions spray guns maintain a reasonably coherent flow stream through a certain pressure range and then within a narrow pressure band the flow stream transitions into what behaves more like an atomized flow. There are many variables that determine the particular pressure at which this transition takes place; however, there is a direct relationship between fluid tip pressure and emissions. Understanding this fact is an important aspect of equipment set-up and operation.

Why are Non-Atomized Resin and Gel Coat Applications Different?

The following table summarizes the differences between non-atomized resin and gel coat application.

Compared to matrix resin application, gel coat presents two challenging aspects due to the nature of the product. Film thickness is a critical attribute of finished product performance. It is easier to produce a more uniform film thickness with atomized application than with a coherent flow stream. Likewise, porosity is a determining factor of

finished gel coat quality. Porosity is more likely to be present with non-atomized applied gel coat, than with a highly atomized application. When considering resin void inclusion (of the size that would affect gel coat) is reduced by vibration and is not a major issue.

Comparison of Non-Atomized Applications

	Resin	Gel Coat
Flow Rate	Less Critical	More Critical
Applied Thickness	Less Critical	More Critical
Initiator Mixing	Less Critical	More Critical
Air Entrapment	Minor Issue	Major Issue
Cosmetic Requirement	Minor Issue	Major Issue
Application Technique	Less Critical	More Critical
Material Sensitivity	Minor Issue	Major Issue
Temperature Sensitivity	Minor Issue	Major Issue

Gel coat can be successfully applied with low-emissions equipment; however, the application parameters are more critical than with resin application. The equipment may require pressure settings in an operating range just below the threshold of atomization. While successful in some facilities, and for particular levels of quality, at this juncture it remains to be seen if 'non-atomized' gel coat can satisfy the quality requirements across the broad spectrum of the open molding industry.

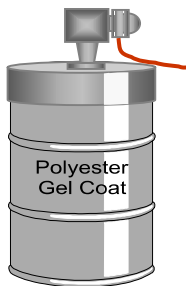
The combination of the type and set-up of equipment and the specific gel coat formulation is more critical than with any other open molding material application. Experience shows that gel coat

application requires careful fine-tuning of the 'equipment/materials system' to achieve acceptable quality.

Proper Equipment Set-Up for Low-Emissions Application

The set-up of low-emissions equipment is a highly critical aspect of the process. The use of a 'non-atomized' application device does not guarantee the result is a non-atomized flow stream that meets the UEF emissions criteria. With excess pressure it is possible to cross the line where the spray pattern converts from meeting non-atomized parameters to that of an atomized fan pattern. This conversion takes place when the ligaments and large droplets forming at the end of a coherent flow stream are converted into small high velocity particles signaling the onset of atomization.

Establish the appropriate fluid pressure for every combination of material and spray gun, including non-atomized and atomized units. This procedure produces the minimum achievable emissions from any combination of spray gun and material.

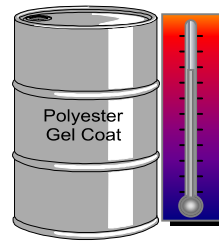


● Step One: Mix the Material

Verify that the material has been properly mixed within 24-hours of use according to the manufacturers' recommendations.

Effective mixing requires the use of a device that can impart a low shear to the material such as an air-motor powered drum-top paddle mixer or a screw-type mixer. Attempts to mix material by bubbling air through the drum are highly detrimental to the quality of the material and completely ineffective in mixing, as are attempts at mixing by rolling a drum on the floor. It is imperative to use an

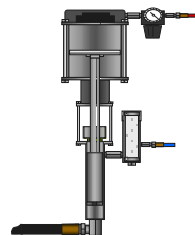
air-powered mixing device to properly mix the material into a homogeneous blend before use.



● Step Two: Adjust and Verify Temperature

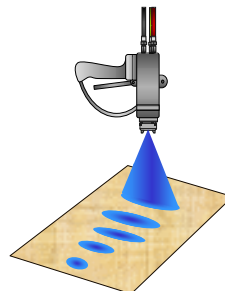
The temperature of the material in the drum is a critical element of the application process.

The effect of temperature on viscosity plays a critical role in the pressure required to pump the material to the spray tip. Most manufacturers recommend 70°F as the *minimum* material temperature for application. (Refer to the manufacturer for a product-specific recommendation). The use of in-line heaters for gel coat application has been found to enhance the sprayability of the product, but in-line heaters are not a substitute for obtaining the proper temperature of material in the drum.



● Step Three: System Checks

Unrestricted fluid flow from the pick-up tube in the drum, through the pump and within the fluid lines, is essential to consistent pressure settings. Check and clean the pick-up tube screen and high-pressure in-line filters. Clean filters are required to provide the least restricted flow in the system. Check the wear condition of the spray tip: tips erode through the abrasion of high-energy flow and must be replaced on a routine basis to maintain optimal spray patterns.



● Step Four: Calibrate Gun Pressure

The lowest fluid tip pressure that results in a practical spray pattern will produce the

lowest emissions for that combination of equipment and material. This pressure calibration procedure works with all spray guns, non-atomized and atomized, and with all materials including both resin and gel coat. While the quality of a spray pattern may be somewhat subjective and dependent on required quality, there are common characteristics of a workable spray pattern:

- The spray pattern is of sufficient width at the required distance from the mold.
- The spray pattern is uniformly ovoid or elliptical in shape.
- The fluid stream is evenly distributed across the width of the spray pattern.

The Pressure Calibration Procedure should be performed at the beginning of each day or shift, or if significant environmental changes during the day require pressure modifications. This procedure is simple, effective, and takes no more than a few minutes to accomplish.

► **Step 1:** (if the spray gun uses external shaping air)
Set the air-assist pressure in the middle of the normal operating range. Set the external mix initiator pressure at the required level.

► **Step 2:** Turn the fluid pump pressure down to the point where the pump will not stroke when the spray gun trigger is pulled.

► **Step 3:** Hold the spray gun perpendicular to, and about 12" to 18" from, a disposable covering on the floor. Pull the trigger and increase the pump pressure in increments until a workable spray pattern is formed. Once the pressure is

near the optimum pattern formation, quickly pull and release the trigger to take a 'snapshot' of the fan pattern shape. Adjust as necessary to refine the pattern with the goal of using the lowest pressure possible.

► **Step 4:** (if applicable)
Fine-tune the external shaping air and/or initiator mixing as required. Again, use the lowest pressure that produces a workable spray pattern.

► **Step 5:** Observe the non-atomized flow stream to be sure the transition to atomization has not taken place. If the coherent flow stream is degenerating into excess fine particles, repeat the set-up process and lower the fluid pressure.

► **Step 6:** Record the pressure settings in a daily log.

This procedure will produce a repeatable equipment set-up that can be optimized for a wide range of equipment, materials, conditions, and quality requirements.

In Calibration Step 5, if a coherent flow stream cannot be established into a workable fan pattern, it may be necessary to make adjustments to the combination of material and equipment type. It is recommended that molders work closely with material formulators and equipment suppliers to develop the appropriate combination of material, spray gun set-up parameters and application conditions.

The use of non-atomized application is a significant benefit to composites open molding production. However, misuse of the process by over-pressuring the

spray gun may lead to higher than expected emissions. By understanding the emissions mechanism and the techniques for calibrating equipment, the objective of reducing process emissions an achievable goal. The resulting increase in transfer efficiency not only leads to emissions reduction, but also provides measurable cost savings and cleaner production environment.

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MACT and the Cast Polymer Industry: *understanding the EPA regulation*

What is MACT?

When Congress amended the Clean Air Act in 1990, it directed EPA to list categories of *sources* that emit any of 189 *hazardous air pollutants*. The list of HAP established by Congress included styrene, methyl methacrylate, and methylene chloride, and in 1992 EPA listed Reinforced Plastics Composites Production as a category of sources emitting HAP.

Congress also told EPA to establish control requirements for each listed category of HAP sources. For each category, the requirements were to be based on what EPA determined was the *maximum achievable control technology*.

EPA promulgates MACT requirements in the form of National Emission Standards for Hazardous Air Pollutants. The NESHAP for Reinforced Plastics Composites Production was published in the Federal Register on April 21, 2003. On August 25, 2005, EPA published a Federal Register notice making certain corrections and modifications to the rule. The composites NESHAP is codified as Subpart WWWW, of Part 63, of Title 40, of the Code of Federal Regulations. Official references to the MACT rule will often take the form of *40 CFR Part 63 Subpart WWWW*.

The scope of the rule includes cast polymer manufacturing. The rule requires many composites manufacturers to adopt state-of-the-art pollution prevention controls or, in a few cases, capture and oxidation controls. Existing sources are required to comply by April 21, 2006, and new sources on start-up.

Many cast polymer manufacturers will be exempt from MACT requirements. Those facilities that are not exempt will only have work practice, record keeping, and other administrative requirements; they do not have engineering control requirements. However, no manufacturers should casually assume they are exempt. Even the smallest manufacturers are likely to face certain administrative requirements to establish that they are in fact exempt from the MACT rule.

Who has to comply with MACT?

Any reinforced plastics composites production operation located at a *major source* must comply with the composites production NESHAP. A reinforced plastic composites production facility is one in which reinforced and/or non-reinforced plastic composites products or molding compounds are manufactured using thermoset resins and/or gel coats that contain styrene.

A major source is a facility with the *potential to emit* 10 tons per year of any single HAP, or 25 tpy or more of any combination of HAP. Major sources of HAP are required to have *Title V operating permits* from their states. Note that a cast polymer manufacturing operation with one gel coat gun can be a major source—and hence subject to Title V and MACT requirements—since the potential to emit calculation assumes continuous operations, 24 hours/day, seven days/week, 52 weeks/year.

Avoiding MACT

Sources with actual emissions below the 10 tpy MACT threshold can avoid major source designation and Title V permit and MACT requirements by obtaining a federally enforceable state operating permit that limits operations so that emissions do not exceed the threshold. These permits, commonly called synthetic minor permits, will typically limit hours of operation or material usage, so that the source cannot legally exceed the major source emission threshold.

Sources with synthetic minor permits can apply for a Title V permit if they need to increase production at a later time. However, this process can take some time, so any company that expects emissions to exceed the 10 tpy MACT threshold in the next few years should consider getting a Title V permit now, even though this will mean that MACT compliance is required earlier.

ACMA strongly encourages all composites manufacturers to have federally enforceable air emissions permits. Sources with emissions of 10 tpy or more, or who expect to emit this much in the near future, should have Title V permits. All other composites manufacturers should have federally enforceable synthetic minor permits.

The only reliable way to know if a company needs to comply with MACT is to refer to its federally enforceable operating permit.

Some states have told small composites manufacturers that they do not need a permit. We believe this is bad advice, and that these states are trying to reduce the number of permits they issue. If a source is told by a state not to apply for a permit, the company should carefully document this instruction, and on an annual basis should formally request the state to review its permit status. Operating without a required permit is a violation of federal law, and companies must be very cautious about accepting state guidance that permits are not required.

MACT requirements for polymer casting operations

The MACT rule contains the following definition for “polymer casting:”

Polymer casting means a process for fabricating composites in which composite materials are ejected from a casting machine or poured into an open, partially open, or closed mold and cured. After the composite materials are poured into the mold, they are not rolled out or worked while the mold is open. The composite materials may or may not include reinforcements. Products produced by the polymer casting process include cultured marble products and polymer concrete. 40CFR63.5935.

While polymer casting is included in the list of operations at “affected sources” (i.e., those required to comply with MACT; 40CFR63.5790), there are no control requirements for polymer casting. However, polymer-casting operations at affected sources must still fully comply with the administrative provisions of the rule. Further, any cast

polymer manufacturer required to comply with MACT who applies gel coat, stores or mixes resin, or cleans equipment, will have to comply with the control requirements for those processes. These requirements are summarized in the table below.

in compliance with an issued permit, is a federal felony, punishable by a fine of \$25,000 per day and jail time for business owners and managers. The only way for a company to be certain of its Title V and MACT requirements is to have a federally enforceable operating permit from its state – either a Title V permit or a synthetic minor permit.

Get a permit, then read the rule

Operating a major source of HAP without a Title V permit, or without being

Summary of some possible MACT control requirements for cast polymer manufacturing

Gel coat type	Comply with these HAP-monomer limits (higher limits allowed for non-atomized application; see the rule)
Clear production	44.0
White/off white pigmented	30.0
All other pigmented	37.0
Tooling	40.0
CR/HS or high performance	48.0
Fire retardant	60.0
 Cleaning	<p>Do not use cleaning solvents that contain HAP, except that styrene may be used as a cleaner in closed systems, and organic HAP containing cleaners may be used to clean cured resin from application equipment. Application equipment includes any equipment that directly contacts resin.</p> <p>Use mixer covers with no visible gaps present in the mixer covers, except that gaps of up to 1 inch are permissible around mixer shafts and any required instrumentation. Close any mixer vents when actual mixing occurs, except that venting is allowed during addition of materials, or as necessary prior to adding materials or opening the cover for safety. Keep the mixer covers closed while actual mixing occurs except when adding materials or changing covers to the mixing vessels. Containers of 5 gallons or less may be open when active mixing is taking place, or during periods when they are in process (i.e., they are actively being used to apply resin). For polymer casting mixing operations, containers with a surface area of 500 square inches or less may be open while active mixing takes place.</p>
 Mixing	<p>Keep containers that store HAP-containing materials closed or covered except during the addition or removal of materials. Bulk HAP-containing materials storage tanks may be vented as necessary for safety.</p>
 Resin storage	

Once a source has a Title V permit, it must then comply with all applicable MACT rules. While MACT control requirements for polymer casting operations have been summarized above, the rule is complicated, and there are many record keeping, reporting and other administrative requirements. Sources required to comply with MACT must carefully read the rule, work out compliance plans, and have their permits modified to reflect the applicable MACT requirements.

A cast polymer manufacturing operation with one gel coat gun can be a major source, and hence subject to Title V and MACT requirements. The only reliable way to know if a company needs to comply with MACT is to refer to its federally enforceable operating permit.

For more information:

General information on the composites MACT, including links to EPA MACT sites:

www.acmanet.org/ga/mact.cfm

State air permitting offices:

www.cleanairworld.org/scripts/stappa.asp

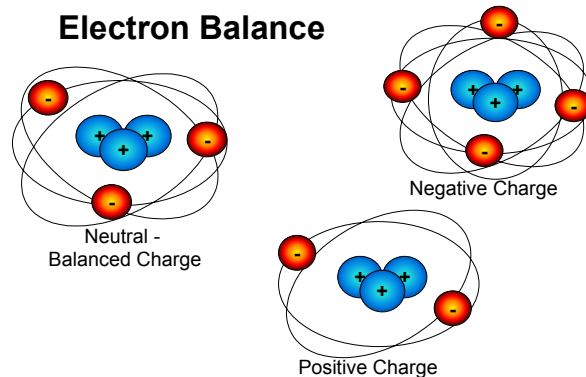
Electrostatic Discharge (ESD): hazards in composites operations

Things were humming along as usual in the mold shop of a large boat manufacturing plant. The relatively new plant was clean, well organized and busy producing a well-known line of sport fishing and motor yachts. As a flow chopper operator leaned in toward a mold for better reach, he felt a small static shock from the mold. The outside air was cool and dry, with typical winter humidity in the 30% range. The chopper operator leaned in again, stretching for the far side of the mold, and ZAP – static spark – the mold was on fire!

There is nothing scarier than fire in a composites plant. Things happen faster than you can imagine, the smoke is black and dense, and chaos ensues. In this case the plant's response was good. Fortunately, the mold was located near an overhead door, which was immediately opened, the mold was pushed out of the building, and the fire was extinguished. No injuries, no building damage, and only minor mold damage occurred. However, the outcome could have been much more serious had the circumstances been slightly different.

The problem in this example is electrostatic discharge or ESD. In this case several factors came together to create a new set of conditions. This boat plant was using a flow chopper and

conductive molds (FRP molds built using conductive tooling gel coat.) This combination, coupled with low atmospheric humidity, produced a situation warranting serious attention.



What is static electricity?

All matter is composed of atoms. Atoms consist of electrons orbiting a nucleus. In the state of equilibrium, the positive charge of the nucleus equals the negative charge of the electrons. Electrons, however, come and go as the electrostatic equilibrium of surrounding atoms change. If electrons leave an atom, the atom becomes positively charged. If an atom gains extra electrons, it develops a negative charge. Given the opportunity to reach a neutral state, electrons from negatively charged atoms will migrate to positively charged atoms until an electrostatic balance is achieved.

The development of a 'static charge' occurs when an insulator is introduced into the atomic system. An insulator prevents the flow of electrons up to the point where a great enough charge (push) develops to bridge the insulated gap. In this case, great quantities of electrons are transferred almost instantaneously. On a small scale this is a static spark; on a large scale we know it as lightning.

The ability of a material to either shed electrons or attract electrons is known as conductivity. Good conductors, such as copper, have a rigid molecular structure that does not allow electrons to be easily released. Poor conductors such as thermoplastics and FRP composites will surrender their electrons easily by contact, friction or pressure. Not only do many non-conductive materials easily lose electrons, but they also act as insulators, causing a buildup of excess electrons on their surfaces. When the electron imbalance is large enough, a discharge takes place to the nearest conductive material. Electrostatic discharge (ESD) occurs to bring atomic equilibrium back into place. The discharge can range from a few thousand volts developed while petting your cat, to millions of volts witnessed in an earth-to-cloud lightning discharge.

The level of static discharge we come into contact with on a normal basis ranges from 1,500 volts up to as high as 35,000 volts. Remember that when dealing with humans and electricity it is *amperage* that determines the potential hazard. The term *volt* refers to the quantity of electrons that are available for a discharge. Amperage measures the 'push' behind the flow of electrons. In terms of contact with electrical discharge, high voltage at low amps is many times just an annoying static zap. On the other hand, low voltage with amperage can be deadly. For example,

typical household current of 120 volts at 15 amps can cause a severe shock hazard, whereas 220 volts at the same amperage can easily cause death by electrocution. With static electricity we are talking about high voltage and low amperage. For example, walking across a carpet may generate 1,500 to 35,000 volts. Opening a plastic bag can produce 2,000 to 12,000 volts. When you feel a static discharge you are experiencing a minimum of 3,000 volts – anything less is below the threshold of human sensation.

Fiberglass composites have high dielectric strength, the level of conductivity of a material. Copper and steel have low dielectric strength because they are good conductors. Glass fiber laminates are poor conductors and resist electrical transmission by being good insulators. However, by virtue of being a poor conductor, a glass fiber laminate may accumulate very high static surface charge. Electrons build up on the surface of a mold, and because it is a good insulator, they cannot easily bleed off in a controlled incremental fashion. The surface charge on an FRP mold surface can reach 30,000 to 60,000 volts under certain conditions. When an open mold develops 'dust stars' on the surface, a charge of at least 6,000 volts is present.

How is Static Electricity Generated?

There are two primary mechanisms to generate an electrostatic charge: friction or contact and separation. We are all familiar with friction-caused static. When you walk across carpet, friction charges your body, which promptly discharges when you touch an object (such as the doorknob.) When the humidity is low and you walk across the FRP shop, you generate static within your pants legs, which draws fiberglass

dust up your legs. If you wear pants made of synthetic fiber, a much higher charge is developed and more dust is drawn higher up your legs. To avoid immense discomfort, wear only cotton clothing in the shop in the winter!

There are other ways of developing friction that may become hazardous. For example, fluid flowing through a spray gun hose causes a static charge to develop. Even a liquid such as acetone, being poured out of a drum spout will develop a static charge. But the most hazardous of all static generators in the FRP shop is the chopper gun. Non-conductive gun roving is pulled through roving guides at high speed. The friction that results turns a chopper system into a virtual static generator.

Static generated by contact and separation is experienced when we remove a part from a mold. We have all experienced the typical scenario – you've driven the wedges in around the flange and the part is loose in the mold. You then grab the flange and lift the part from the tool. The first thing you feel is all the hair on your arms stand-up, then all the resin particles leap onto your cloths, and as you lift the part further... ZAP. A discharge takes place: 30,000+ volts equalize the surface charge. That is contact and separation.

Understanding Static in the Shop

Spray guns develop an electrostatic charge because of the friction of fluid moving through the spray lines. Typically high-pressure fluid lines have an inner lining of high-density polyethylene, which is a non-conductive thermoplastic. As resin or gel coat flows through the line, friction occurs, which produces a charged fluid stream. When the fluid exits the spray tip, a contact and separation charge may also develop.

Chopper guns add to the problem by pulling gun roving through a series of roving guides on the way to the gun. Using metal roving guides (or homemade cardboard tape roll cores) creates a very high charge as the roving is pulled through the guides at high speed. This action charges the spray rig boom as well as the gun roving. If grounded properly, the boom will bleed off the charge, but the non-conductive glass roving will retain a considerable charge. Additionally, as the already charged roving runs through the chopper mechanism, a substantial charge may be imparted between the cot and the blades. The glass will retain a very high charge out of the chopper chute if the unit is not properly grounded.

Surface charge on molds is another aspect of this problem. Since typical FRP molds are non-conductive, they cannot be effectively grounded. Even if a mold has a metal sub-structure and the metal is grounded, the mold will still retain a surface charge. The charge may bleed off slightly in the areas of metal framework, but for the most part the laminate effectively insulates the grounded frame from the mold surface. Molds become charged by several means – removing parts, friction from rubbing the surface during waxing, and accumulating electrons from charged chop on the surface.

The non-conductive nature of FRP molds works for and against us. Electrostatic charge cannot be effectively bled off the surface. However, when an electrostatic discharge (EDS) occurs, it only discharges a local portion of the surface and not the entire surface. This phenomenon reduces the severity of EDS by reducing the quantity of electrons transferred during the discharge.

Dealing with Spray Guns

Much of the electrostatic discharge issue involves resin or gel coat application equipment. Because of this all fluid-handling equipment MUST be properly grounded. Electrical continuity must be established from the body of the spray gun, through the fluid hoses, to the pump and to a known ground. High-pressure fluid lines have a ground wire incorporated in the hose jacket. This ground wire must be in contact with the fittings at each end of the hose. (Check with your equipment supplier for specific procedures to establish a ground with your fluid lines). It is highly recommended that a separate ground wire be run from the spray gun back to the resin pump. This wire should connect the metal body of the gun and be bundled with the hoses leading back to the pump unit. The pump in turn should be connected to a confirmed earth grounding point. It is easy to confirm a complete ground circuit using a low cost continuity meter.

Please take note that it is an OSHA requirement to have all spray equipment properly grounded. You will be fined if improperly-grounded fluid-handling equipment is noted during an inspection. Additionally, your insurance company requires proper grounding. Poor handling of this important aspect of safety could affect your premiums.

Chopper Gun Precautions

The chopper system is a highly effective static generator, but there are several methods to reduce potentially hazardous discharges.

- 1) Always use ceramic roving guides from the roving creel out to the end of the overhead boom. Never use plastic funnels, tape roll cores, or plain metal guides. The ceramic

guides substantially reduce the charge of the roving flowing through the guides. Do not allow shop personnel to place non-standard roving guides in the system.

- 2) Ground the overhead boom and confirm continuity from the end of the boom to a known earth ground.
- 3) Be absolutely certain the chopper unit is properly grounded to the spray gun. Again confirm the continuity from the chopper chute to a known ground point.

Flow Choppers: A New Problem

With the increasing use of flow choppers there is growing notice of a greater static problem with these units as compared to traditional spray guns. The chop (chopped glass exiting the chopper chute) seems to be more highly charged than is normally noted with an atomized chopper gun. Additionally, there is anecdotal evidence that gun roving from different manufacturers may be either positively or negatively charged! In certain cases the chop 'fluffs' on the mold surface, being repelled by the charge in the mold. This phenomenon has caused some operators to change suppliers or even mix two strands of roving from different suppliers.

The flow chopper EDS problem: With a traditional atomized spray gun, the electrostatic charge of the material exiting the spray tip is carried by the atomized particles. The fan pattern presents considerable surface area and allows much of the accumulated charge to bleed off into atmospheric moisture. With a flow coater, the coherent streams of resin present minimal surface area, minimizing the opportunity for the charge to be neutralized by natural means. Additionally, the multiple streams of a flow coater present many contact and separation points at the fluid

tip compared to only one on an atomized spray gun. Where an atomized spray pattern seems to have the ability to carry off a charge, multiple flow streams seem to generate greater electron imbalance.

Because of the higher levels of charge apparent in flow coaters, for the first time the sizing on the continuous strand roving has become an electrostatic issue. *Sizing* is the chemical treatment on the surface of glass fiber filaments. The sizing enables the handling of the filaments and more importantly acts as an interface to bond the resin to the glass fiber. Sizing formulations are proprietary from each of the glass manufacturers, and are designed with the handling, wet-out and laminate properties of the glass in mind. It appears that different sizing formulations can produce either a positive or negative charge as the chopped glass exits the chopper chute.

In observing the interaction of the glass-charging phenomenon, it appears that if the chop is positively charged and the mold is negatively charged, the chop lays down well. On the other hand, if the chop is negatively charged and the mold is negatively charged, the chop seems to be repelled from the mold surface resulting in the observed 'fluffing' of the chop.

As a result these problems it is much more critical to *ground* all components of a flow chopper. Some flow chopper manufacturers have installed a separate grounding lug on the chopper chute to bleed off as much charge as possible at the last contact with the ejected chop.

Conductive Surface Molds: A Warning

Conductive tooling gel coat was

originally developed to promote electrostatic gel coat application. In electrostatic spraying the mold is negatively charged and the spray pattern is positively charged. The sprayed material is attracted to the mold surface, which promotes even coverage. While electrostatic gel coating has not been successful for several reasons, the use of conductive gel coat has continued. Many fabricators have found that the conductive gel coat produces a durable, high gloss tooling finish – regardless of its electrical properties.

Conductive surface molds present a new level of challenge and awareness in terms of dealing with ESD. As previously mentioned, a typical non-conductive mold will only bleed off the surface charge from a local area during a discharge. However a conductive surface mold, by virtue of being conductive will discharge the entire mold surface in one contact. Because of this conductive surface molds have a much higher potential for a high voltage discharge than their non-conductive counterparts.

In the electrical world a *capacitor* is two conductive surfaces separated by an insulator. When the charge of one of the conductive surfaces becomes great enough to bridge the insulating gap, a discharge takes place to the other conductive surface. A mold made from conductive tooling gel coat is a big capacitor. The conductive surface accumulates a charge and is insulated by the non-conductive laminate. When another conductive object, such as the human body, comes close enough the capacitor discharges the entire mold surface.

Molds with conductive tooling gel coat surfaces *must be grounded* at all times to prevent hazardous ESD. There are two recommended methods of

grounding conductive surface molds. One is to drill a countersunk hole on the mold flange and place a flathead brass bolt in contact with the tooling gel coat. The bolt is then grounded. The second method is to place a fine copper screen in the wet gel coat around the mold flange during mold construction, then mount a brass ground bolt through the flange. The grounding lugs must then be connected to a known grounding point.

Preventing Hazardous ESD in Composites Operations

There are several aspects of static discharge mitigation to consider, including equipment, molds, environmental conditions, and devices to reduce static electricity.

Equipment – Ground all fluid handling equipment and pay particular attention to grounding flow coaters and flow choppers.

Molds – Ground all conductive molds. This includes molds with conductive tooling gel coat surfaces and metal molds. Ground all metal fittings in non-conductive molds, such as blowout ports or metal trim edges. Ground the metal structure on the backside of a non-conductive mold in *not* an effective method of bleeding static charge off the mold surface, it can however prevent shocks from touching the metal structure.

Environmental Conditions – Low humidity is a prime factor in ESD. When atmospheric moisture drops below 50% relative humidity (RH) and static problem may develop. In the winter it is important humidify the plant production areas. On the high end humidifiers can be incorporated into forced air-heating systems or auxiliary humidifiers can be placed in critical molding areas, and several different types are available. As

a last resort there is a no cost method of maintaining plant humidity – simply wet the shop floor periodically during the day. Keeping the floor damp provides a good method of evaporating large quantities of water over a large area. It also helps keep the dust down.

Ionization – Treating the plant air or compressed air from blowguns by ionization can reduce ambient static development, or can be used to treat a local area. For example, blowing off a mold with ionized air will neutralize the surface charge for the moment. This may be used when blowing off dust prior to waxing the mold. However the act of rubbing the mold surface will create a surface charge. This will require the application of ionized blowgun air repeatedly during the waxing procedure. Ionization blowguns are nuclear powered, using Polonium 210 isotopes that have a half-life of about 138 days, so they need to be replaced on a regular basis. The radiation produced by this isotope is not harmful to humans.

Electrostatic discharge is no joke as witnessed by the chopper operator at the boat plant. In this specific case the new combination of a flow chopper – with increased static levels, the non-grounded conductive mold, and the low humidity conspired to cause a near disaster. The fortunate aspect is, “Houston, we have an answer”. By paying attention to these recently discovered aspects of ESD you can avoid potentially hazardous situations.