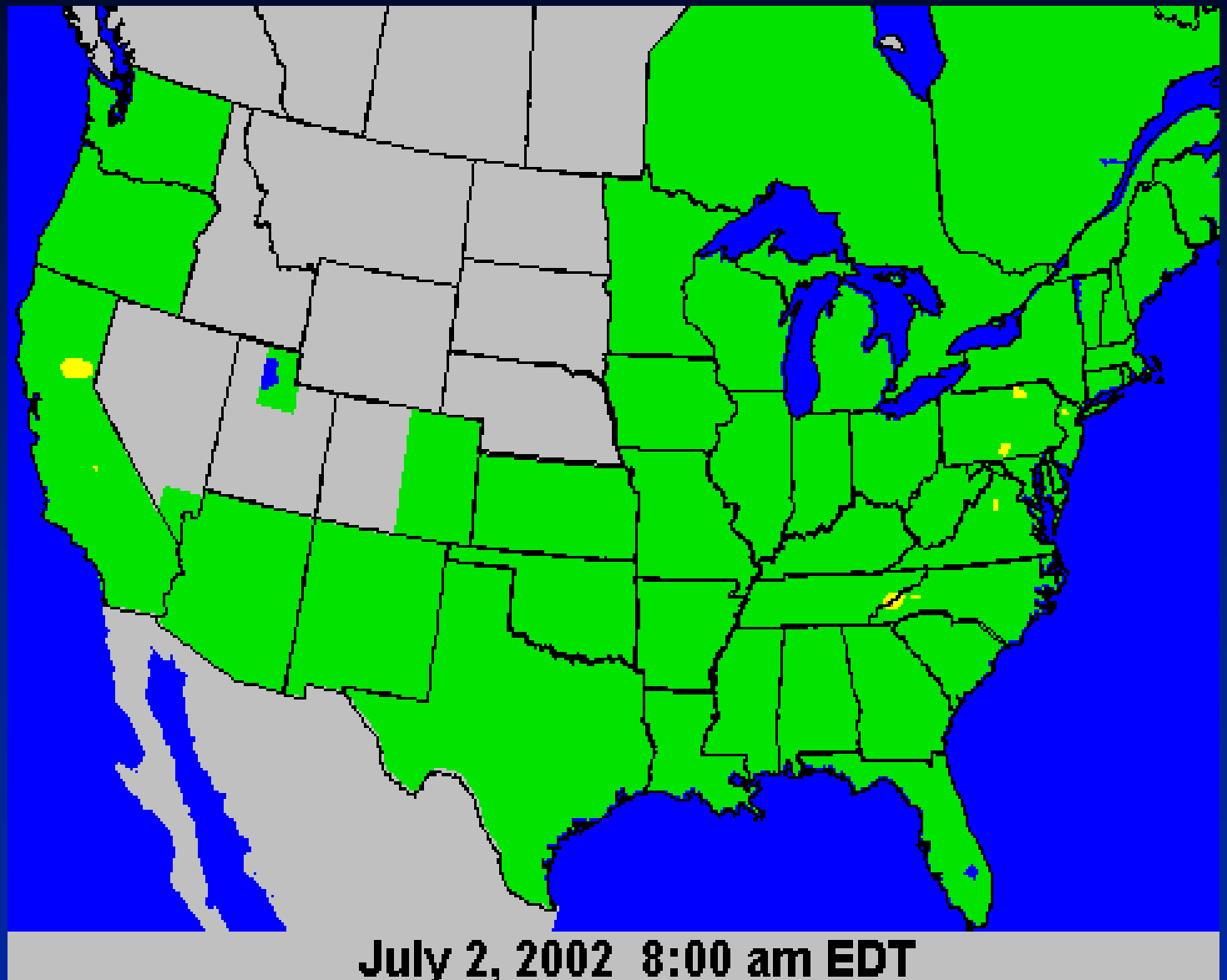
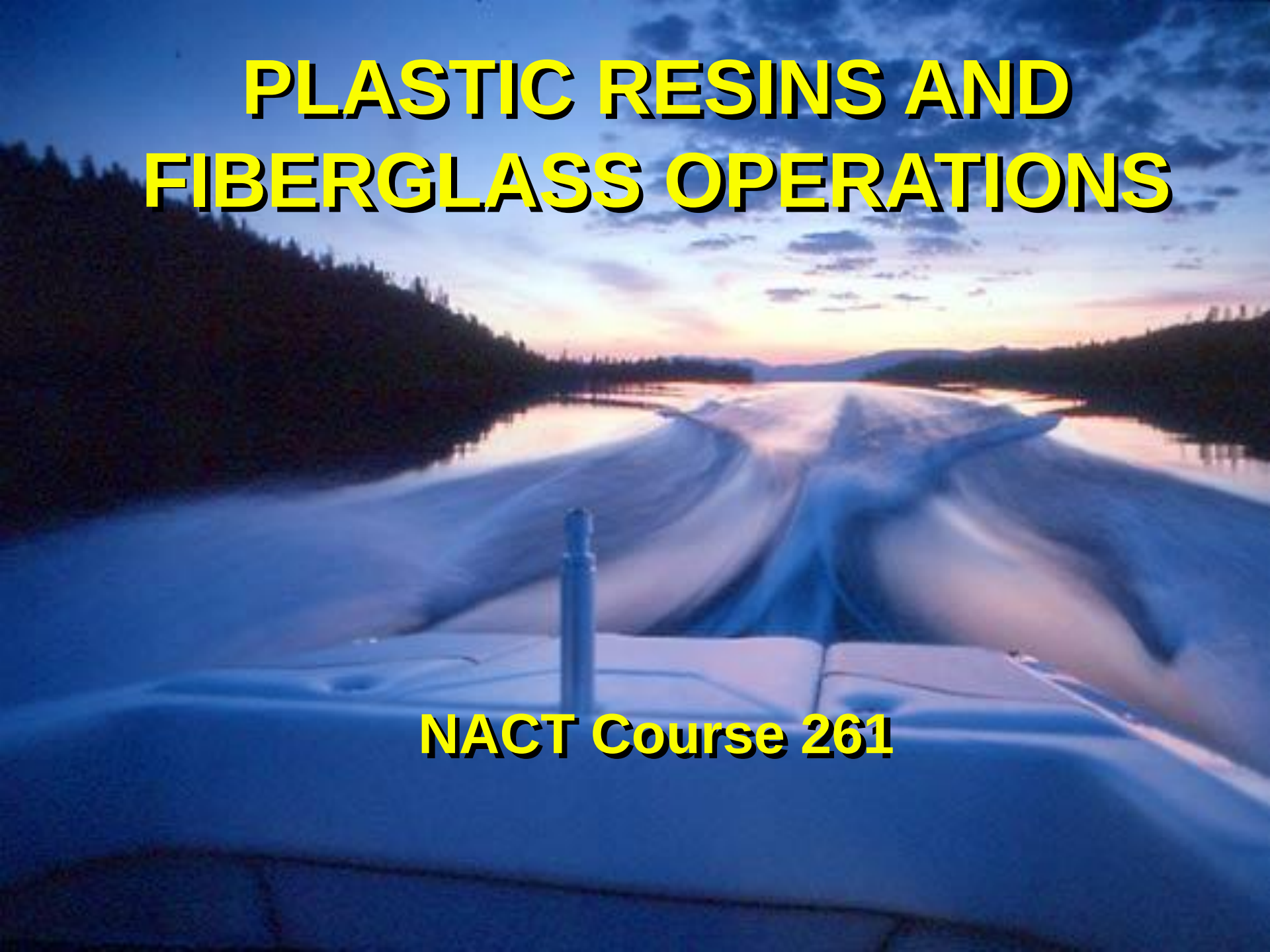
OZONE Formation



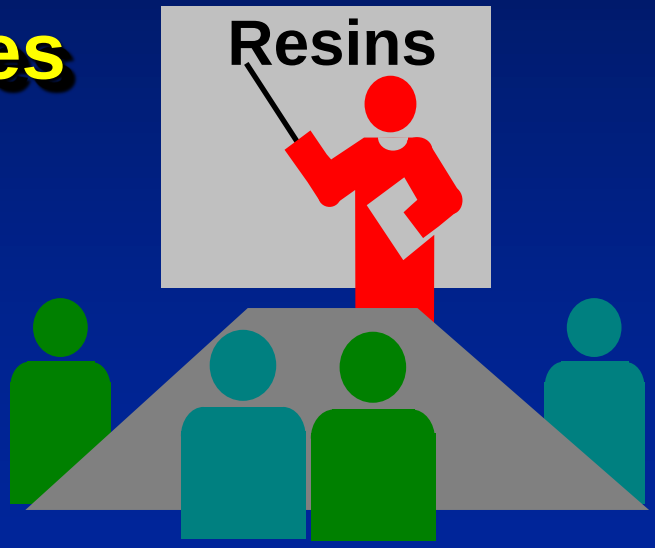


PLASTIC RESINS AND FIBERGLASS OPERATIONS

NACT Course 261

Course Overview

- Plastic resin uses
- Plastic resin theory / operation
- Air pollution control devices
- Implementing regulations
- Typical permit conditions
- Inspection procedures
- Federal regulations



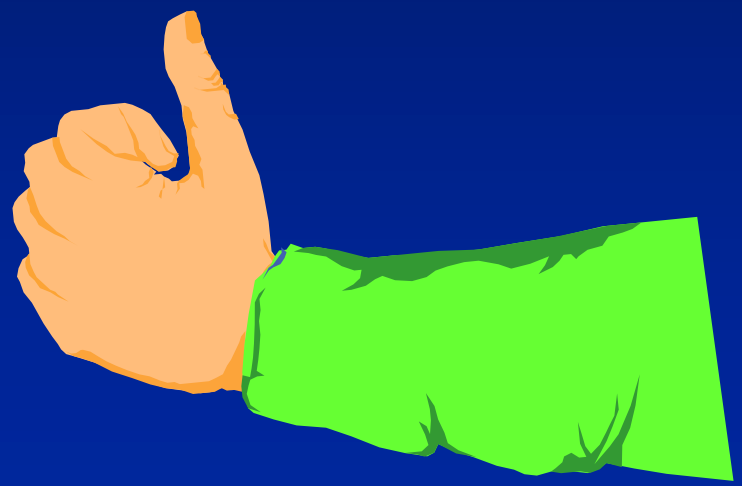
Uses of Polyester Resins

- Aircraft / Aerospace / Automotive
- Marine / Railroad applications
- Electrical / Electronic components
- Construction / Building materials
- Packaging materials
- Consumer / Institutional products
- Corrosion resistant products
- Business equipment
- Furniture / Furnishings


Composite Decking

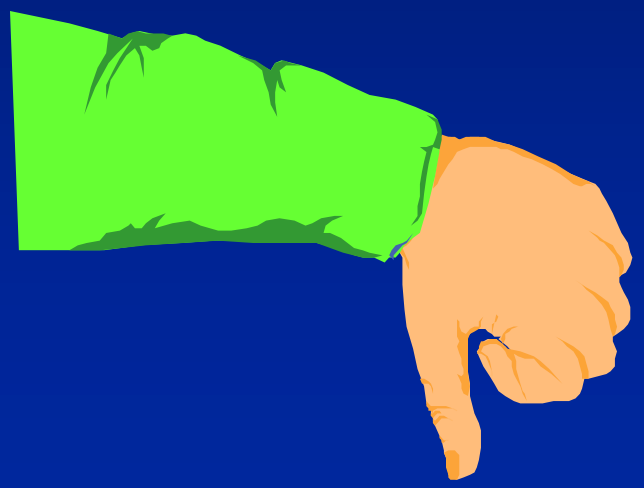
Advantages

- Structural strength & rigidity
- Heat resistance
- Corrosion resistance
- Dielectric strength
- Design flexibility
- Low finish cost
- Moisture resistance
- Reuse & recycle
- Light weight
- Durable



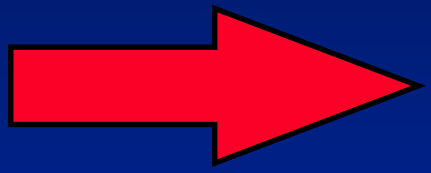
Disadvantages

- VOC emissions
- Toxicity issues
- Flammability
- Storage
- Disposal



Emissions From Polyester Resins

Resins & Glass Fiber



- Ethylene
- Styrene / MMA
- Ethylene Glycol
- Pentane
- Acetone / MEK
- MEKP
- Dibasic Ester

Coming to Terms

- **Plastic**
  - Organic compounds that can be molded
- **Polymer**
  - Two or more like molecules joined to form a more complex, physically different molecule
- **Resin**
  - Carbon compound polymers used in reinforced products to surround and hold fibers

How are Plastics made?

- Consist of building blocks : HC
  - derived from petroleum or NG
  - Monomers (mono=one, mer =unit)
  - bonded into chains → Polymers

- Reaction known as Polymerization
  - Ethylene → Polyethylene
  - Propylene → Polypropylene


Let's Discuss Common Plastics

Common Plastic Materials

- Polycarbonate
- Polyethylene
- Polystyrene
- Polypropylene
- Polyurethane
- Polyvinyl Chloride
- Polyesters

Polycarbonates

- Created to compete with die-cast metals
- Strong, tough & rigid
- Excellent electrical insulators

- Mostly electrical uses

Polyethylene : PET

- Clear, very tough polymer
- Excellent barrier against O_2 and CO_2
- Good chemical resistance

- Soft drink bottles
- Fiber (the polyester 70s!!!)
- Magnetic tape (audio & video)


OLN
SM
OUTDOOR LIFE
NETWORK
Polyester Fiber Jacket


POLARTEC
Fleece Made From
Recycled “PET”


PET
Product

High Density Polyethylene

- High density version of PE
- Excellent protective barrier properties & Strong

- Milk, juice & H_2O container
- Household chemicals
- Detergents

High Density Polyethylene

Low Density Polyethylene

- Low density version of PE
- Offers clarity & flexibility
- Provides ductility

- Grocery & garbage bags
- Shrink & stretch films


Composite Decking

Polypropylene

- “Workhorse” of plastics
- High tensile strength
- High melting point
- Good chemical resistance

- Packaging & carpeting
- Automotive & appliances

Polystyrene

- Foamed or Expanded Polystyrene : EPS
- Exceptional insulation properties

- Foam cups & containers
- Foodservice products
- Packaging & protecting


Expanded Polystyrene Foam

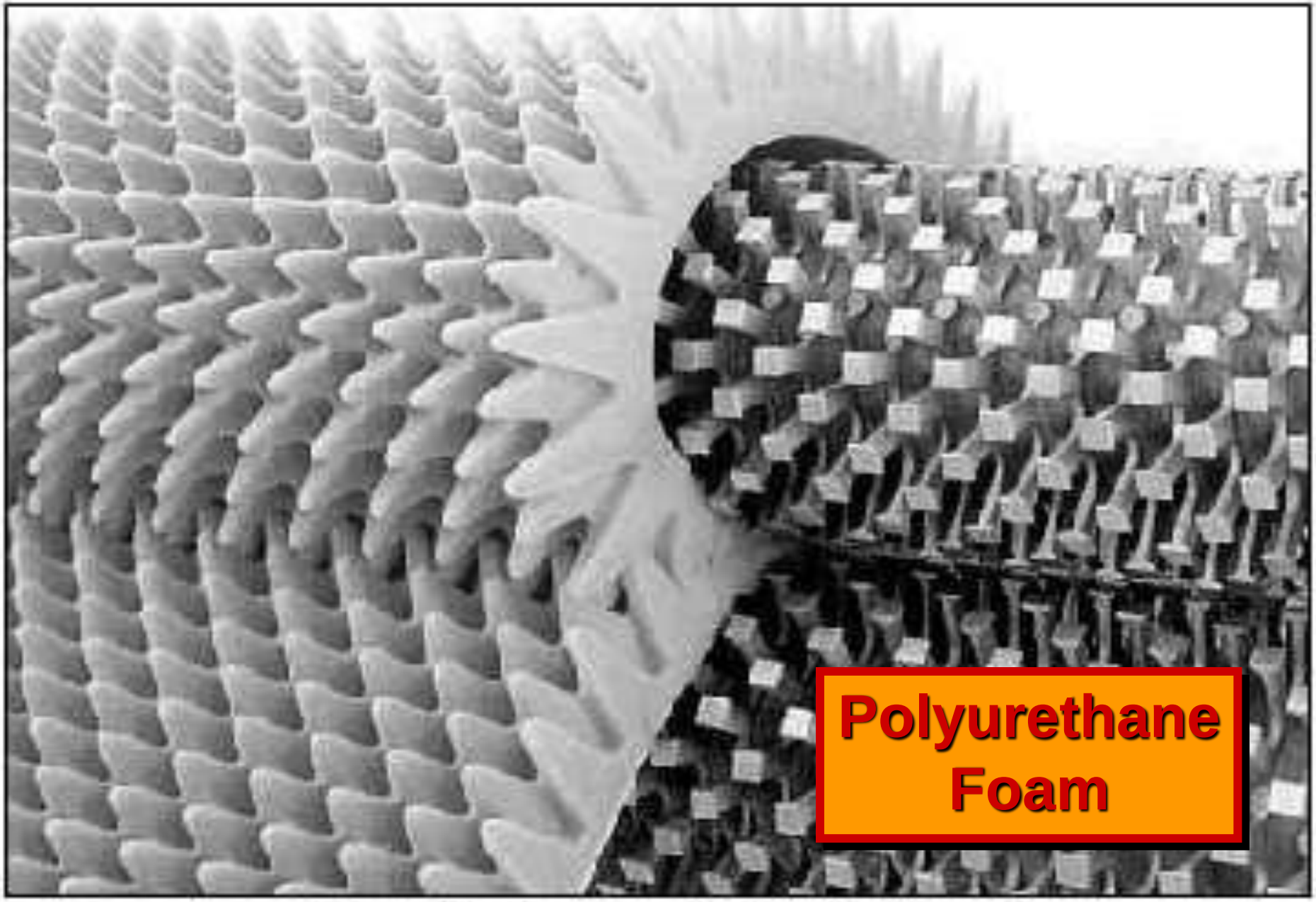

Recycled
Polystyrene


Recycled Polystyrene
Baseboard Molding

Polyurethanes

- Foam : bedding, auto seats, cushioning, carpet underlay

- Insulation & flotation
- Polyurethane coatings
- Abrasion resistant : printing rolls, conveyor belts, gaskets & seals



Convoluters use patterned dies to efficiently produce profile shapes from sheets of foam.

Polyvinyl Chloride (PVC)

- Chemical, abrasion & weather resistance

- Pipes & sidings
- Leather-like upholstery
- Gloves, boots & apparel


What are Composites ?

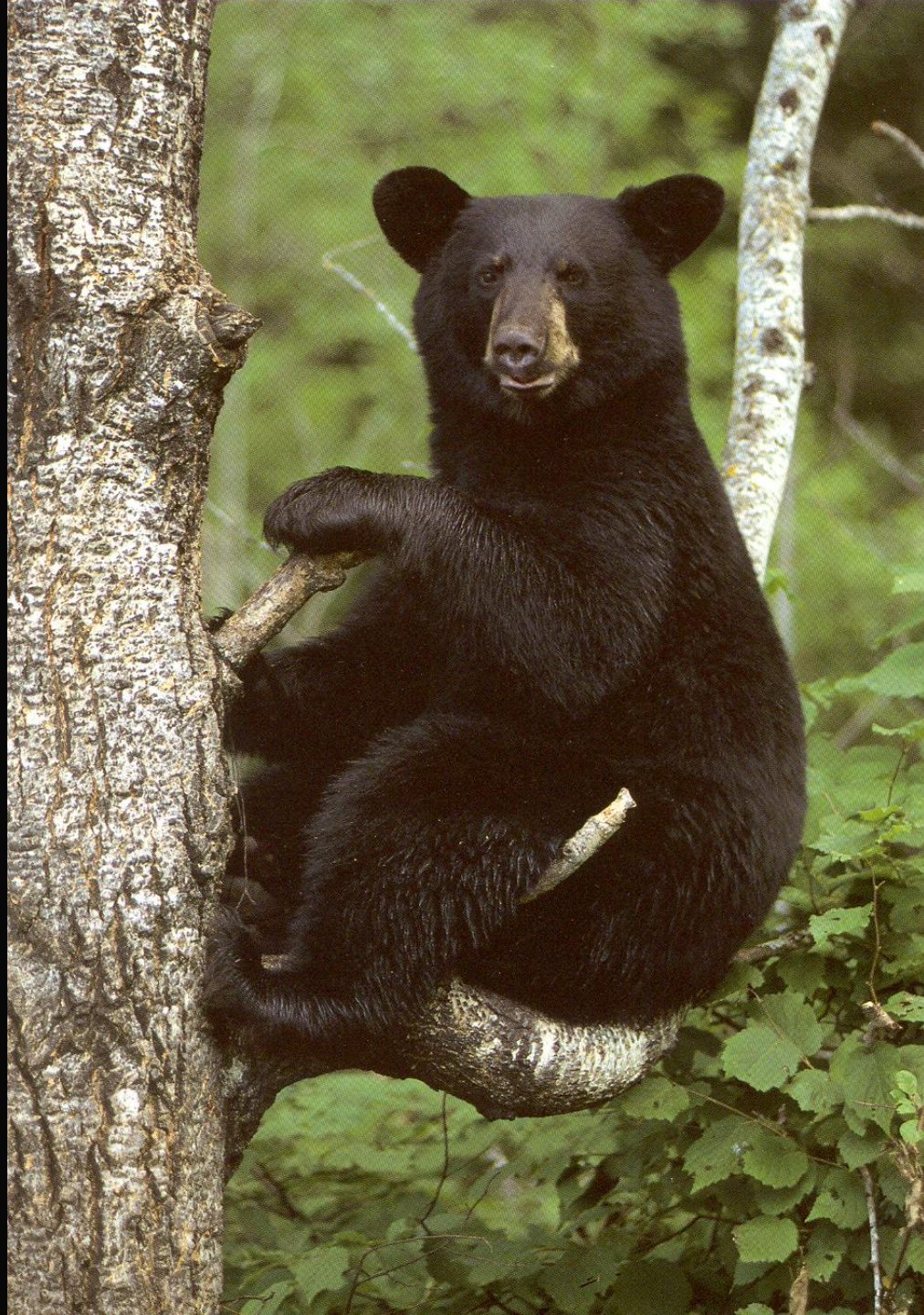
Introduction to Composites

- Made up of 2 or more components
  - Fibrous reinforcing network embedded in the cured resin matrix
  - Types of reinforcements → Fiberglass, Carbon fiber & Kevlar®
  - Thermosetting type resin is a plastic that cures from a liquid to a solid state
    → Polyester, Vinyl, Epoxy & Urethane


Composite
Material

Types of Reinforcements

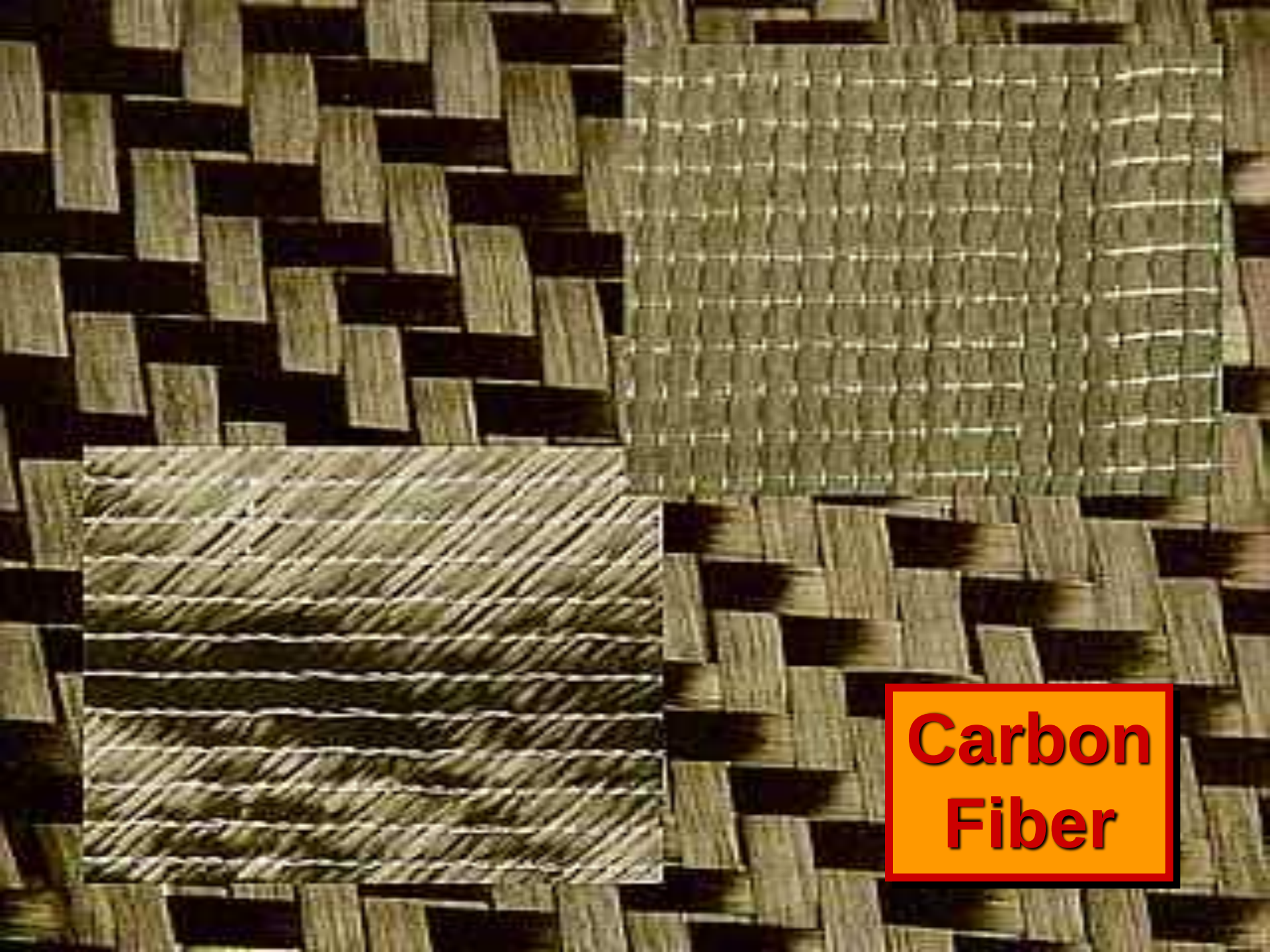
- Fiberglass
- Carbon Fiber
- Kevlar



Carbon Fiber

- Stiffest & strongest reinforcing fibers for polymer composites
- Used together with epoxy

- Race cars
- Space applications
- Sporting equipment


Carbon
Fiber


Carbon Fiber

Carbon Fiber Product

Fiberglass

- Made of silicon oxide
- Produced by a spinning process
- Pulled through a nozzle from molten glass

- Reinforcing materials
- Automotive and naval industries, sporting equipment

Fiberglass Forms

Fiberglass Forms

- Surfacing Mat (Veil)
- Chopped Strand Mat
- Roving (Spool)
- Woven Roving
- Cloth (Hand Lay-up)


Fiberglass
Forms


ANCOR
BLACK&DECKER
Spacemaker
Fiberglass
Forms

Fiberglass Advantages

- High strength
- Low price
- Dimensional stability
- Temperature resistance
- Corrosion resistance
- Low weight
- Excellent dielectric properties

Fiberglass Product


Fiberglass
Spa

Types of Fiberglass

- E-glass and S-glass
- E-glass → Good electrical properties
- S-glass → Very strong, stiff, and temperature resistant

Glass Fiber Reinforced Resin

- Most used composites
- Temp resistance & strength
- Impregnating fibers with liquid epoxy resins

- Aircraft components
- Casings for missiles, pipes, tanks, pressure vessels

Kevlar®

- Lightweight Flexible Comfortable
- High Tensile Strength
- Excellent Dimensional Stability
- High Flame Resistant
- High Chemical Resistant
- Used with epoxy or vinyl resin


Kevlar Product

Kevlar®

- Protective & Performance Apparel
- Composites : aircraft parts/boats
- Fiber-Optic Cables
- Tires
- Ropes & Cables
- Brake Pads & Clutch Linings
- Power Transmission Belts / Hoses


Kevlar
Product


Let’s Discuss Types of Plastic Materials

Types of Plastic Materials

- **Thermoplastic Resins**
  - become fluid upon heating
  - repeatable & reversible process
  - no chemical change
  - no permanent change in physical prop.
  - readily extruded or molded

  e.g.. film, fibers, bottles etc.

  Polyethylene, Polystyrene & Polypropylene

Types of Plastic Materials

- **Thermosetting Resins**
  - irreversibly polymerizes and solidifies
  - chemical structure permanently altered
  - cannot be resoftened
  - process called curing or hardening

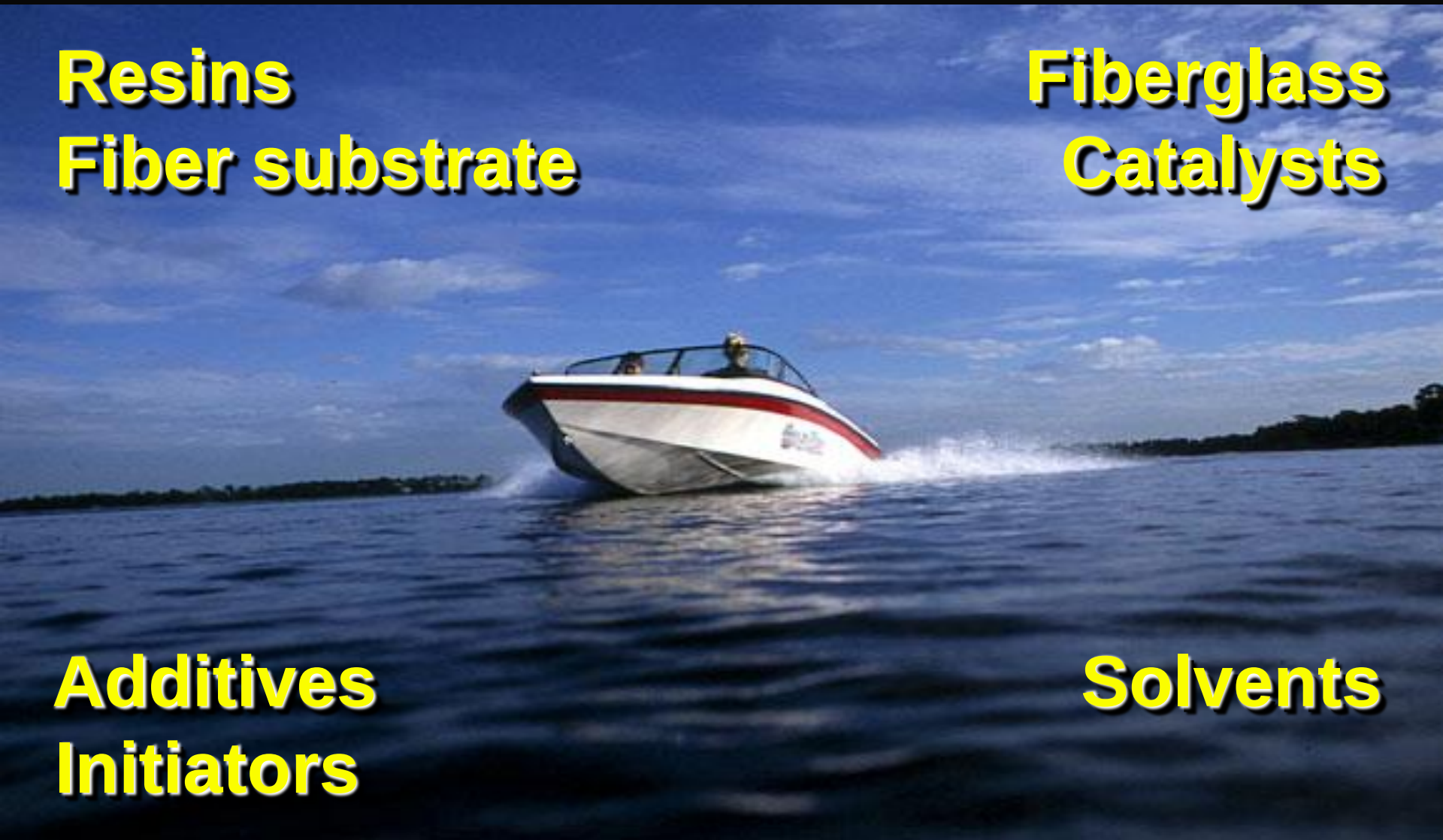
  e.g.. Molding, casting, powder coating

  Polyurethanes, Polyester & Epoxy resins

Thermoplastic vs. Thermosetting

Thermoplastic	Thermosetting
Faster molding Lower emissions Lower costs Easy recycling Low labor intensity	Design constraints Limited unit production Performance requirements Market demands

Raw Materials



Resins
Fiber substrate

Fiberglass
Catalysts

Additives
Initiators

Solvents

Typical Raw Materials

What is a Resin?

Thermoset Resins

- Two Common Types
  - → Epoxy & Polyester
  - → Molding, Laminating, Casting ….

  - – Epoxy
  - → Higher Performance & Higher Price
  - → High Strength, Weight Critical
  - → Dimensionally Accurate Applications


Epoxy
Resin
Product
UNITED STATES AIR FORCE
USAF

Polyester Resins

- **Building Blocks for Polyester Resins**
  - → Acids & Glycols Cooked Together
  - → Dissolved in Styrene Monomer
  - → Inhibitors Added to Delay Reaction

- **Product Added to a Peroxide Catalyst**
  - → Unsaturated Portions of Monomer and Polyester React Together
  - → Hard Solid Mass


Polyester Resins

Fabrication With Polyesters

- → Reinforcements such as a Glass Fiber in a Mold
- → Saturated with Polyester Resin
- → Resin Mixed with Catalyst Causing Crosslinking Reaction
- → This Causes Resin to Harden from Liquid to Solid

- → Polyester Resin in Fiberglass Boat Mfg.


Let’s Discuss Fabrication With FRP

Fabrication With FRP

→ Fabricating with Metals : Structure is Produced & External Paint is Applied

→ Fabrication with FRP : Reverse

→ Start with Mold

→ Pigmented Polyester Coating (Gel Coat) is Applied to the Mold

→ Structural Reinforcement is Built Using Fiber Glass & Polymer Resin

→ Finished Part is Removed from Mold

First Step : Mold


Second
Step : Wax
Application
Meguiar's
MIRROR
GLAZE
Serving Professionals Since 1901
8
Maximum
Mold Release
Wax
CONTAINS CARNAUBA
WAX


Gel Coat Applied to Mold


Chopped
Fiberglass
Application


Chopped Fiberglass Application


Chopper Gun

Gel Coat Application : Spray Booth


Gel Coat :
Spray Booth

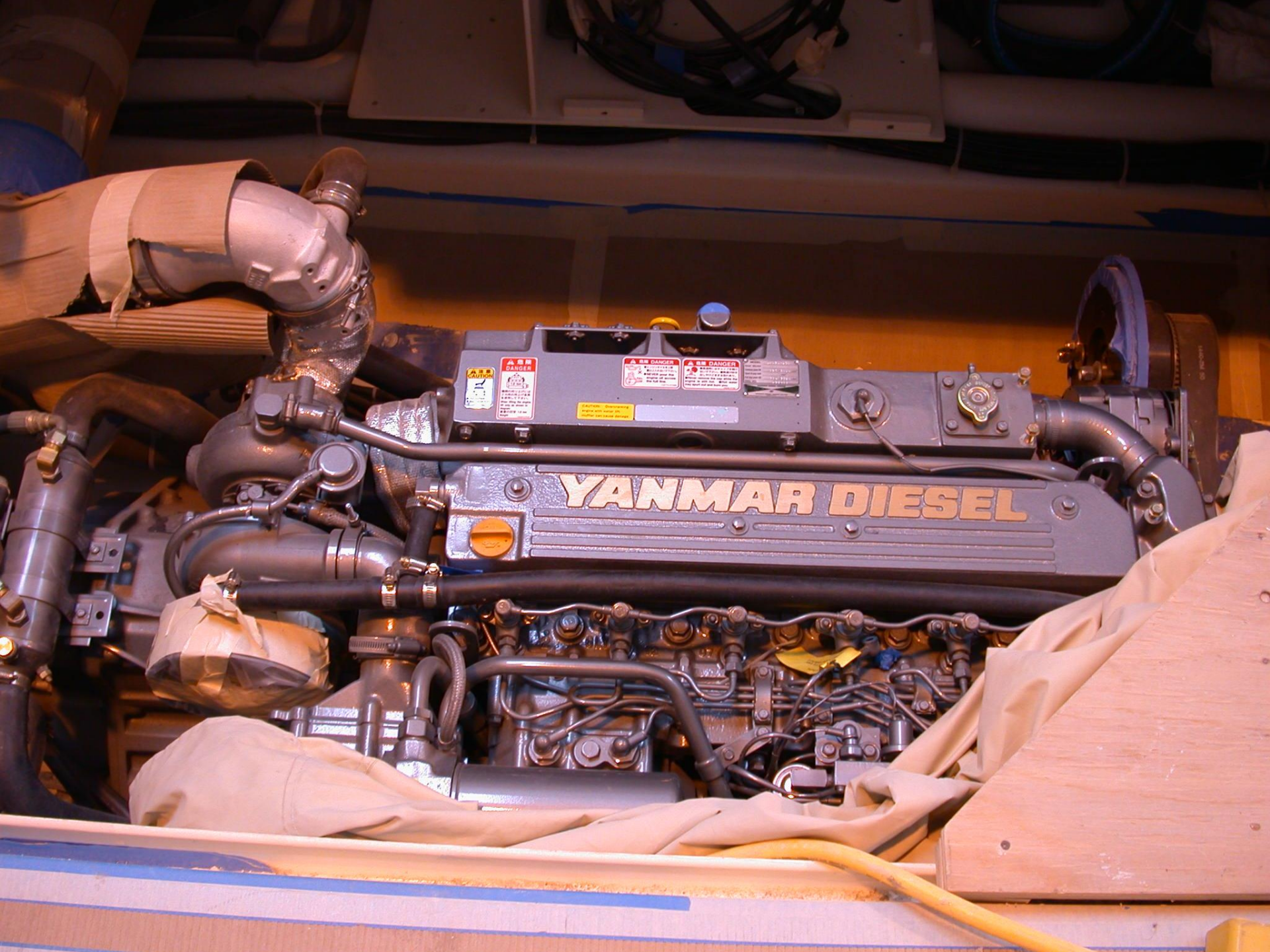

Gel Coat Applied to Mold

Fiberglass Reinforcements


Saturating with Resin


Curing Process


Curing
Process


YANMAR DIESEL


Assembly Line

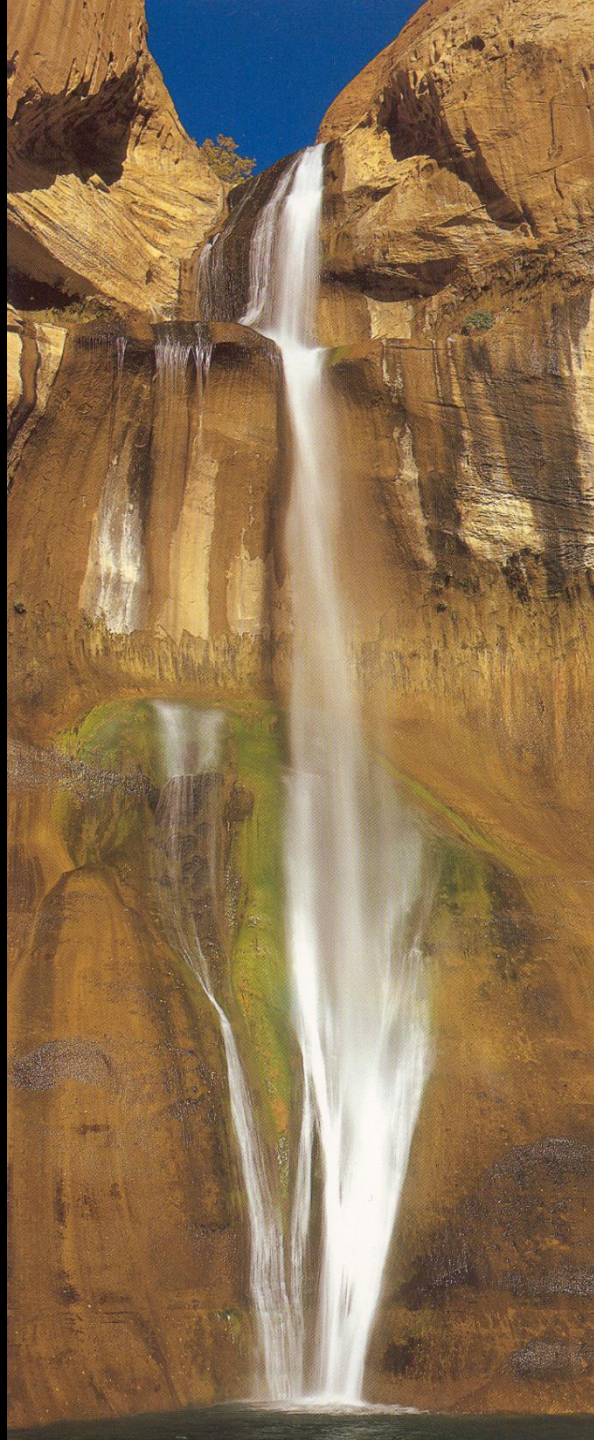

Finished Product


Finished Product


Let's Discuss
Fabrication of
Cultured Stone

Types of Cultured Stone

Cultured Marble
Cultured Granite
Cultured Onyx



Cultured Marble

- Consists of →
  - Crushed Marble & Stone (Mined)
  - High Strength Polyester Resin
  - Protective Gel Coat on the Surface

- Mixture is Poured into a Mold
- Allowed to cure and shrink
- Part is trimmed and polished


Protective
Gel Coat

Fabrication of Cultured Marble


Cultured
Marble
Products


Trimming & Polishing


Cultured
Marble
Product

Cultured Onyx

- **Consist of →**
  - Alumina Trihydrate
  - Polyester Resin Content 28 - 35%
  - Protective Gel Coat on the Surface

- **Products are translucent**
- **They have an added visual depth or a 3-D effect**


Cultured Onyx Product

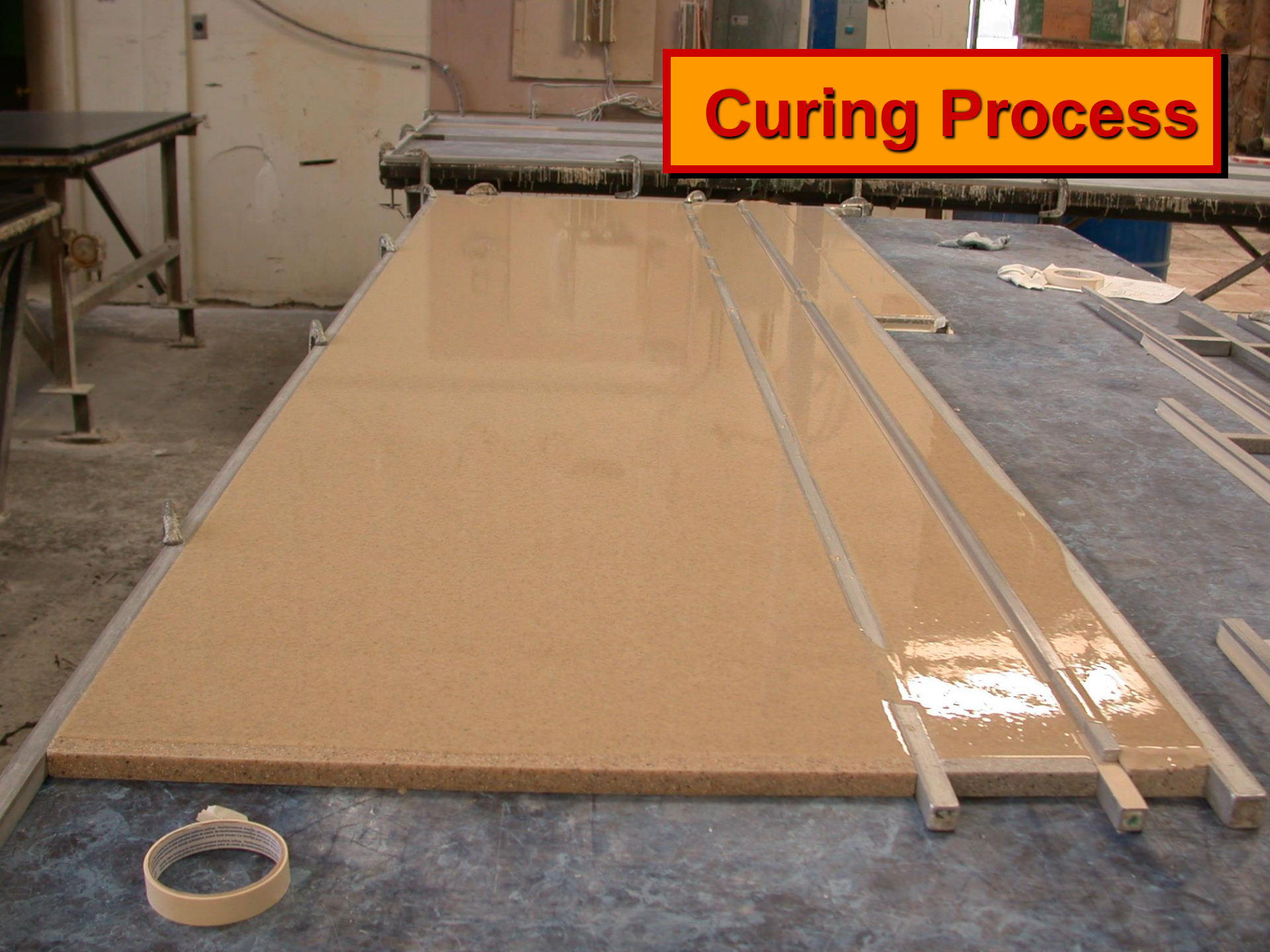
Cultured Granite

- **Consists of →**
  - Crushed Stone & Mineral Chips
  - Polyester Resin Content 40%
  - Protective Gel Coat

- **Offers the Beauty of Quarried Granite**
- **Low Cost**
- **Stain Resistant Coating**


Crushed
Stone
GRANITE
Elite
GRANITE


Polyester Resins


Curing Process


Cultured Granite

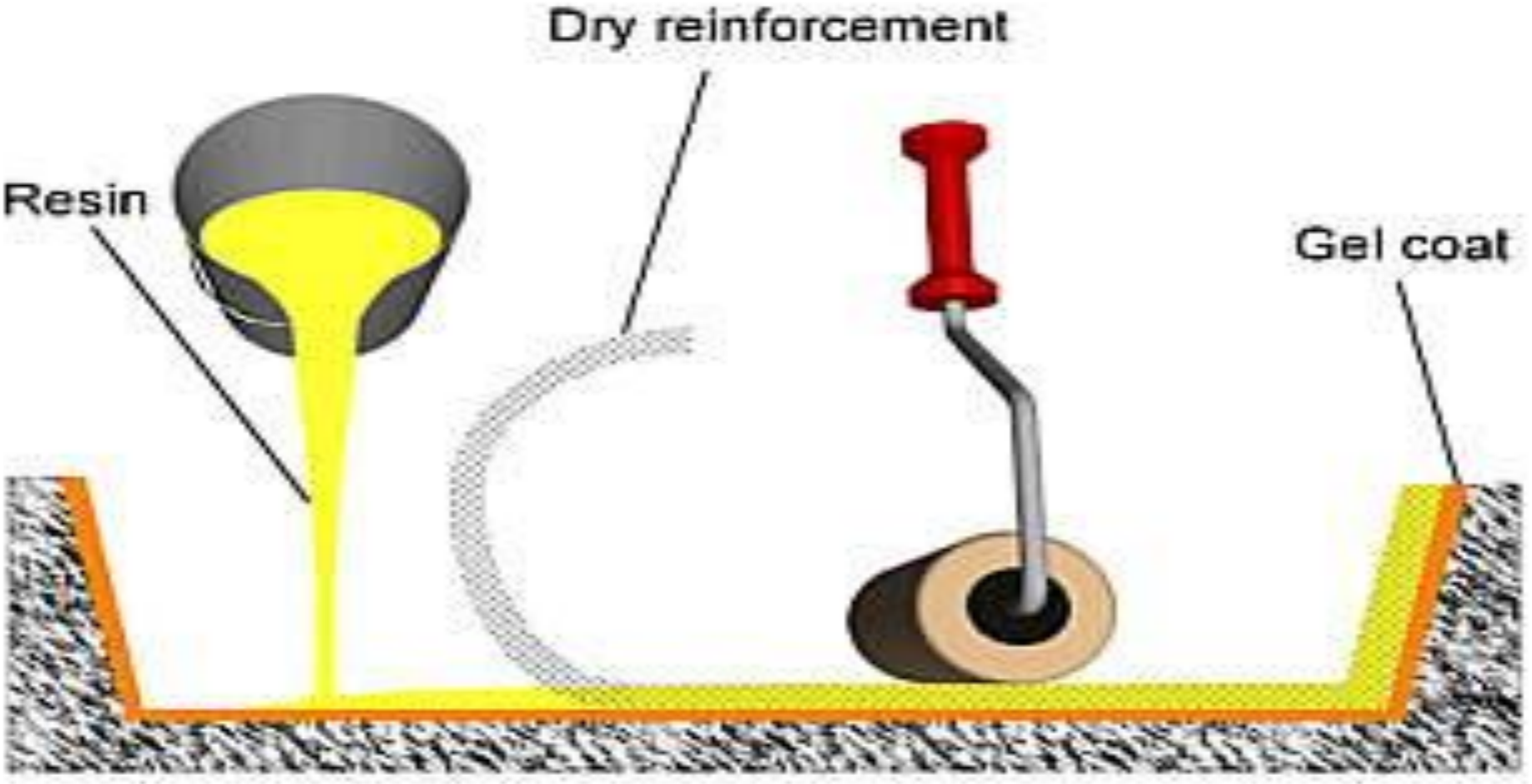

Let’s Discuss Open
Molding Operations

Process and Control

- Types of Open Molding Operations
  - Hand lay-up & Spray-up
  - Continuous lamination
  - Pultrusion
  - Filament winding
  - Casting or molding
  - Infusion or scrimp

Hand Lay-Up

- Simplest Type / Very Flexible
- Apply Gel Coat, Resin, Fiberglass by Hand
- Roller or Brushes Used for Resins
- High Strength to Weight Ratio
- High Styrene Emissions
- Suitable for Prototypes & Low Volume Production


Dry reinforcement
Resin
Gel coat


Hand Lay-Up

Examples of Hand Lay-Up Operations

Hand Lay-Up Product

Let's Discuss Hand Lay-Up Product : Surf Board Manufacturing

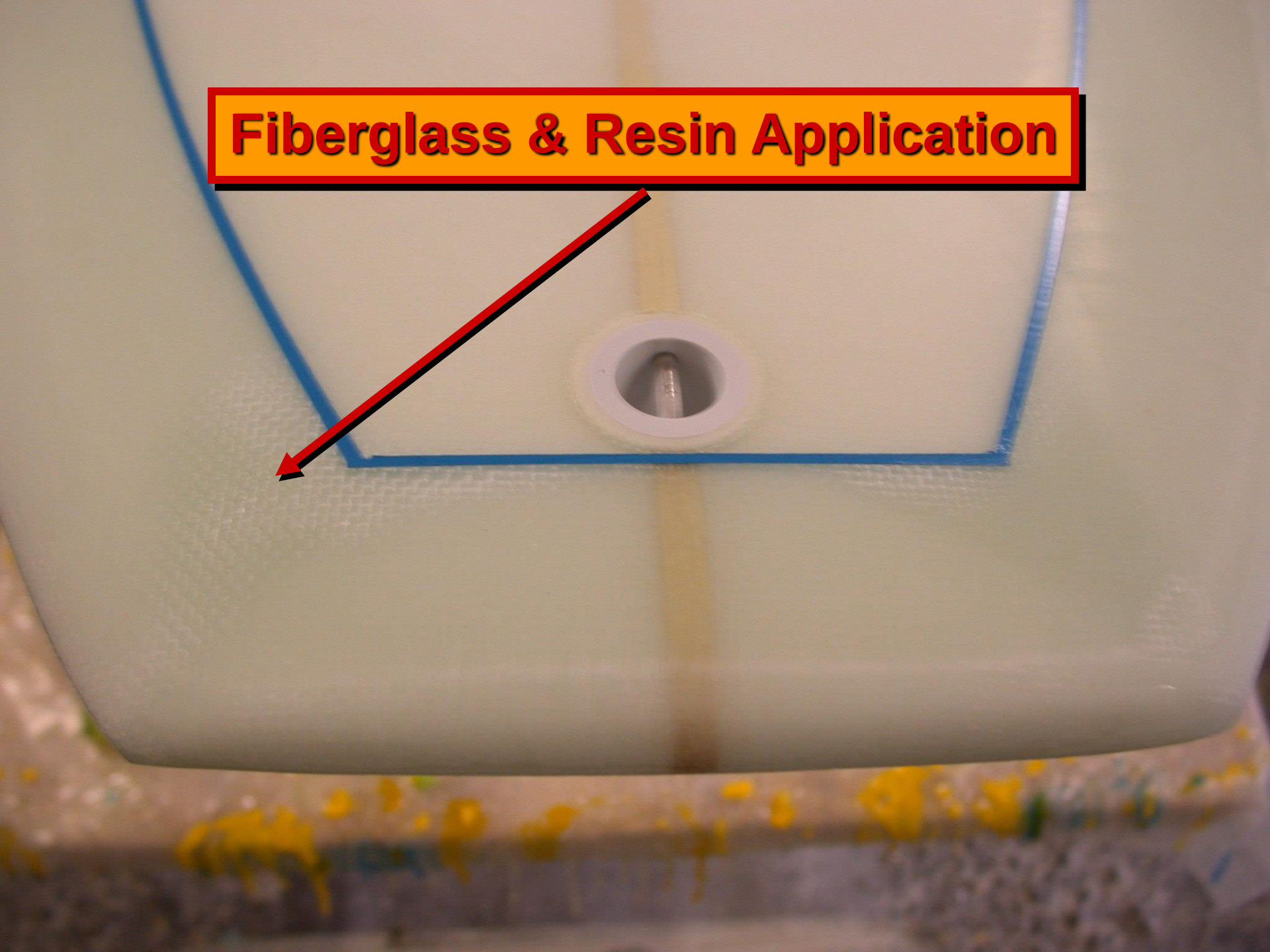
First Step :
Foam Core


Foam Core :
Shaping & Sizing


Fiberglass
Surfacing
Mat


Fiberglass & Resin
Applied to Core


GREAT WHITE


Fiberglass & Resin Application


Grinding & Sanding
Operation

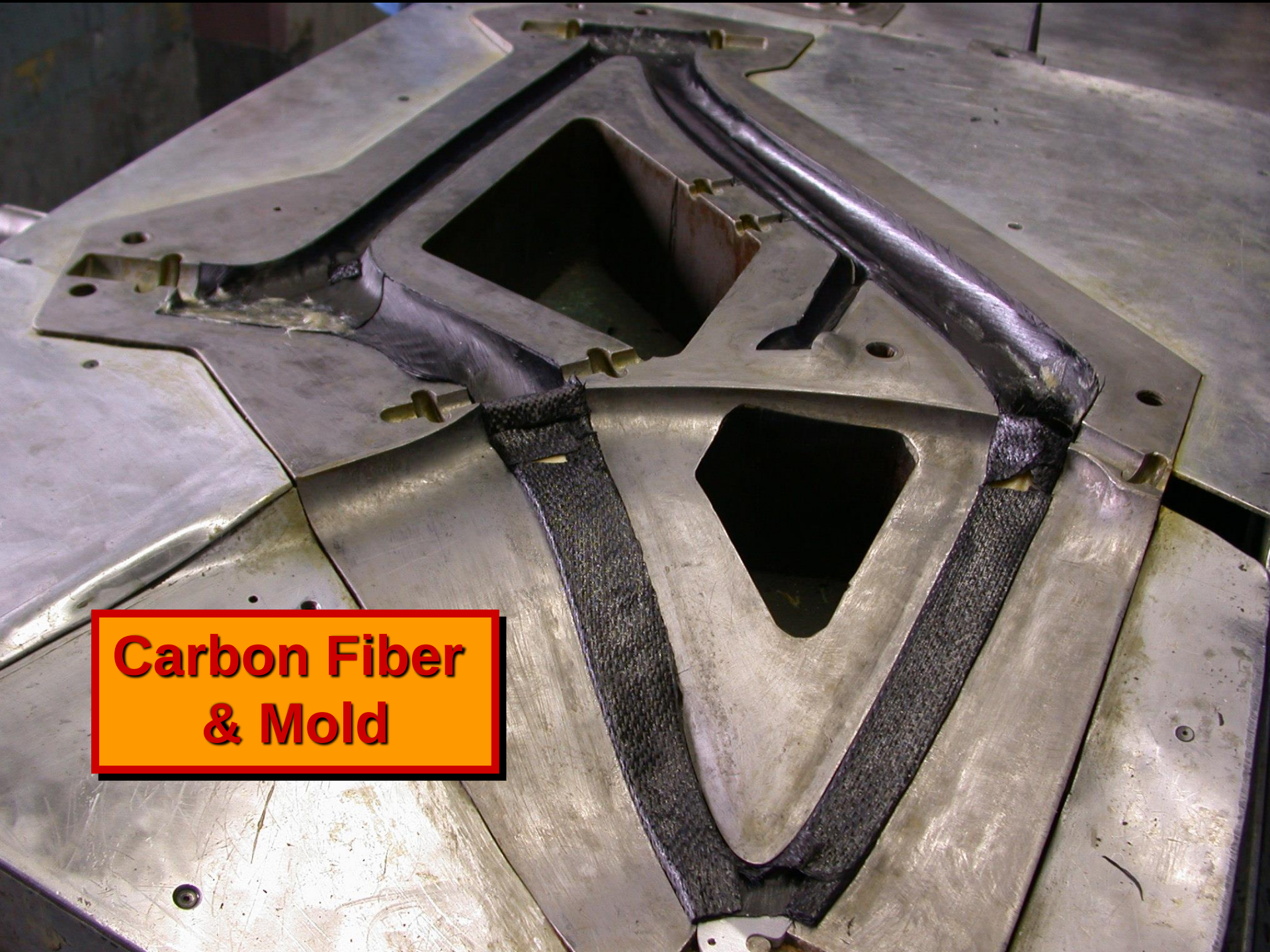
Grinding & Sanding Tools


Waxing & Coating
Operation

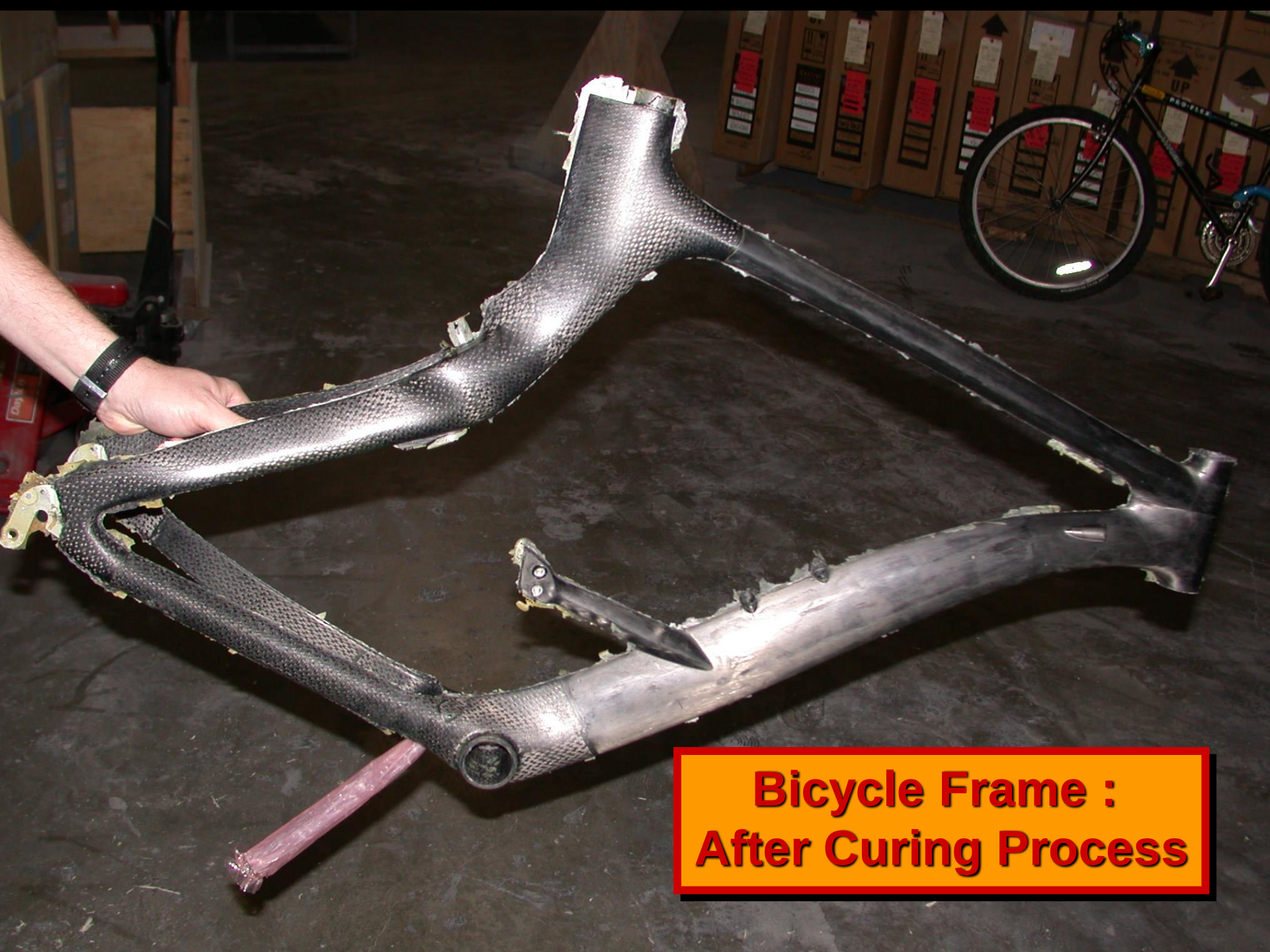

Curing Operation


Let's Discuss
Carbon Fiber
Epoxy Resin Mfg.


Bicycle Frame
Components


Carbon Fiber
& Mold


Top & Bottom
Half of Mold


Bicycle Frame :
After Curing Process


Spray Painting
Operation

Bicycle Frame : Finished Product

Spray-Up

- Versatile Process
- Cost Effective Method of Producing Large Open-Molded Parts

- Chopped Fiberglass is Sprayed With
  - → Catalyzed Resins onto Gel Coat
  - → Compacted

Spray-Up

Spray-up

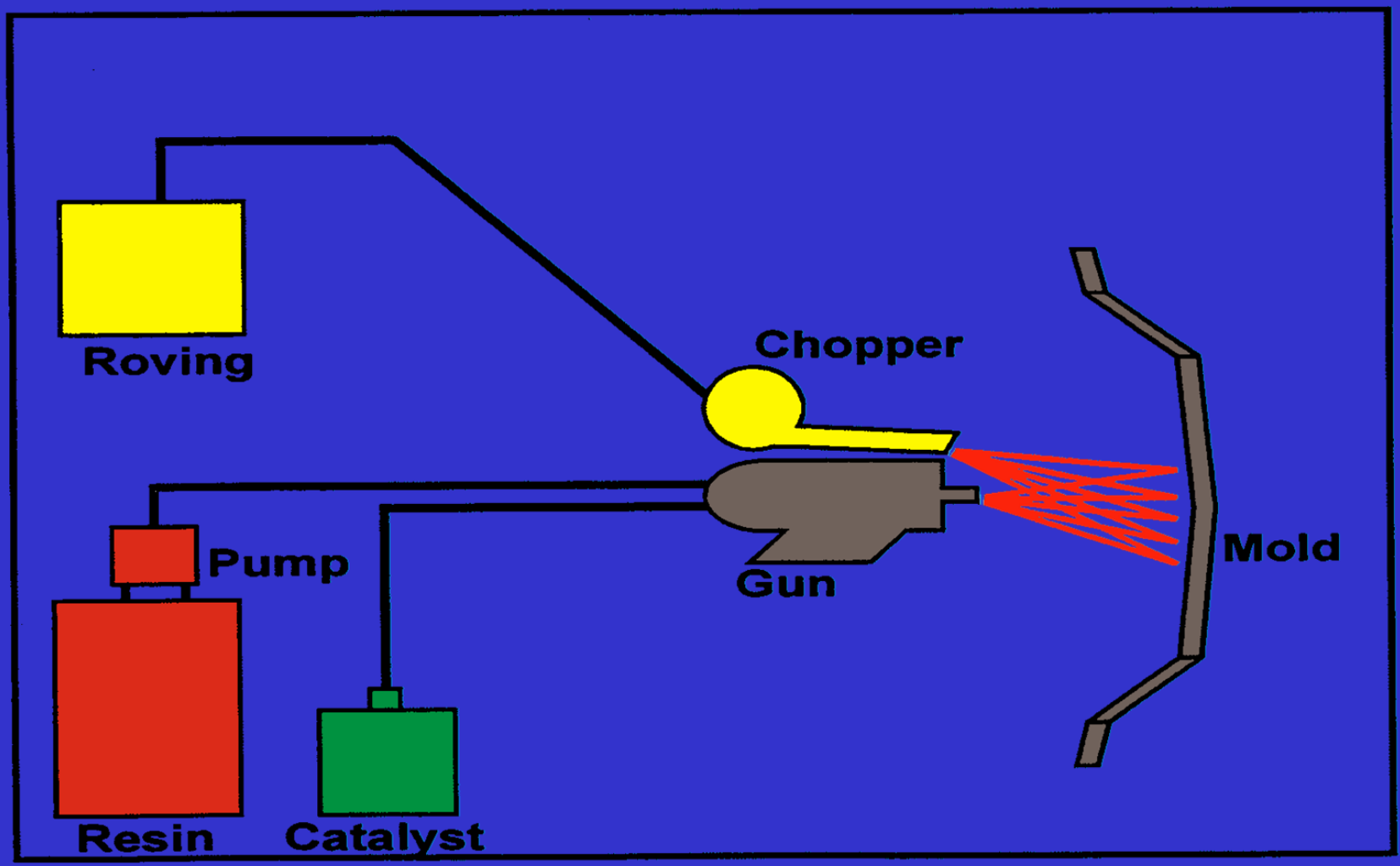


Figure 300.3: Spray-Up

Chopped Fiberglass Spray-up Operation

Controlled Spraying

- Reduces styrene emissions
- Increases transfer efficiency
- Low fluid tip pressure
- Employee gun handling training
- Close containment flanges


Gel Coat Application

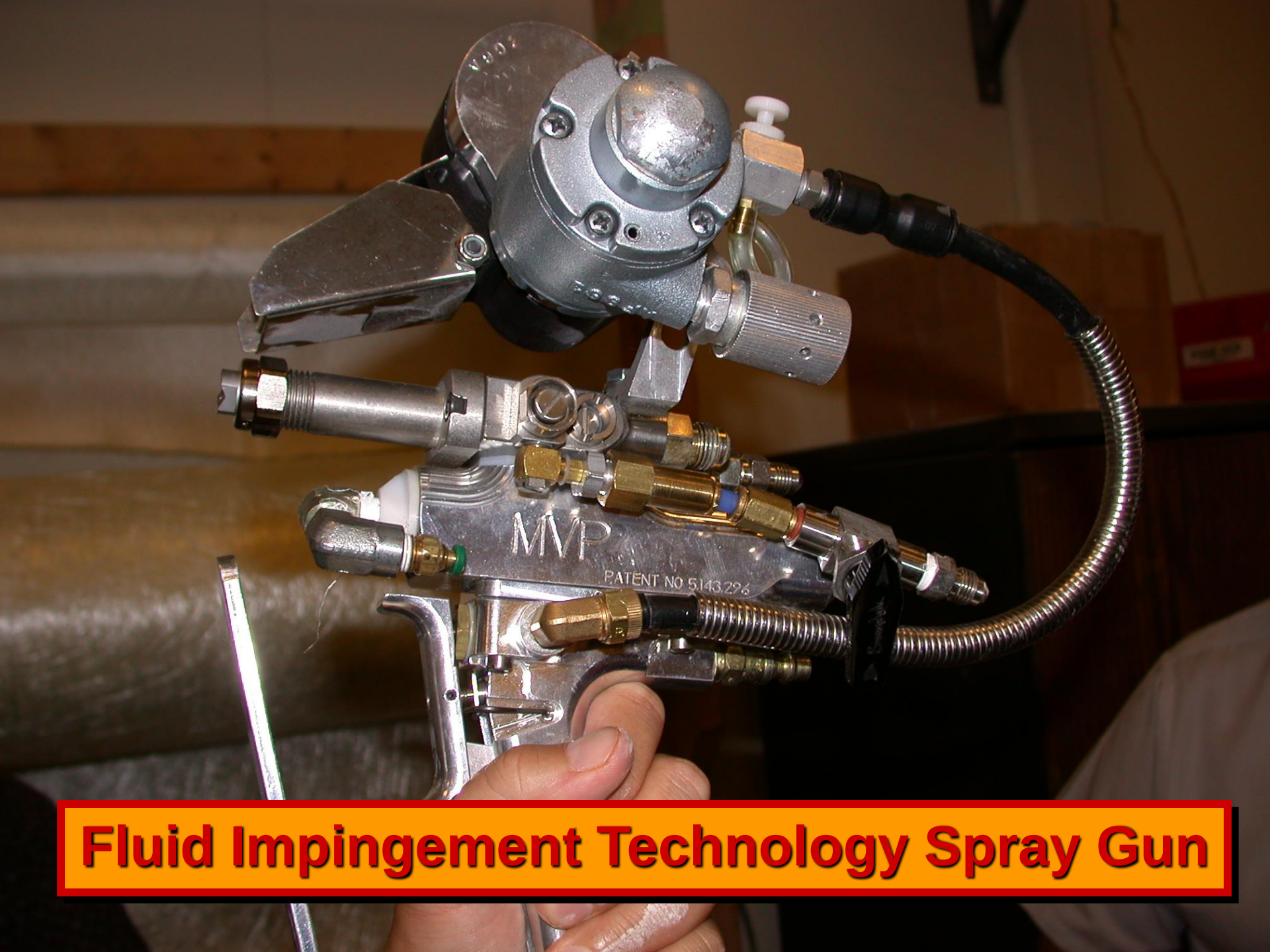

Gel Coat Application in a Spray Booth

Gel Coat Storage

Approved Spray Guns

- High Pressure Airless Guns
- Air-Assist Airless Guns
- Electrostatic Spray
- High Volume Low Pressure (HVLP) *
- Fluid Impingement Technology (FIT) Spray Gun *

HVLP Spray Gun



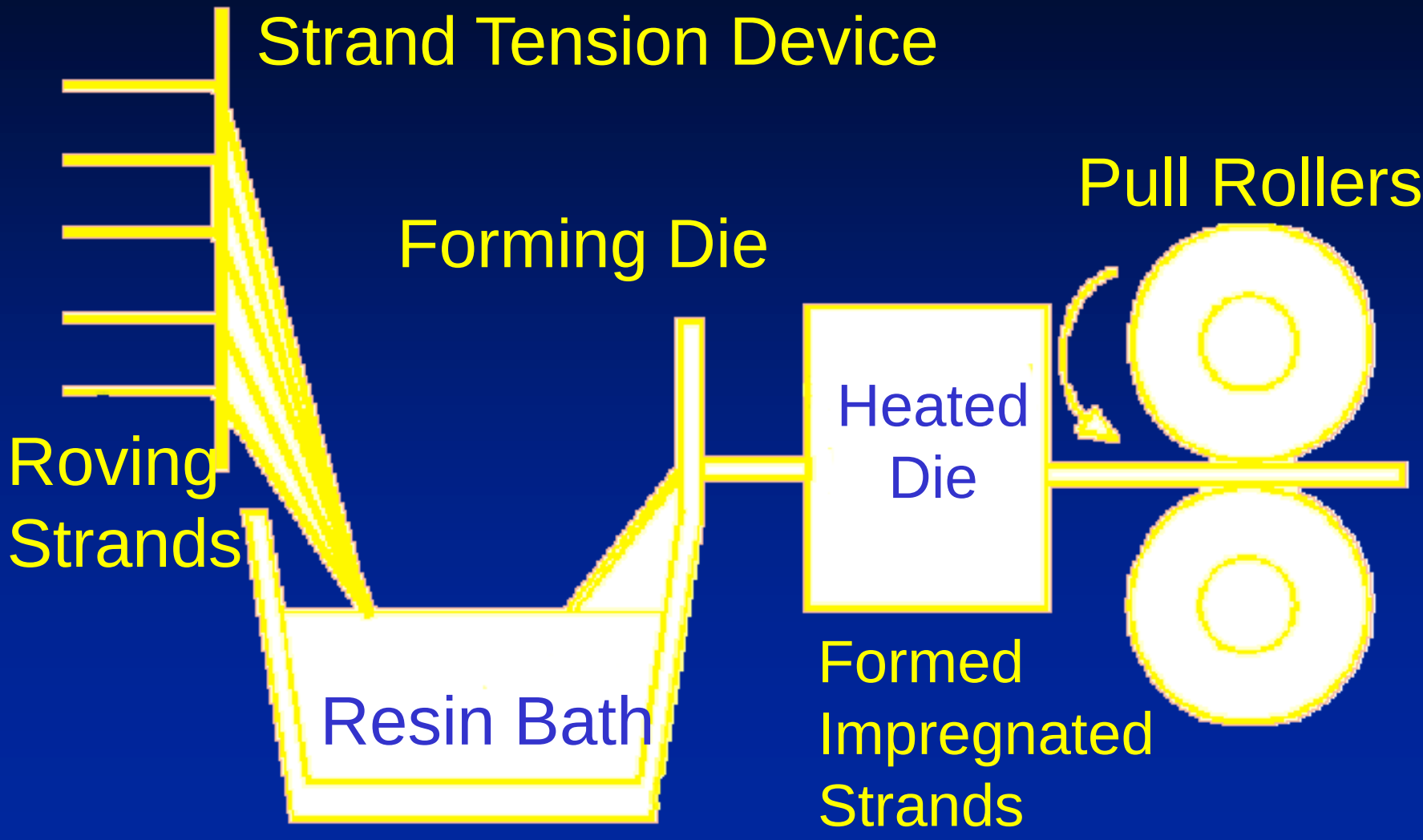
Fluid Impingement Technology Spray Gun


Let’s Discuss other Open Molding Operations

Pultrusion

- Pulled extrusion process
- Fiberglass under tension
- Immersed in Resin bath or injection
- Pulled through forming dye
- Pulled through heated dye to cure
- Produces flat stock for cutting
- VOCs at resin bath and forming area

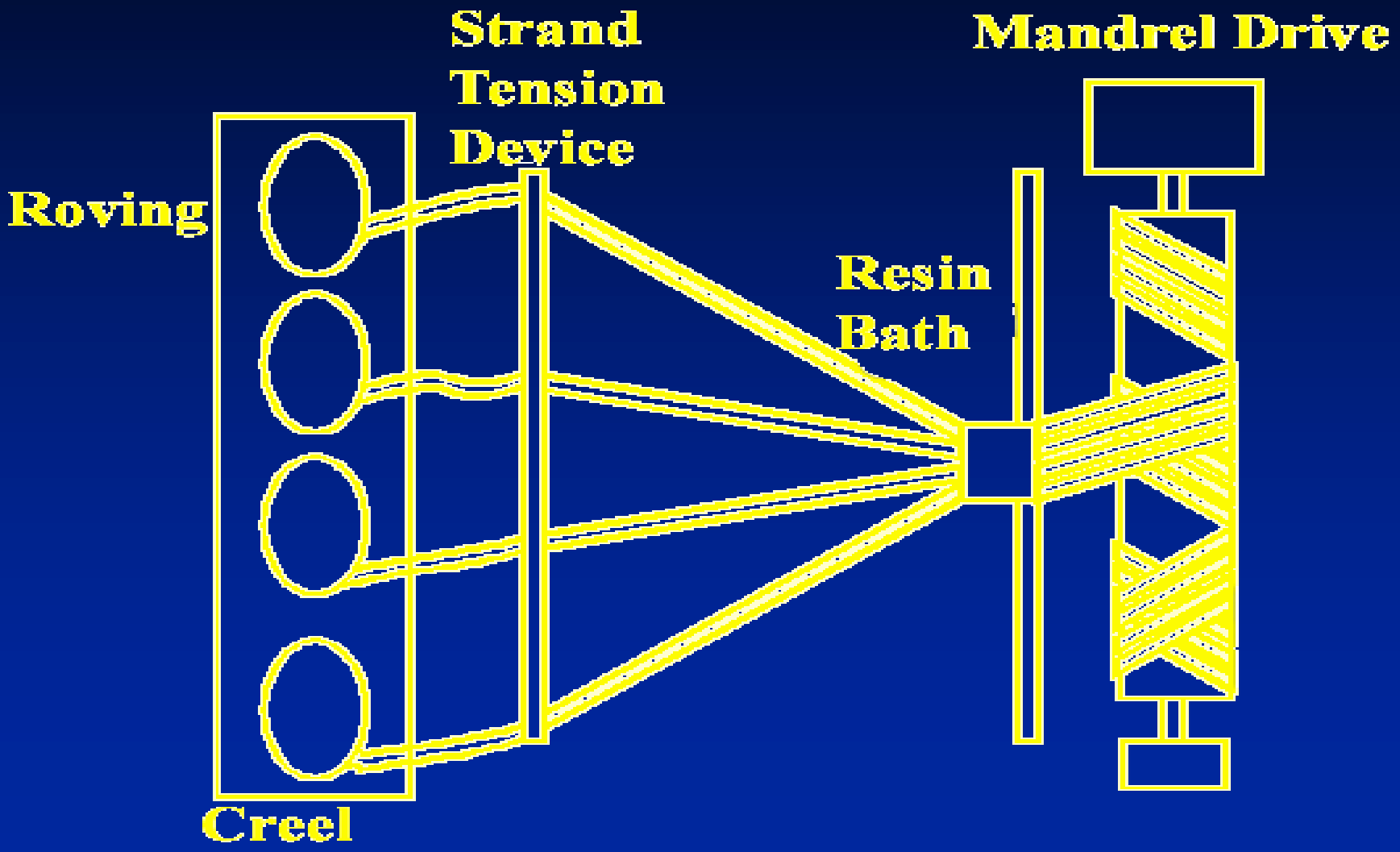
Pultrusion


Strand Tension Device
Pull Rollers
Forming Die
Heated Die
Roving Strands
Resin Bath
Formed Impregnated Strands

Filament Winding Operations

- Used in Manufacture of:
  - large pipes and storage tanks
  - hollow vessels subject to high internal pressure
- Strand Rovings are Pulled under Tension into a Resin bath
- Wound into Shape & Cured

Filament Winding




Let’s Discuss Closed Molding Operations

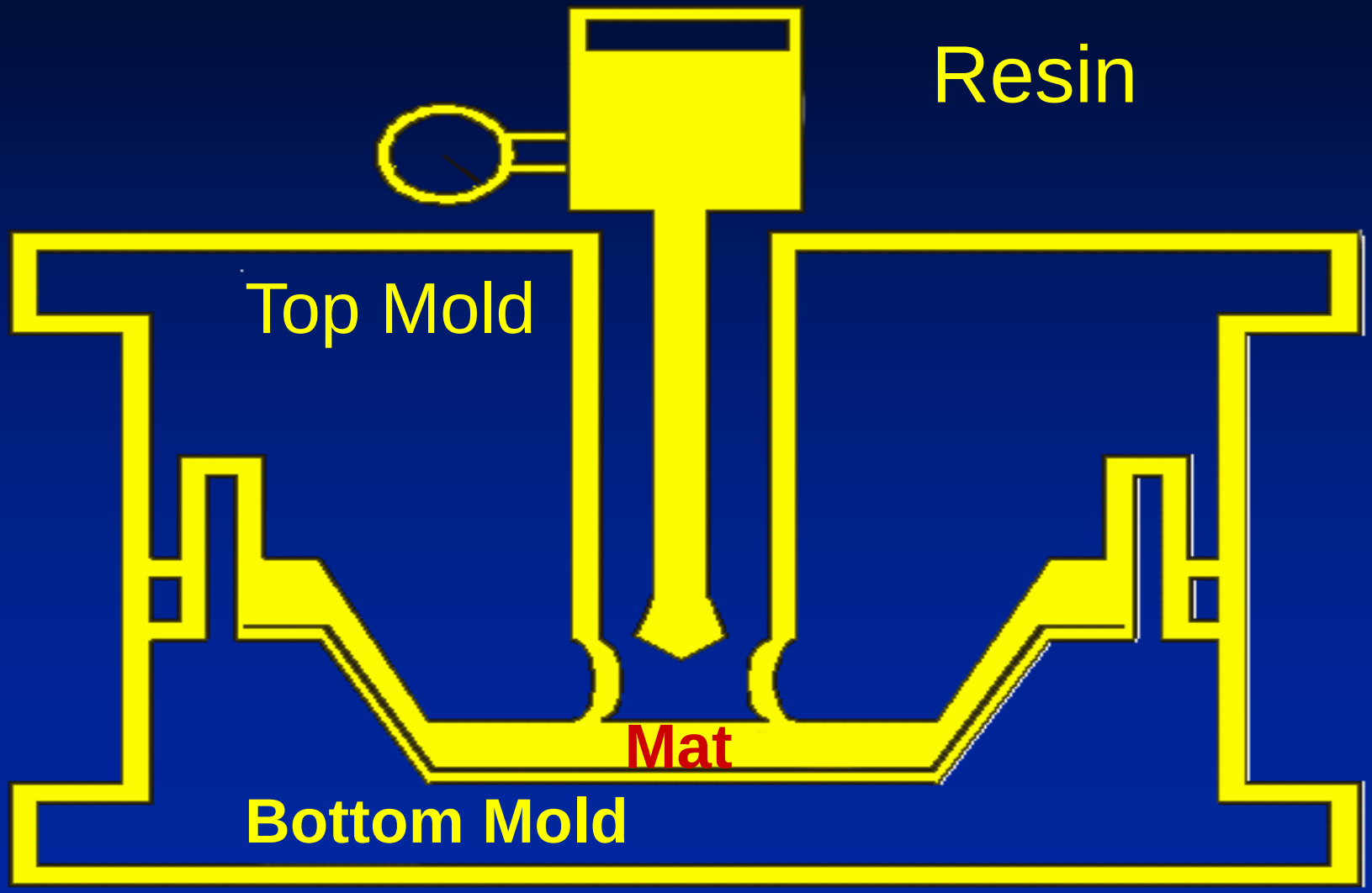
Resin Transfer Molding

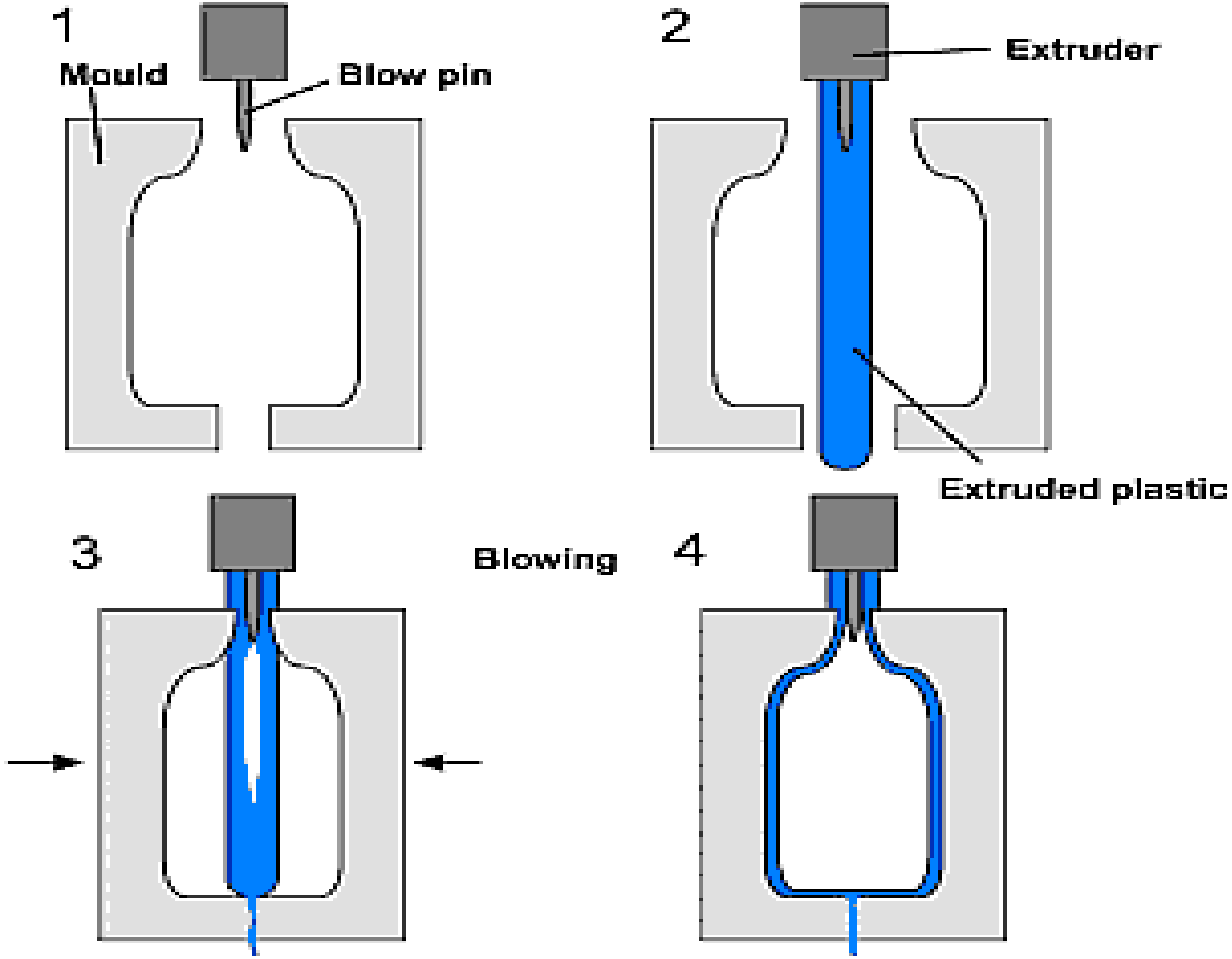
- Gel Coat is Applied to Mold
- Reinforcing Fibers are Placed into the Mold Cavity
- Mold Halves are Closed & Clamped
- Liquid Resin is Injected into the Mold Cavity

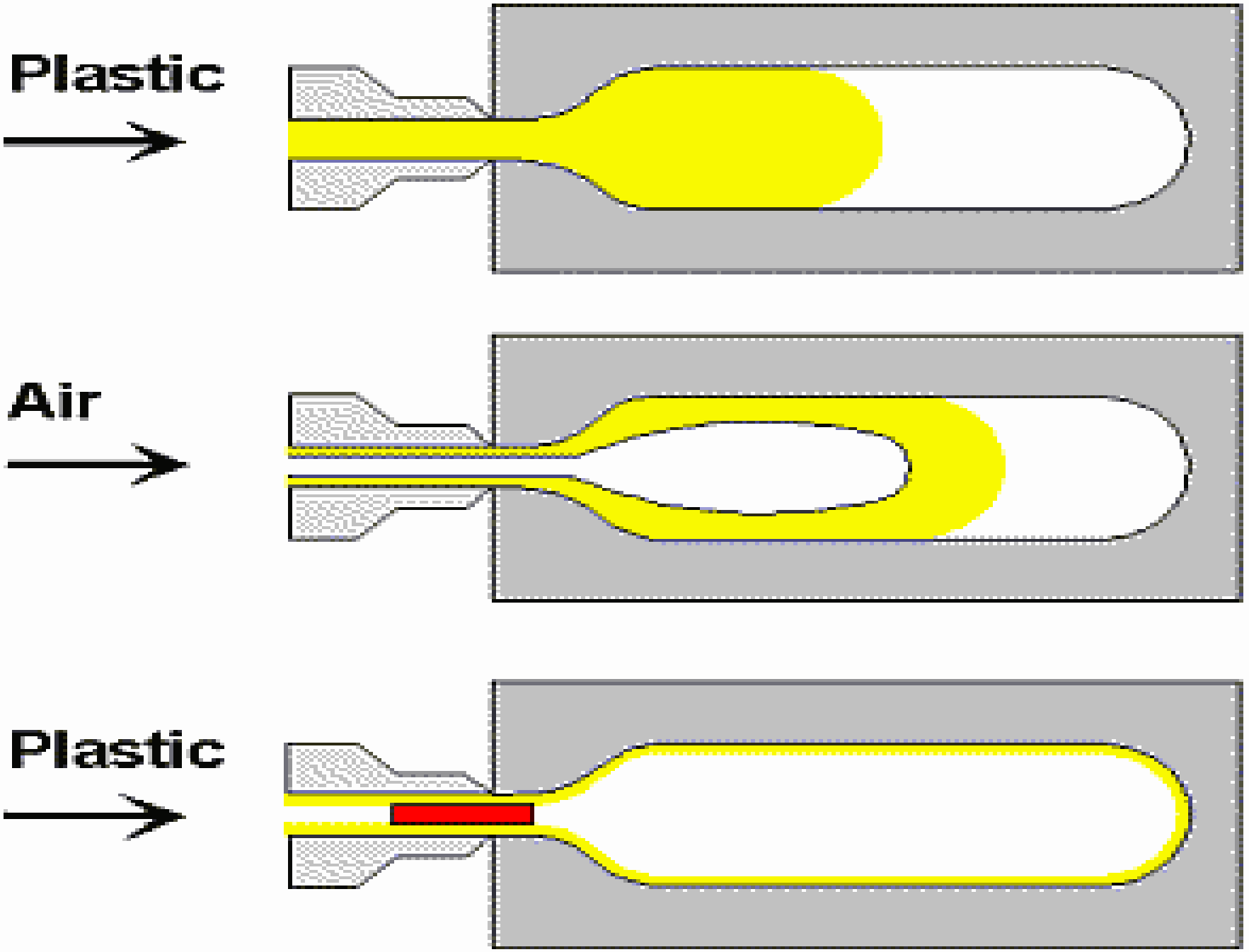
→ Suitable for High Vol. Production

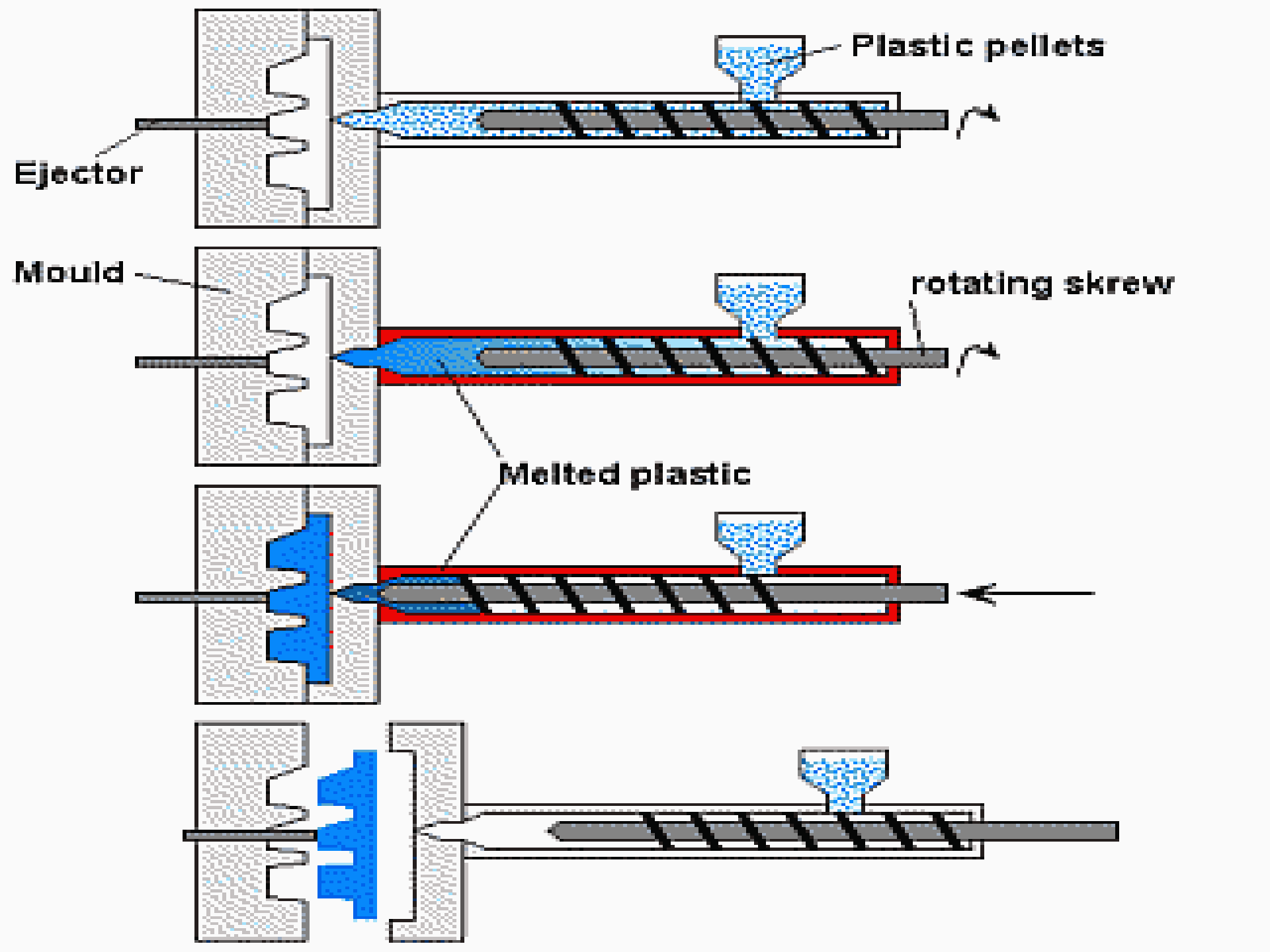
→ Reduced VOC emissions

Resin Transfer Molding




1
Mould
Blow pin
2
Extruder
Extruded plastic
3
Blowing
4


Plastic
Air
Plastic


Plastic pellets
Ejector
Mould
rotating skrew
Melted plastic


Let’s Discuss Emissions & Controls

Emission Sources

- Gel coat - Styrene Emissions
  - Application (atomization)
  - Curing
- Resin
  - Styrene most common monomer
- Mixing
- Clean-up solvents

Application Step	38% Monomer	25% Monomer
Loss due to Atomization	5-7%	2-4%
Loss due to Curing	6-11%	4-9%
Total Loss	11-16%	8-11%

Process Materials

- General Purpose Resins : 35% styrene
- Specialty Resins : <50% styrene
- Most AQMD Rules : 35% styrene
- Tough Low Profile Resins <35% styrene
  - Higher viscosity
  - Need better surface prep
  - Need good wet-out procedures

Solvents

- Acetone (widely used)
- Methyl Ethyl Ketone (MEK)
- Dibasic Ester (DBE)

  - less volatile, less flammable than acetone

- Water-based resin emulsifiers

  - detergent cleaners


Open Acetone Container


CAUTION HAZARDOUS MATERIAL
ACETONE
CAUTION HAZARDOUS MATERIAL
ACETONE

Clean-Up Rules

- Cleaning with Compounds 50 to 200 g/liter VOC
- Closed containers
- Self-Closing Containers
- Styrene soaked rags in closed containers


Open Containers


Potential Emissions ??

Let's Discuss Styrene Emissions

Styrene : HAP Source

- Unsaturated aromatic HC
- Petroleum By-Product
- In Polyesters :

  → Reactive Diluent
- Styrene : HAP (Hazardous Air Pollutants)

Styrene : HAP Source

- Foamed or Expanded Polystyrene : EPS
- Exceptional insulation properties

- Foam cups & containers
- Foodservice products
- Packaging & protecting

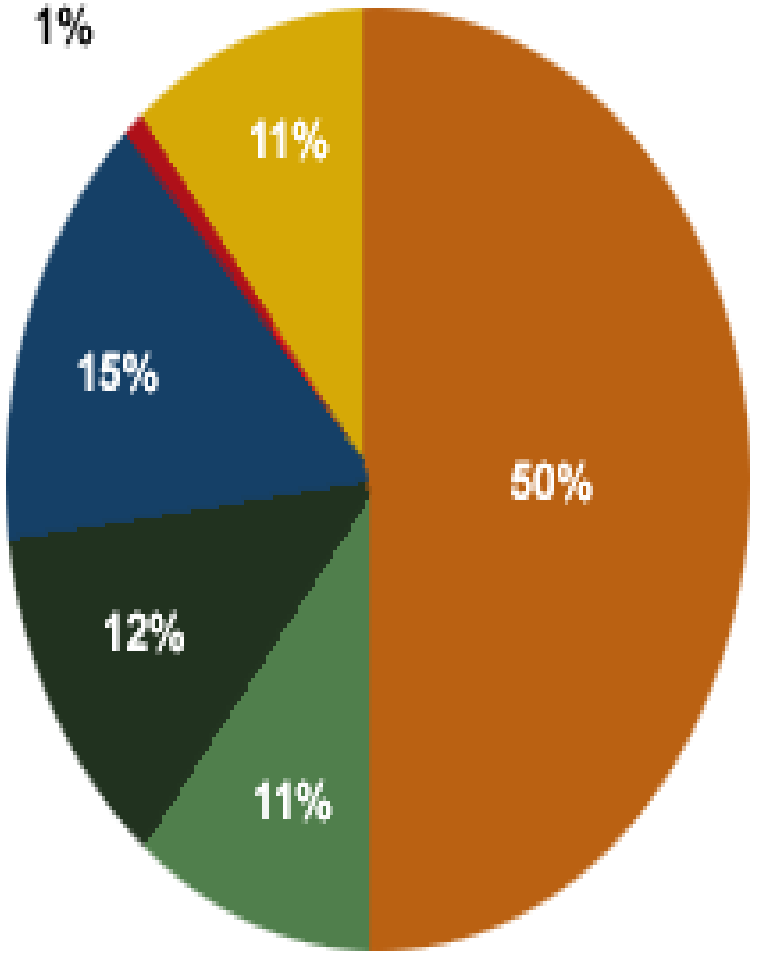
Styrene Emissions Determination Models

- A 540 lb. Drum of Gel Coat
  - → 38% VOC
  - → Applied by "Uncontrolled Spray" Techniques
  - ⇒ Emit 100 lb. of Emissions

- Two Drums of Gel Coat/day
  - ⇒ 25 Tons of Emissions/Yr

6 Major Styrene Resin Families (20 million tons, more than 40 billion pounds)

- **PS - Polystyrene**
  cups, plates, toys, packaging, dairy containers, building constr., cassettes
- **ABS - Acrylonitrile-butadiene styrene**
  appliances, transportation, business machines
- **SAN - Styrene-acrylonitrile**
  appliances, battery castings, packaging, automotive materials, housewares
- **SBR - Styrene-butadiene rubber**
  tires, automotive applications
- **SBL - Styrene-butadiene latex**
  carpet and upholstery backing, coatings
- **UPR - Unsaturated polyester resins**
  boats, bath tubs, shower stalls, spas, hot tubs, cultured marble



Industry Estimates


Let's Discuss VOC Control

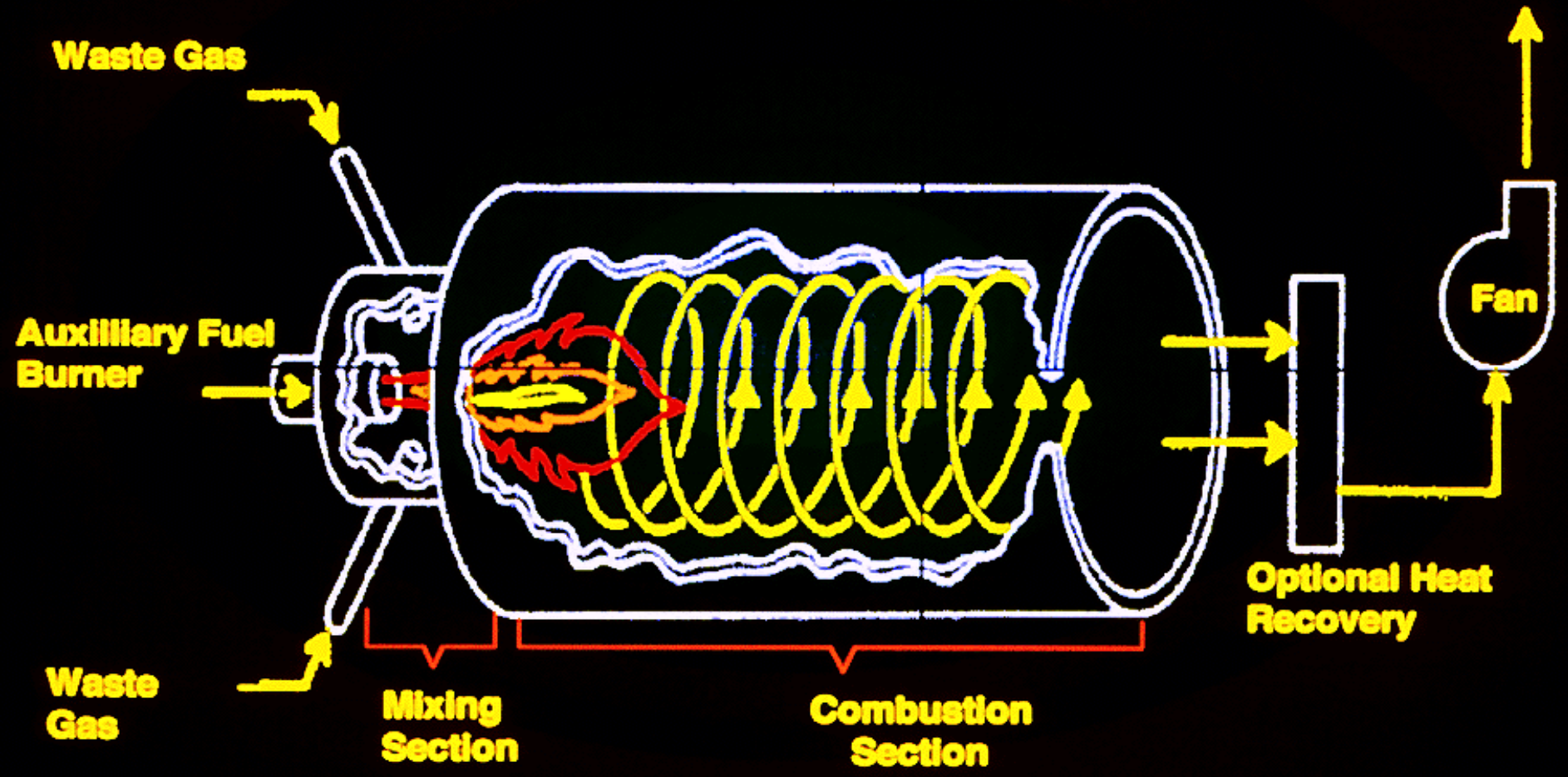
Control of VOC Emissions

- Process change to control monomer emissions
- Low VOC Gel Coat
- Change from acetone to less volatile solvent
- Reclaim acetone (distill)
- ADD-ON equipment

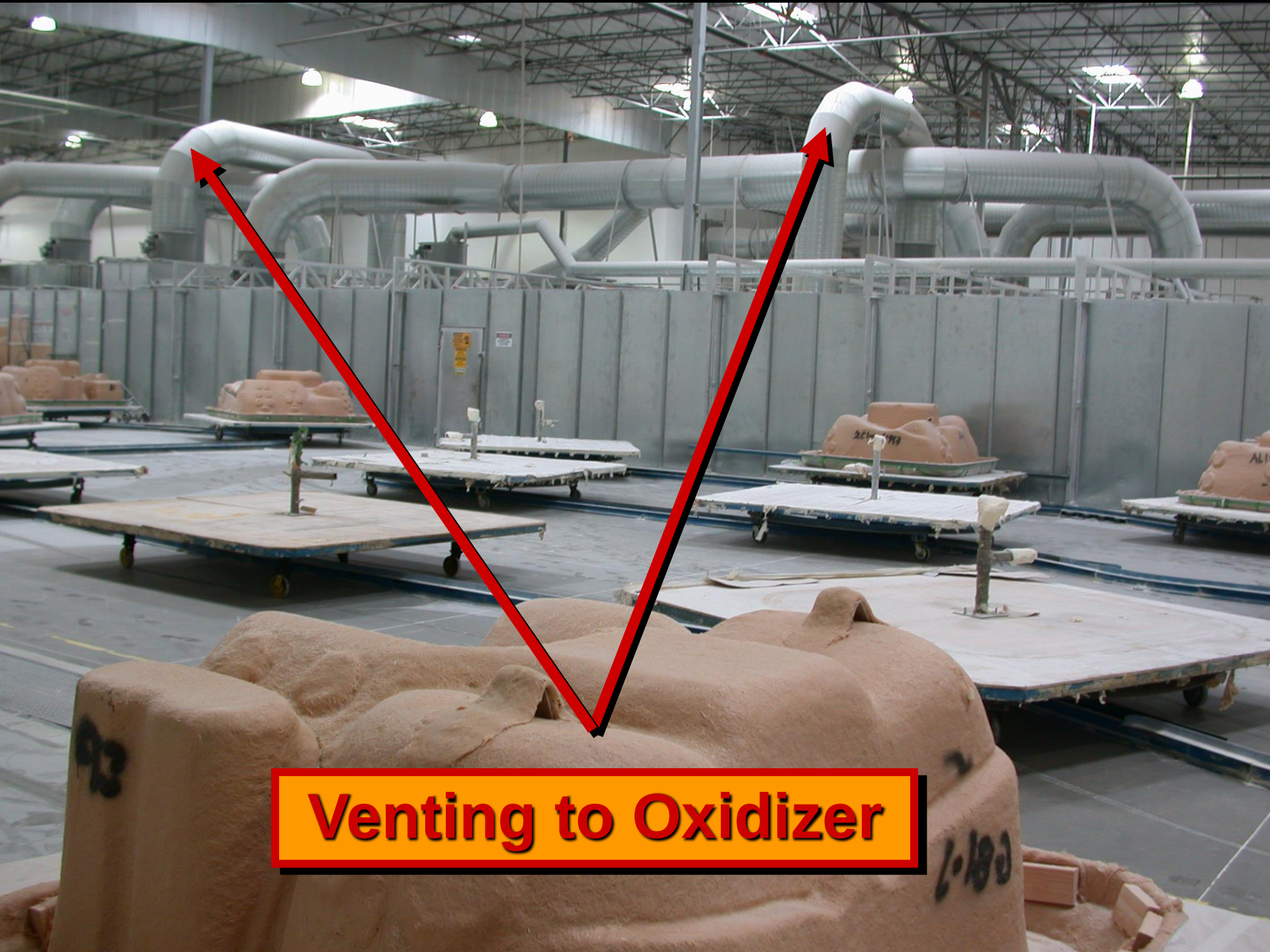
Add-On Control Methods

- Incineration
- Absorption
- Adsorption
- Condensation

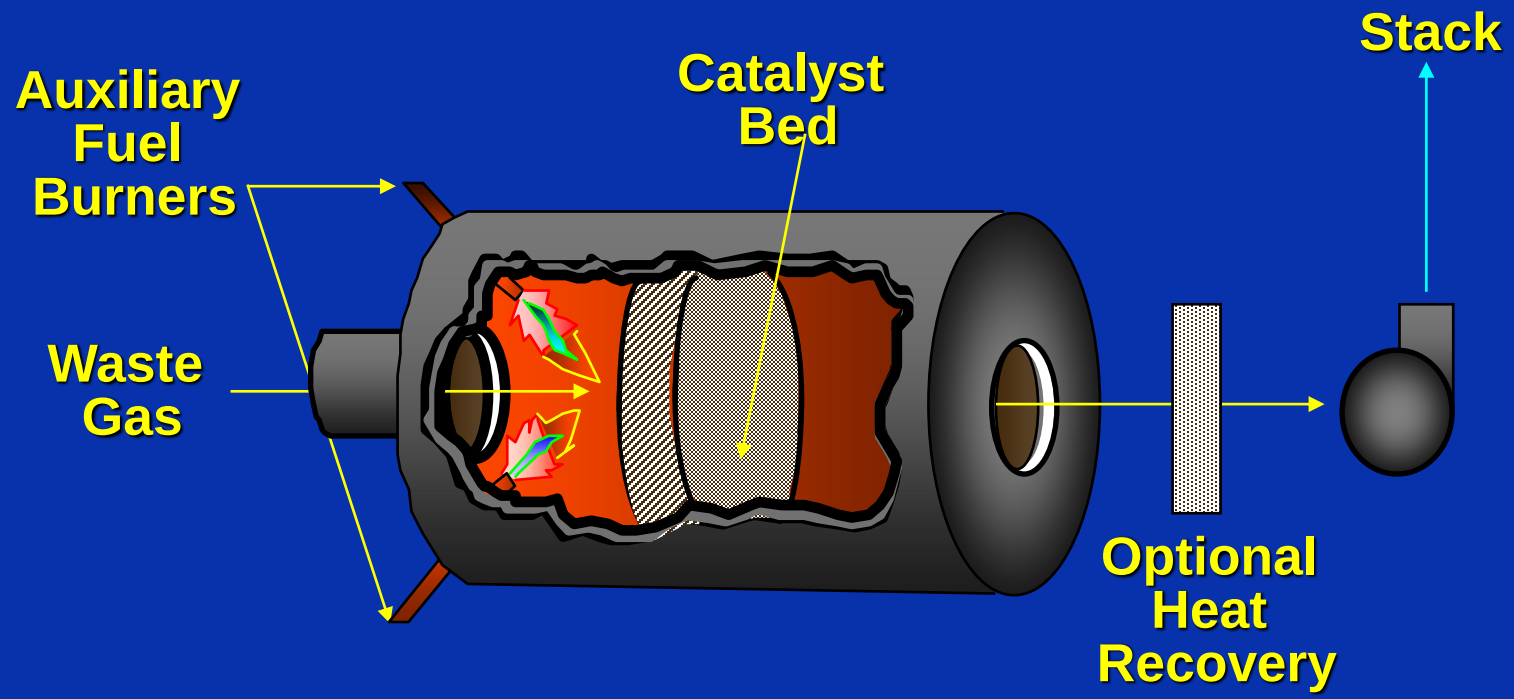
Thermal Oxidizer/Afterburner

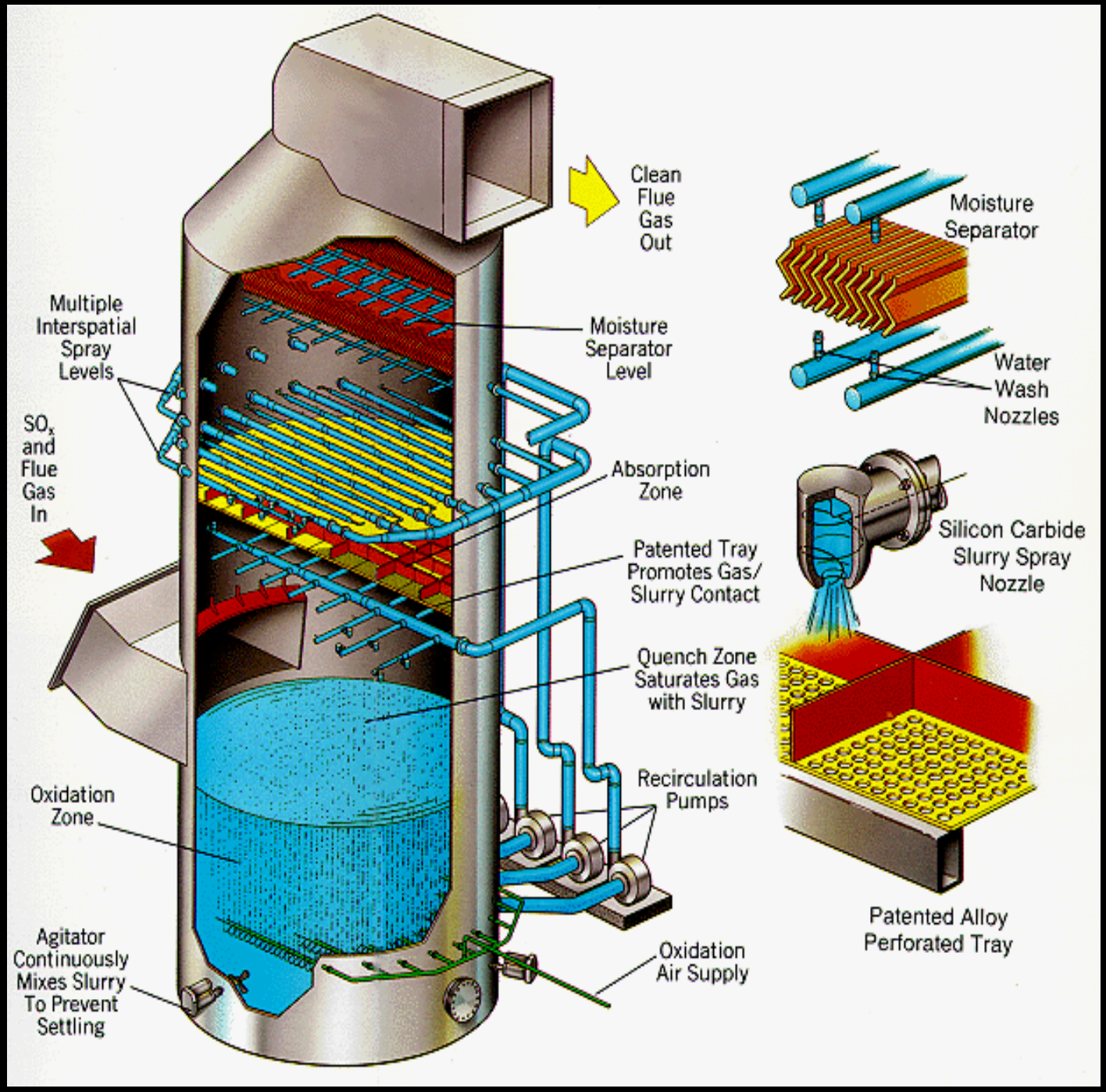


Thermal Incinerator


Venting to Oxidizer

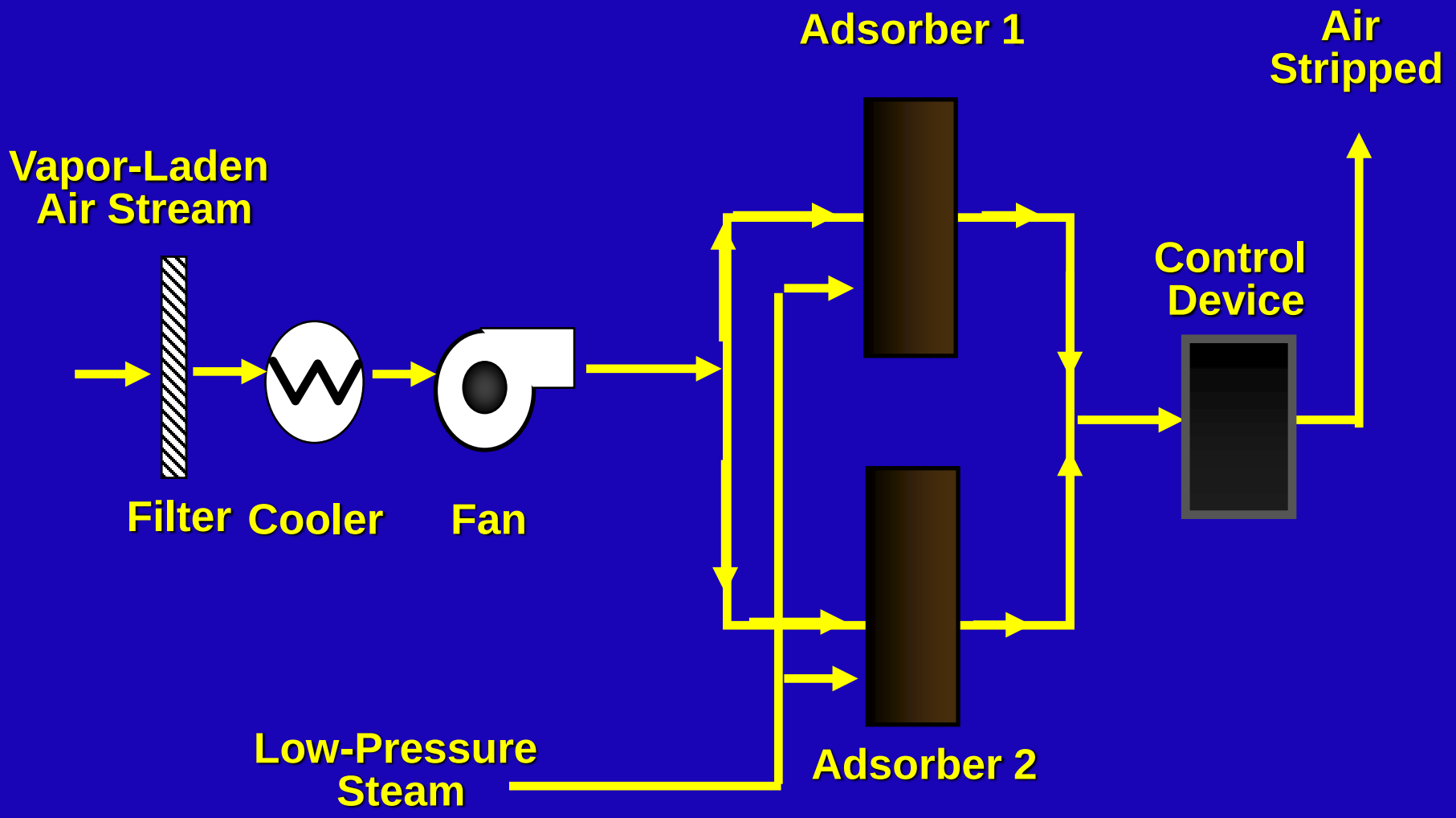
Catalytic Oxidizer/Incinerator





Wet Scrubber

Carbon Adsorption System



Remediation System with Carbon Adsorbers


Regulatory
Requirements

Regulatory Requirements

- Federal, state, and local requirements
- Resin specific limits
- Permit requirements
- Monitoring requirements
- Visible emission limits
- Nuisance regulations
- Breakdowns & variances.

Federal Regulations

- 1990 Clean Air Act
  - NESHAPS : National Emissions Standards for Hazardous Air Pollutants
  - HAPS : Hazardous Air Pollutants
  - MACT : Maximum Achievable Control Technology
  - New & Existing Major Sources

Federal Regulations

- 40 CFR Part 63 Subpart VVVV -- NESHAP for Boat Manufacturing
- 40 CFR Part 63 Subpart MMMMM -- NESHAP for Flexible Polyurethane Foam Fabrication

- 40 CFR Part 63 Subpart U -- NESHAP for Group I Polymers & Resins
- 40 CFR Part 63 Subpart JJJ -- NESHAP for Group IV Polymers & Resins

Federal Regulations

- 63 WWWW – Reinforced Plastics Composites Production
- 63 III – Flexible Polyurethane Foam Production
- 63 6O – Area Source Flexible Polyurethane Foam
- 63 YY – Generic MACT Acetal Resins, Polycarbonate, etc.
- 63 W – Group II Polymers and Resins
- 63 OOO – Group III Polymers and Resins
- 63 6L – Area Source Acrylic and Modacrylic Fiber Production
- 63 7H – Polyvinyl Chloride and Copolymers Production
- 63 6D – Area Source Polyvinyl Chloride and Copolymers
- 63 4H – Wet Formed Fiberglass Mat
- 60 HHH – NSPS for Synthetic Fiber Production
- 60 VVV – NSPS for Polymeric Coating for Supporting Substrates

Operation (Open Mold – Boat Mfg)	Application Method	HAP Weight %
Tooling Gel Coat	Any Method	40%
Pigmented Gel Coat	Any Method	33%
Clear Gel Coat	Any Method	48%
Production Resin	Atomized (Spray)	28%
Tooling Resin	Atomized (Spray)	30%

BACT and BARCT

Polyester Resin Material	Monomer Weight %
General Purpose Resin	<35%
Specialty Resin	< 50%
Clear Gel Coat	<50%
Pigmented Gel Coat	<45%

Typical Permit Conditions

- Daily Emissions Limits
- Gel Coat Monomer Content (weight %)
- Resin Monomer Content (weight %)
- Amount of Material Used
- Cleaning Material
- Logs


Inspection Procedures

Reasons for Inspections

- Compliance determination
- Complaint investigation
- Source plan approval
- Review or renewal of permits
- Special studies.

Pre-Inspection

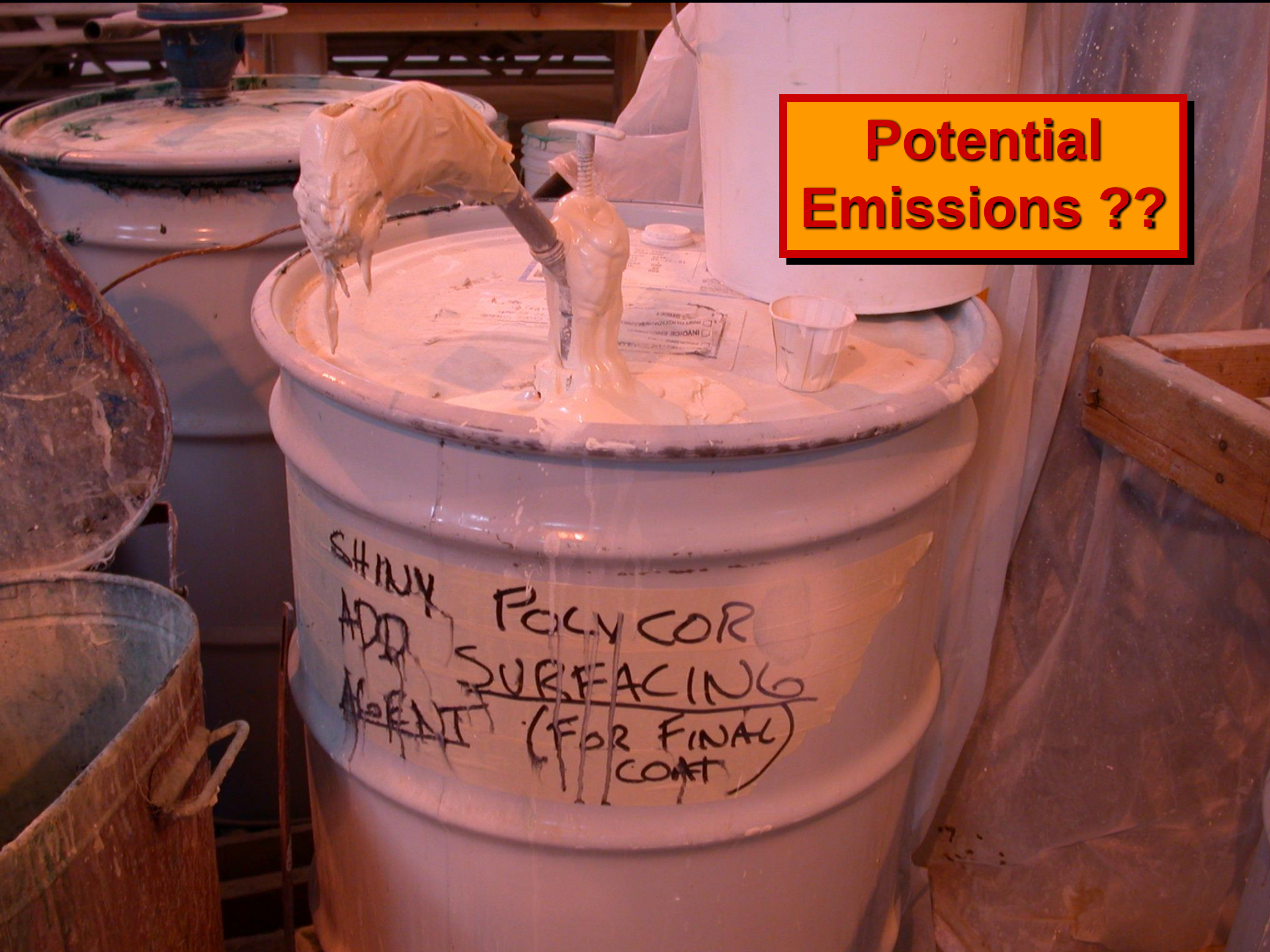
- Prepare inspection report form
- File review
- Regulation review
- Equipment check
- Pre-entry & entry
- Pre-inspection meeting
- Permit check.

Inspection

- Visible emission evaluation
- General upkeep & maintenance
- Maintenance records
- Operational records
- Any open containers?
- Self-closing containers
- Rags and waste in closed containers

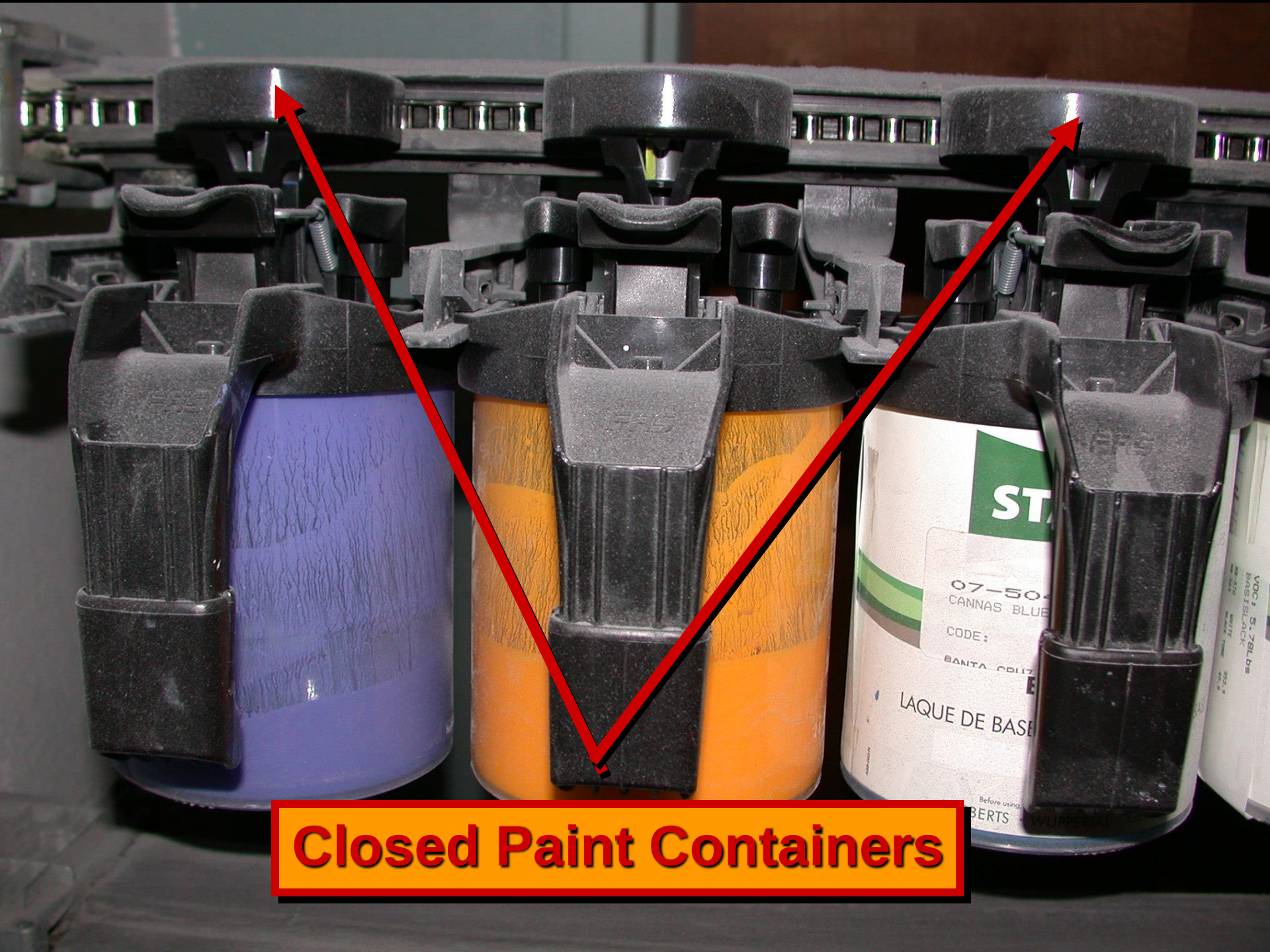
Closed Containers


Open
Container


Potential
Emissions ??
SHINY POLY COR
ADD SURFACING
AGENT (FOR FINAL
COAT

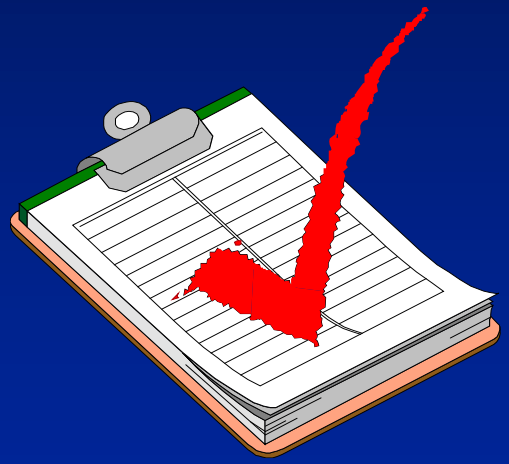

Catalyst (MEKP)
Emissions


Self - Closing Container


Closed Paint Containers

Inspection

- Coating Application Equipment
- VOC content of solvents and other chemicals
- MSDS
- Spray Booths
- Dust control equipment
  - Filters and screens
  - Cleaned as often as necessary




Compliant
Spray Gun


Spray
Booth


Spray Booth Filters


Spray Booth Application
Kestrel
Kestrel

Filter Inspection

Inspector Safety

Proper equipment
Plant evacuation
Inhalation hazards
Hazardous materials
Chemicals & Machinery


The End