3D SYSTEMS

RESIN

SAFETY & HANDLING

GUIDE

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Introduction

Stereolithography Technology

Stereolithography is made possible by a process called photopolymerization in which a resin is converted to a solid polymer upon exposure to an ultraviolet (UV) energy laser beam. The degree to which photopolymerization occurs, and thus the degree of solidification, is dependent on the total UV energy absorbed.

The polymerization of resin is not a new technology and has been used in such applications as ultraviolet inks, coatings, varnishes, and printed circuits for more than twenty-five years. However, the use of lasers as the energy source is a more recent innovation.

The photopolymers used in stereolithography are composed of two basic materials. The first is a photoinitiator which absorbs the laser energy and forms reactive initiator species. It is this initiator species which starts the photopolymerization process. Photopolymers also contain functionalized monomers and oligomers which polymerize upon exposure to an initiator source.

Typical components of UV-curable materials may include: a reactive resin, a multifunctional cross-linker, and a reactive diluent.

These components may be formulated with photoinitiators, stabilizers, and other additives, depending on their use and application.

Currently, all CIBATOOL® Stereolithography (SL) resins are based on acrylate and/or epoxy technology. Acrylate-based materials are cured by a free radical mechanism, and utilize oligomers and reactive diluents. Epoxy-based materials are cationically cured. These resins also utilize a variety of resins and modifiers to achieve end results.

Storage of Resins

Stereolithography resins are composed of reactive monomers and oligomers. If improperly stored or handled, these compositions could undergo polymerization resulting in the evolution of heat. Improperly stored resins increase in viscosity, and eventually result in a gelled (polymerized) product in the storage container. Products should be stored in conformance with applicable fire department and insurance company regulations and other applicable laws, regulations, codes and guidelines.

Containers

Resins manufactured by Ciba Specialty Chemicals ("Ciba") are shipped in polyethylene bottles or steel containers that are either polymer coated or plastic lined. Polyethylene bottles or liners are acceptable as long as they are opaque to ultraviolet energy, and have not been contaminated with other chemicals prior to use as storage containers for stereolithography resins.

To ensure product stability, CIBATOOL SL resins should not be allowed to come in contact with iron, copper, or alloys containing copper. Plastic containers made from monomer-soluble materials such as polystyrene or polyvinylchloride (PVC) also should not be used for storage.

Container lids must be tightly sealed in order to protect the product from contamination and/or stray UV energy when resins are not in use. Accidental spillage of resin can be minimized if the container lid is sealed tightly.

Shelf Life

CIBATOOL SL resin products have a self life of one year in undamaged, unopened containers, starting from the date of manufacture as printed on the container. Therefore, inventory provisions should be made to insure that the resin purchased first is used first. The material in the vat should be checked for viscosity and photoreactivity on a regular basis to insure optimal performance.

Vat Life

Vat Life of a resin is defined as the useful life of the resin after having been poured into the vat of an SLA. No guarantee or warranty is made or implied by either 3D Systems or Ciba as to vat life. However, to extend the vat life of CIBATOOL SL resins, certain conditions should be maintained. These conditions include: temperatures not exceeding 40°C (104°F), a dust free environment, humidity control, UV light protection, properly maintained equipment, and no aggressive vapors, (e.g. acids, amines, solvents, etc.).

The resin retains its usefulness in the vat until a buildup of viscosity or a change in photoreactivity prevents further processing in the SLA. To extend vat life, do not leave parts in the vat for extended periods of time. Also, resin drained from QuickCast™ parts should not be poured back into the vat.

Light

Resins should be shielded from sunlight or other sources which produce UV actininc radiation such as fluorescent or mercury vapor lights. Exposure to UV energy leads to an increase in product viscosity and eventually to product solidification.

Care should be taken to minimize laser scatter in the SLA build chamber. If significant scattered light is observed, 3D Systems' Customer Support should be called to correct the problem.

Temperature

Containers of resin products should be kept indoors in a cool, dry area with adequate ventilation, and at temperatures preferably between 16°C (60°F) and 27°C (80°F). Always keep containers out of direct sunlight.

Contamination

Avoid contamination from free radical sources such as phenolic compounds, peroxides, and contaminants such as iron or copper. Also avoid strong oxidizers such as amines and strong acids. These contaminants can retard the cure rate of the resins.

Accidental contamination of the resin system with another resin system or other foreign material may change resin performance characteristics such as critical exposure and depth of penetration, (Ec and Dp) to such an extent that acceptable SL parts can no longer be created. Therefore, resin photo properties should be tested if contamination is suspected.

Polymerization

Signs of premature polymerization in the container include bulging, leaking, the emission of heat, or an unusual odor emanating from the container. The following precautions should be taken if polymerization is suspected (particularly in the case of drums or other large containers):

Safety Precautions

- Unnecessary personnel should be evacuated from the area.
- Heat input, if in use, should be discontinued, and cooling initiated immediately through internal coils, internal heat exchangers, or cold water spray.
- If polymerization continues, as evidenced by a continued increase in temperature, one part of an inhibitor solution composed of 25% hydroquinone dissolved in 2-butoxyethanol (butyl cellosolve, Union Carbide) should be added to 600 parts of material and mixed thoroughly with air sparging and/or mechanical agitators or pumps.

  If the container housing the resin is too hot to touch, do not attempt to use this inhibitor solution. Instead, isolate the container and provide as much cooling as possible. Inhibitor solution should be maintained on hand for emergency use.

Storage of Full Vats

Oxygen from the air plays an important role in increasing the storage stability of resins. Dissolved oxygen reacts with free radicals that tend to form naturally and slowly with the aging of the resin, thus preventing polymerization.

An idle vat which has previously been used to build many parts presents a special storage problem. Fragments of laser cured parts which sink to the bottom of the vat can be an additional source of free radicals, consuming oxygen more rapidly.

Oxygen diffuses very slowly through an unstirred vat of resin. In normal operation the stirring action of the platform insures adequate oxygen levels at the bottom of the vat. Vats should be stirred at least once a month when not in use.

Vats should be stored indoors in a cool, dry area with adequate ventilation, and at temperatures preferably between 16°C (60°F) and 27°C (80°F)

Transfer and Handling

Transferring Resins

During transfer of resins, it is essential to protect the material from exposure to light and contaminants of any sort. Therefore, it is recommended that the containers be covered, but vented to avoid any pressure buildup. UV-absorbing plastic sleeves should be installed over fluorescent lights in work areas or application areas to prevent premature curing of the product. Likewise, windows should be covered with a plastic barrier or film that will screen out UV light.

Adequate ventilation must be provided during transfer and handling of resins, since small amounts of vapor may be emitted.

Resin can be transferred directly from the containers into the SLA vat.

If for any reason tools are used in the transfer of resin, they should be made of a material which is opaque, essentially non-reactive and not affected by resin, such as stainless steel. Some plastics, such as polyethylene or Teflon, may also be used as long as they are not affected by the resin.

Avoid any alloys containing copper or iron which may result in premature curing (polymerization) and degradation.

Pumps and Pressurized Air

It is advisable to avoid high shear pumps such as gear or piston types, for transferring resins because high degrees of shear may cause the resin to cure and the pump to seize. Centrifugal, peristaltic, diaphragm, or low shear progressive cavity pumps are preferred. Pressurized air can also be used to transfer products, if all of the vessels and lines are certified and capable of resisting the air pressure. A maximum air pressure of 0.35 MPA (50 psi) is suggested.

Flammability

Flammability is the ability of a material to burn. The degree of flammability hazard is often expressed as the flash point of a material or the temperature to which a material must be heated before a flame will ignite the vapors. The flash points of Ciba resins are shown on their respective Material Safety Data Sheets (MSDS). CIBATOOL SL products all currently have flash points greater than 93°C (200°F). The United States' Department of Transportation considers materials with flash points greater than 60°C (140°F) as combustible, rather than flammable.

Special precautions should be taken to prevent exposure of resins to heat, flames, sparks, or any source of ignition. If the containers are exposed to extreme heat, they may burst violently.

Post Processing

3D Systems recommends that excess liquid be removed from the laser-cured Stereolithography part before completing post-processing. Solvent stripping is the most common method for removal of excess resin from SLA parts. The recommended solvent for SLA parts is tripropyleneglycol monomethylether (TPM). After stripping with TPM, a quick rinse water is required. Denatured or isopropyl alcohol can be used to remove any remaining residue.

It should be noted that once a TPM bath has been used to clean a part, it then contains a concentration of the liquid resin. For the purposes of safety, cleaning baths should be handled in the same way as the liquid resin.

Disposal or re-introduction of the contents of a TPM bath, should comply with all applicable local, state, and federal environmental and safety regulations.

QuickCast™ Patterns

Physical removal of excess resins through the use of paper towels and cloth is recommended for epoxy parts. Small amounts of dry, denatured or isopropyl alcohol can be used in the cleaning process. It is important to note that denatured or isopropyl alcohol is readily absorbed.

Health Hazards

Any chemical may exert harmful effects if it enters the body in sufficient quantities. The hazard of a chemical is the likelihood that a chemical will produce damage under specified conditions, and is derived from two main considerations:

1. Toxicity:

Toxicity is the inherent ability of a chemical to produce a deleterious response in a biological system. All materials have some toxicity associated with them which may be high or low. Toxicity can be measured in a quantitative manner through experiments which determine the nature of the toxic effect and the dose which causes it.

In evaluating the toxicity of stereolithography resins, the toxicity of all individual components must be considered. Each potentially hazardous component is listed in the CIBATOOL MSDS (Material Safety Data Sheet).

2. Exposure:

The industrial process determines the probability and extent to which exposure to the chemical can occur. Care should be taken to minimize exposure. The risk of health hazard can be greatly minimized by minimizing exposure.

Skin Irritation

Brief contact with high concentrations or prolonged exposure to low concentrations of acrylate- or epoxy-containing materials may cause tissue inflammation, itching, redness, dry patchy scaling, and/or discharge. Skin irritation is generally confined to the area of direct contact. Prolonged exposure may cause burns. Because direct skin contact may not always cause immediate irritation, skin exposure can easily go unnoticed.

Skin Sensitization

Sensitization dermatitis is the result of an allergic reaction to a given substance. In almost all cases, direct skin contact is necessary to cause sensitization. It is possible for individuals to become sensitized to a substance even after a trouble-free period of exposure. Many factors affect a person's susceptibility including: existing skin conditions, personal habits, and individual sensitivity. Sometimes an exposure of only a minute can trigger a severe outbreak of dermatitis which may spread over the body. Since sensitization is generally permanent, a sensitized individual should be removed from potential contact with the sensitizing agent.

WARNING:
Do not allow uncured material to contact skin.

Resin products may contain materials that are potential sensitizers. To avoid sensitization, do not allow uncured material to contact skin. Some epoxy resins are skin sensitizers, while others are not. Consult the appropriate MSDS for specific information about the sensitization potential.

Inhalation

Inhalation of resins has been regarded as less of a problem than skin or eye contact due to their low volatility, although volatility does vary by composition. Vapors may accumulate in areas without adequate ventilation, however, and some vapors do irritate the nose, throat and lungs. Therefore, all areas where resins are handled should be thoroughly ventilated.

WARNING:
Work in well ventilated areas when handling resin.

Occupational Exposure Limits

Neither the U.S. Occupational Safety and Health Administration (OSHA), nor the American Conference of Governmental Industrial Hygienists (ACGIH) have established occupational exposure limits for the majority of resins contained in ultraviolet electron beam (UV/EB) curable materials. If additional information is available regarding exposure limits, it will be found in *Section II* of each (Ciba Specialty Chemicals) Material Safety Data Sheet.

Ingestion

Resins may be toxic by ingestion. Therefore, these materials must not be present where food and drink are stored, prepared or consumed.

Handling of Cured Parts

The cured plastic parts can be handled and stored with no special precautions. Typical applications include concept modeling, prototyping, and tool pattern generation.

WARNING:

Current CIBATOOL resins are not intended for medical implant nor food or drink handling applications.

If the parts are not completely cured, low levels of volatile compounds may remain. If these compounds volatilize in an area with poor ventilation, irritating airborne contaminate levels could develop.

Burning of the cured parts, as required for investment casting applications, may result in toxic gas formation depending on specific formulation and burn temperature. Higher temperatures will assist in complete combustion of the plastic. The ultimate combustion products for cured plastics include carbon dioxide, water, and nitrogen.

Exposure Control

Three types of controls are used to reduce exposure to chemicals:

1. Engineering controls are the preferred method for reducing employee exposure and include local exhaust ventilation and closed process systems.
2. Administrative controls include rotating employees to different jobs in order to reduce the exposure time to hazardous materials. Reduced exposure time does not correspond to a reduction in the risk of sensitization since the number of employees exposed to the material is increased by using job rotation. Therefore, this approach is not considered useful in protecting employees from sensitization.
3. Personal protective equipment is used in some cases where engineering or administrative controls are not feasible or adequate.

The following section gives personal protection controls and equipment recommendations to be adhered to when working with curable materials.

Skin Protection

Water soluble barrier cream should be applied to hands and other skin areas which may be exposed to UV/EB-curable materials. Chemically resistant gloves should be worn at all times. In cases where fine work is being performed, disposable nitrile gloves may provide some protection but should be used only for brief periods. The use of a cotton glove underneath the nitrile glove will allow absorption of perspiration and improve comfort. If a hole appears in a glove, it must immediately be removed and discarded. Hands should be cleaned and new gloves put on if work is to continue. Glove manufacturers should be consulted as to appropriate glove type.

When handling large quantities of UV/EB-curable materials, long-sleeved, chemically-resistant uniforms should be worn including both tops and bottoms. Disposable uniforms provide only limited protection against UV/EB-curable materials. Shoe coverings such as rubber boots or disposable booties should also be worn.

Eye Protection

Safety glasses with side shields should provide adequate protection when working with small quantities of curable materials. Face shields should be used where exposure to large quantities is possible. Contact lenses should not be worn. Where medically necessary to wear contact lenses, splash-proof eye protection must also be worn.

Respiratory Protection

Respiratory protection is often not necessary if engineering controls and safe work practices are implemented. Good shop hygiene will help keep odors under control.

The need for respiratory protection must be evaluated for each use of stereolithography resin. If respiratory protection is indicated, a respiratory protection program complying with 29 CFR 1910.134 must be implemented.

A dust mask should be worn when sanding or post-finishing parts.

Hygiene

Good hygienic practices should be rigorously followed including washing before meals, breaks, smoking, applying cosmetics, using toilet facilities and after work. Barrier cream should be reapplied after meals and breaks. Do not apply barrier cream after exposure. Moisturizing hand creams should be applied after the skin is washed after work to prevent skin drying.

Safety Shower and Eye Wash Stations

Eye wash stations should be installed in all work area locations to ensure employees ready access in case of exposure. Employees should be trained in their use. Locating safety showers near the work area is also suggested.

Housekeeping

Good housekeeping should be practiced in the work area. Employees must be alerted to the need to clean and rinse off any contacted surface immediately in order to prevent the contamination of other employees. Solvents should be used for cleaning equipment only if provision for vapor removal has been made, if appropriate respiratory protection is worn, and if a safe means of disposal is available. Disposable wiping towels should be used rather than reusable rags, and towels should be discarded immediately after use.

Training

Employees must be trained in the hazards and control of stereolithography materials. Such training should be provided to new employees before they begin working.

Maintenance, Cleanup, and Disposal

Maintenance Practices

Maintenance employees must be informed about the hazards of resin materials prior to working on SLAs or performing other duties which may result in exposure to resin. Whenever possible, maintenance work should not be performed until the equipment has been thoroughly cleaned of resin. Tools which may be contaminated with resin must be thoroughly cleaned prior to reuse.

Clean-up

Organic solvents are normally required to clean equipment and tools. The following solvents are recommended:

- Denatured alcohol
- Isopropyl alcohol
- Tripropyleneglycol monomethylether (TPM), and water

Of the three organic solvents noted, TPM is a less aggressive non-flammable solvent whose use is preferred for health and safety reasons. However, where better solvency is necessary, denatured alcohol does a better clean up job. A final wash with soap and water will remove the last traces of excess resin.

Worker safety, flammability, solvent strength, equipment materials, and cost are all factors to consider when selecting an appropriate solvent for clean up. In any event, solvent suppliers should always be contacted for information on the proper handling of solvents.

Spill Controls

Small Spills

Small spills, loosely defined as two gallons or less, can be cleaned up using disposable towels, non-reusable rags, or absorbing materials such as sawdust, clay, diatomaceous earth, activated charcoal, etc.

All clean up materials should be placed in sealed, labeled containers. The spill area can then be cleaned with denatured or Isopropyl alcohol, followed by a thorough washing with soap and water.

Large Spills

Large spills, (larger than two gallons) can be cleaned up using the following procedure:

- Cleanup Personnel must wear proper protective clothing and NIOSH/MSHA approved respiratory equipment. Adequate oxygen levels must be maintained at the site.
- The area should be isolated immediately and diked to contain the spill.
- The spill must be covered with absorbing materials such as sawdust, clay, diatomaceous earth, activated charcoal, etc.
- After the absorbent is saturated, it should be removed and placed in a sealed, clearly labeled container, and disposed of properly.
- The spill area should be thoroughly cleaned with solvent or soap and water and the waste disposed of properly.

Workers Cleanup

- Liquid resin should be wiped from protective clothing with clean disposable towels.
- Protective clothing should be removed in the following order: boots, gloves, face protection, and suit. After removing gloves, use disposable towels to protect hands from contact with the resin.
- Place contaminated clothing in a sealed, labeled container for proper disposal.
- All personnel should shower with soap and cool water.

Disposal Procedures

- Fully cured stereolithography resins often present no special safety or health related disposal issues. Nonetheless, some areas may still regulate cured resins as hazardous industrial waste.

  The disposal of fully cured SLA resins, should comply with all applicable local, state, and federal environmental and safety regulations.
- Partially or uncured resin waste may be classified as hazardous in some areas, thereby requiring special packaging, transportation and disposal.

  The disposal of partially cured or uncured SLA resins, should comply with all applicable local, state, and federal environmental and safety regulations.

The packaging, transportation and disposal methods used must prevent any form of human contact with the waste, even if it is classified as non-hazardous or unregulated. This precludes the use of disposal methods which result in groundwater or surface water contamination. Small quantities of resin may be cured by pouring thin layers (<2 cm) into trays and exposing them to sunlight or placing them in a Post Curing Apparatus (PCA). The disposal of cured, partially cured, or uncured SLA resins, should comply with all applicable local, state, and federal environmental and safety regulations.

- Clean up solvents (containing resin) should be isolated in sealed, labeled containers and disposed of as “Hazardous Waste” in accordance with all applicable laws and regulations.
- Clean up materials, soiled clothing, empty containers, etc., should be disposed of in accordance with the preceding guidelines and applicable laws and regulations. Whenever any of these contain uncured or partially cured resin, the disposal method must preclude any form of human contact, including any method which could result in ground-water or surface water contamination.
- Discard contaminated shoes by isolating in a sealed container and disposing of as solid waste.
- Empty plastic bottles should be punctured, drained thoroughly, and disposed of as solid waste.
- Empty five gallon pails may be disposed of by removing the lids, curing the plastic liners in the sun or a PCA, and packaging as solid waste in accordance with local regulatory regulations.
- Containers with closed lids should be emptied to a drip-free state, punctured, and disposed of in accordance with local regulatory regulations.

Fire Fighting Procedures

Extinguishing media that should be used on fires involving these materials are National Fire Protection Association Class B extinguishers such as carbon dioxide, dry chemical, or foam.

Vapors and combustion products from burning resin can be irritating to the respiratory system and must be avoided. If it is necessary to approach a fire or smoldering resin, wear eye, skin, and respiratory protection equipment with self-contained breathing apparatus.

Water may be used to cool closed containers to prevent pressure buildup and possible auto-ignition or explosion when exposed to extreme heat. If water is used, fog nozzles are preferable.

First Aid

This section includes first aid procedures in the event of exposure to CIBATOOL Stereolithography Resins. Always refer to the resin container label or the MSDS for information specific to the product being handled.

Skin

If resin comes in contact with the skin, immediately wash the contacted area thoroughly with soap and cool water, and then remove contaminated clothing. Particular attention should be paid to flushing the hair, ears, nose and other parts of the body that are not easily cleaned. The use of cool water is important to avoid opening the pores which may allow more material to penetrate the skin. Do not use solvents to clean skin.

If large areas of skin have been exposed, or if prolonged contact with resin results in blisters, a physician must be consulted. During first aid procedures, avoid the accidental transfer of resin from the hands to other areas of the body, especially to the eyes. Do not reapply barrier cream until the skin has been completely cleansed.

Clothing should be professionally laundered. Do not launder contaminated clothing at home. Dispose of contaminated shoes, belts and other leather items because they can absorb resin and may re-expose the user at a later date.

Eyes

Safety glasses should be worn to prevent accidental splashes into the eyes. If contact with eyes occurs, flush immediately with large amounts of water for 15 minutes and avoid sunlight, fluorescent light, or other ultraviolet light. Eye wash facilities should be provided with a first aid kit situated close to the resin.

Contact Lenses

Wearing of contact lenses is not recommended. However, if contact lenses are worn, verify that flushing the eye with water removes the lens from the eye immediately. Get medical attention.

WARNING:

Contact lenses that come in contact with liquid resin should be discarded.

If eye itching or burning occurs, remove contact lenses and do not refit new lenses to the eye until symptoms disappear. Also, clean and disinfect lenses with appropriate lens cleaner before refitting.

Ingestion

If resin is swallowed, consult the container label for specific instructions. Get medical attention immediately.

Inhalation

Vapors from resins as well as their combustion products can be very irritating to the respiratory system. Upon inhalation exposure to vapors or the products of combustion, immediately expose the affected individual to fresh air. If breathing has stopped, immediately begin artificial respiration or cardiopulmonary resuscitation. **Get medical attention immediately.**

Oxygen should be administered by authorized personnel only. The patient should be kept warm but not hot. An unconscious person should never be given anything by mouth.

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