



Abstract

The technique of three-dimensional (3D) printing can be utilized to create not only simple parts but those with complex geometries as well. These 3D objects are generated via the deposition of successive layers of materials comprising various polymeric and metallic substrates. 3D printing, also known as additive manufacturing, can be easily automated to produce product in commercial quantities. As 3D printing technology has advanced, its use has rapidly increased across a wide range of industries, including life science, healthcare, and medical products, among others.

This TechBrief focuses on the critical cleaning of a wide range of hard surfaces utilized in 3D printing processes across industries, such as extruded plastics, photosensitive substrates, metals, and metal alloys. We use the term critical cleaning to denote situations where the level of cleaning directly impacts the value of the end product or materially increases manufacturing efficiency.

Wide Variety of Materials

Different resins/materials are preferred for specific 3D printing applications depending on the 3D printing process and printer that is used and the design and function of the target part/product being produced. Different applications require materials to be clear or colored, rigid or flexible, and/or tough and durable or soft. They may also need to be of a specific grade, such as those for medical and dental applications. Consequently, biocompatibility, toxicity, biodegradability and other factors of the resins must be considered. It is possible to choose pure or composite materials with chemical, fatigue, impact, heat, UV, and water resistance. There are soluble, elastic, flexible, rigid, and soft materials as well.

Material Selection for Specific Applications and Printing Approaches

Additive manufacturing is a general term referring to a number of different 3D printing processes that in 2015 were classified into seven categories within the <u>ISO/ASTM 52900</u> standard: extrusion, vat polymerization, powder bed fusion, material jetting, binder jetting, direct energy deposition, and sheet lamination The seven categories themselves each encompass many different 3D printing technologies used by different 3D printers today

The choice of 3D printing process will be dictated by the printer cost and capabilities, the speed of the process, the quality of the parts produced, and the practical implementation of the method. Most importantly, the properties of the product must meet the expectations of the end user.

The choice of material will depend on the type of printing process, the capabilities of the printer, and the nature of the part — complexity, functionality, color, texture, appearance, and so on — being fabricated. In addition, certain filaments are more challenging to work with than others and will likely require more experimentation. The quality of the filament is also important, as chemical contaminants in lower-grade material can have the propensity to clog printer nozzles and lead to poorer-quality parts.

When choosing 3D-printing materials, the first step is to define the performance requirements for the printed part. These requirements can then be translated into appropriate material properties. Examples for plastic filaments include tensile strength, flexural modulus (the tendency of a material to bend), elongation, impact strength, hardness, creep, and compression set. Often, the combined set of material properties will point to just one or two optimal choices.

End-Use Applications

Additive manufacturing has been employed for rapid prototyping since the late 1970s. Today, it is also used for the rapid manufacturing across a broad range of <u>precision manufacturing</u> industries. Here, we highlight examples of the use of 3D printing in a variety of industrial and precision manufacturing settings, all of which Alconox Inc. can and has provided critical cleaning assistance to.

Automotive

In the automotive industry, 3D printing is used not only for rapid prototyping but to produce spare parts, tools, jigs,









and fixtures, as well as some car components. It has enabled the auto industry to better achieve lean manufacturing solutions with reduced warehousing and other costs. In addition, people that restore old cars use 3D printing to generate parts that are no longer being manufactured.

Other examples include the 3D printing of custom, theft-resistant locking wheel lug nuts for cars, custom 3D-printed front and rear bumper panels, and 3D printing of up to thousands of components in model race cars for wind tunnel testing.

Aerospace and Aviation

The aerospace sector was one of the earliest adopters of 3D printing, with the first use of the technology going back to 1989. Three decades later, aerospace and defense represents a <u>16.8% share</u> of the \$10.4 billion additive manufacturing market, <u>according to Stratview Research</u>, and heavily contributes to ongoing research efforts within the industry.

As in the automotive industry, 3D printing in the aerospace sector is used not only for rapid prototyping, including of functional prototypes, but also the production of tooling and lightweight components. Real, functional parts are also being 3D printed and used in aircraft and space shuttles. A few examples of parts that can be produced with 3D printing include air ducts, wall panels and even structural metal components

The Boeing 787 Dreamliner uses these 3D-printed fuel nozzles, as well as structural titanium fittings that hold the aft kitchen galley to the airframe.

Other end use applications include industries like architecture, construction and general manufacturing where critically clean surfaces may be required. Advantages of these technologies include enabling more complexity and accuracy, faster construction, lower labor costs, greater functional integration, and less waste.

Method and Material Impacts on Cleaning Requirements

Each material used in 3D printing comes with its own set of strengths and limitations, with many requiring postprocessing steps to finalize the print. In addition, while many parts of 3D printers are similar and have similar cleaning requirements, each 3D-printing method has unique critical cleaning requirements. Alconox Inc. offers solutions that can help your prints become as clean as possible when finished and keep 3D printers clean and performing at a high level.



Materials

Extruded plastics —like acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), and nylon — are among the most common materials used in household printers as well as industrial settings. A scrub or soak in a 1–2% solution of mild, free-rinsing, alkaline detergent to remove residual adhesive, small deposits of material, stringing, and any dirt or dust will provide a critically clean print after printing or removal of the supports. A wash after sanding to remove any particulates is also recommended. As some plastics can be heat sensitive when combined with aqueous detergents, it is further recommended that wash temperatures be lukewarm until compatibility is confirmed.

After each of the two curing processes with photosensitive resins, excess liquid resin must be removed from the print. Cleaning can be achieved with either an aqueous solution or in a solvent bath, often isopropyl alcohol (IPA). Using solvents like IPA comes with a number of challenges, however, including flammability and waste concerns, cost, and effectiveness due to only a single solvent-based cleaning mechanism. A 1–2% solution of a mild alkaline aqueous detergent, on the other hand, is able to clean off most liquid resins without harming the printed piece, and without any hazardous waste generation or flammability concerns.

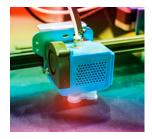
Metals and metal alloy–based 3D printed objects are produced in a bed of powder and often have a layer of powder adhering to their surfaces when pulled from the bed. A detergent bath featuring some agitation can be a great help in removing this layer. Avoiding corrosion is important with metals, so picking a compatible detergent, and quick removal of rinse water for reactive metals is essential.

Dissolvable supports are used to hold up complex prints without leaving unsightly marks and require water or other solvents to remove. Submerging the entire printed part/support assembly in a detergent bath can often help with removal of these supports and any residue the dissolved material may leave on the print.

Printers

Printer beds in 3D printers are typically composed of polyetherimide (PEI) sheets, glass, or an adhesive tape (on non-heated beds). Cleaning them on a regular basis will minimize the chances of any imperfections.





Cleaning of printer beds is similar for all types of printers. Glass beds and beds with a PEI sheet can be cleaned using IPA or other solvents, such as acetone. Acetone, like IPA, will have the same challenges, including flammability and waste concerns, cost, and effectiveness due to only a single solvent-based cleaning mechanism. A mild alkaline, aqueous detergent would again be the safer, more effective option.

Any remaining adhesive should then be washed and gently scraped off. The bed can then be washed with a detergent solution to remove any remaining residue. Older PEI sheets that have seen a lot of use may also benefit from sanding with a fine-grit (1,500+) sandpaper. Beds with adhesive tape are the most difficult to clean, as the tape is subject to breakage. Gentle scraping with a spatula is most effective. These processes may also lend to the generation of particulate residue that mild alkaline aqueous detergents can effectively address.

With vat polymerization printers, the main components that require cleaning are the light-emitting/focusing system and the resin vat. Cleaning the laser emitter and/or mirrors can be performed with a clean cloth and some mild alkaline detergent solution followed by a light rinse to ensure that no dirt or residue is present. The resin vat should be thoroughly cleaned when changing types of resin so that you don't get mixed resins and cross contamination of materials.

For powder-bed printers, it is important to keep the print head or laser system and the powder bed itself clean. Cleaning the print head is important for proper deposition of the binding agent or dye. It is recommended to inspect the print head for obstructions and gently clean with a stiff brush and mild alkaline detergent. Cleaning out the powder bed is generally only a concern when changing materials, as it is undesirable to have leftover powder mixed in with the new, leading to cross contamination.

Printer Nozzles

Fused deposition modeling printers that operate via extrusion also require cleaning of the extruder nozzle to prevent blockages. The exterior of the nozzle can be cleaned while still hot using a damp cloth with detergent if necessary. If that is not sufficient, a wire brush, small blade, or needle can be used.

To prevent nozzle malfunction and blockage, you first need to make sure that the tip of the nozzle and the area around the heating block is clean

Signs of a blocked nozzle include:

- The filament is not extruding uniformly.
- The nozzle extrudes very thin filament.
- Nothing comes out from the nozzle.

Before you begin, you'll need a 2% solution of a mild alkaline detergent, such as <u>ALCONOX®</u> <u>Powdered Precision</u> <u>Cleaner</u> or <u>LIQUINOX®</u> <u>Critical Cleaning Liquid Detergent</u>, a torch, and a very thin wire. Here's how to remove and clean a blocked extruder nozzle::

- 1. Soak the removed nozzle in the warm detergent for about 15 minutes to clean out exterior dirt. Rinse thoroughly. Use a soft cloth to clean the nozzle.
- 2. Place the nozzle on a stone and burn it using the torch for about one minute. Make sure it is extremely hot. You should see slight changes in the color.
- 3. Use a very thin wire to clear the hole in the nozzle. If the wire cannot go through, repeat step 2 until it can go through. Don't force through the hole with the wire.
- 4. If the jam was not caused by ABS or another filament that will dissolve or be cleaned away, you could also use a heat gun or blowtorch to heat it and melt the clog away. Once the nozzle is very hot, you can use a thin, soft wire to check if you can clear a hole through the nozzle.

Support Material

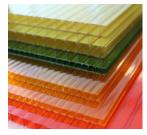
For cleaning soluble support material, you can use a selected choice of alkaline detergents in an Ultrasonic machine. For Ultrasonic cleaning of all the resin from around and inside your 3D prints, we recommend a 2% <u>ALCONOX</u>[®] or <u>DETONOX</u>[®] <u>Ultimate Precision Cleaner</u>; warm temperatures (>130°F/55°C); and an ultrasonic bath. Our powerful emulsive detergent solutions, along with sonication, would be most effective in removing the residue, especially particulates.

For a phosphate-free alternative, <u>LIQUINOX®</u> detergent is an optimal choice.

All three of the above detergents are compatible for cleaning a wide range of polymeric 3D-printing substrates and helping with complete removal of soluble support materials. (It is highly recommended that you verify the cleaning approach in your own setup, conditions, application, and instruments.)







Some sensitive plastics are susceptible to <u>stress cracking</u>, in which case a surfactant-free detergent would be needed. We would highly recommend <u>DETOJET® Low Foaming Liquid Detergent</u> in such a case. Typically, sensitive or stressed plastics are not used in 3D printing applications.

In terms of safety, it is safer to avoid using flammable liquids like alcohol and acetone in your ultrasonic cleaner. There is a risk of your ultrasonic cleaner causing a small spark, and that would be enough to cause a possible fire outbreak. If you have an ultrasonic transducer that fails, the energy from it can transfer into the cleaning fluid, which if flammable, this can also result in a fire outbreak.

Cleaning Chemistry

Since most 3D printing–related soils are light oils and particulates, mild alkaline cleaners are very effective cleaners. Alkaline cleaners remove organics, including oils, resins, extracts, and an array of other soils. Aqueous detergents containing micelle-forming surfactants for emulsifying provide a safe, efficient, effective choice for removing soils.

Alconox Inc. is armed with 75 years of experience recommending cleaners for use in <u>laboratory</u>, <u>cosmetics</u>, <u>medical devices</u>, <u>food</u>, <u>biotech</u>, and <u>pharmaceuticals</u>, where we have gained experience cleaning an array of residues and resins. This same experience allows us to bring great insight into removing residues found in the additive manufacturing process.

When large amounts of residue are attached to manufacturing surfaces, increased detergent concentration is generally required. Typically, a 1–2% (10–20 mL/L or 1.3–2.5 oz/gal) concentration suffices for routine cleaning; however, 2–5% (20–50 mL/L or 2.5–6 oz/gal) is often required for stickier or more dense residues.

Heat is an important variable in the cleaning of photosensitive resin prints. Within reason, higher temperatures increase the mobility of resins via softening, and accelerates the cleaning process residue removal. Using the highest temperature compatible with your prints to be cleaned ensures efficient emulsification of any leftover resin.

Cleaning Methods

Cleaning methods can be generally divided into manual or clean out of place (COP) cleaning, and automated cleaning.

Manual and COP cleaning includes methods that include direct, applied mechanical action. This is where higher-foaming detergents are not only permissible but useful, as they are best for emulsifying. Emulsifying is the preferred approach to remove organic soils, like oils, extracts, and resins. Manual/COP cleaning methods are soaking, scrubbing, and sonication (ultrasonic tanks).

Automated methods include the use of washers, high-pressure sprayers, and clean-in-place (CIP) systems. Low-foaming detergents use surfactants, which foam less and thereby eliminate situations where over-foam can occur. The less efficient surfactants are compensated for by higher alkalinity, chelation, wetting agents, and other methods to ensure that residues are quickly, safely, and reliably removed.

Manual Cleaning / COP Detergents

We would recommend the following detergents for soaking, scrubbing, or sonication of your parts from particulates, resins, and oily residues:

ALCONOX[®] Powdered Precision Cleaner

is a powerful emulsifier of organic and oily residues, used for many decades in manufacturing cleaning. It is biodegradable, drain-safe, and completely free-rinsing. An excellent choice for general cleaning of manual and COP 3D printing applications.

DETONOX® Ultimate Precision Cleaner

is our most potent manual detergent. A liquid concentrate, ideal and safe for hand and ultrasonic use on difficult 3D printing–related residues. It is a non-caustic detergent for exceptional removal of difficult, adherent resin and particulates.

LIQUINOX[®] Critical Cleaning Liquid Detergent

is a phosphate-free liquid alternative to Alconox detergents for manual and COP cleaning.

CITRANOX[®] Liquid Acid Cleaner and Detergent

is a phosphate-free acidic cleaner and metal brightener for the removal of oxidation, scale, salts, and inorganic residues in manual and ultrasonic cleaning. Effective for removal of 3D printing residues in soft and reactive metals.







For each of the approaches above, we would recommend warm to high-heat temperatures $(140^{\circ}F / 60^{\circ}C+)$ and a 1–2% starting concentration. Initial rinse should also be of a similar temperature to avoid thermal shock of the micelles that form.

CIP System and Washer Detergents

For cleaning via washers and other automated high-pressure units (e.g., CIP) necessitating low-foaming detergents, we would recommend:

ALCOJET[®] Low Foaming Powdered Detergent

is ideal for removing 3D printing residues in washers with a cup-in-door designed to hold powdered detergent, often with a door that stays closed during the prewash cycle and then pops open during the wash cycle.

SOLUJET[®] Low-Foaming Phosphate-Free Liquid

is a low foaming liquid concentrate detergent for removal of 3D printing residues in spray CIP system and washers with a liquid dispensing system.

CITRAJET® Low-Foam Liquid Acid Cleaner/Rinse

is a low-foaming, phosphate-free acidic cleaner and metal brightener for cleaning of 3D printing residues from sensitive and reactive metals in low foaming applications including CIP and washer systems.

DETOJET[®] Low Foaming Liquid Detergent

is ideal for cleaning sensitive plastics and stressed polycarbonates with 3D printing residues, as it contains no surfactants and will help avoid stress cracking.

A concentration of 1–2% detergent (10–30 mL/L or 1.25–2 oz/gal) is a good place to start, and the highest temperature that can be reasonably achieved. Recall that heat expedites cleaning and higher concentrations increase capacity or the amount that can be removed by a detergent. Therefore, qualitatively speaking, if there is a large amount of residue, higher concentrations may be needed.

For more information, see Critical Cleaning for 3D Printing in the Life Sciences.





Alconox Inc. Product Innovation

Alconox Inc. is honored to have reached our 75th anniversary milestone. Lets take a look back at some important dates in the company's history.

Pre 1941 While working at a hosiery company, chemist Louis Zisman learned about the emerging chemistry of synthetic surfactants. He discovered that a wetting agent he developed excelled at cleaning glassware without leaving a residue.

1940s Louis Zisman combined his talents with that of William Lebowitz, owner of Standard Scientific Supply Corporation. Standard Scientific was a distributor of products focused on the laboratory market. Together, they began selling and distributing detergent to hospitals and laboratories.

The detergent was first used in commerce on September 1st, 1943 and was coined, ALCONOX[®] Powdered Precision Cleaner.

Alconox Inc. was formed May 28th, 1946, to hold exclusive rights to ALCONOX detergent and its distribution.

1950s Alconox Inc. opens an office on 853 Broadway, New York, NY. Over time, more and more dealers signed up to distribute Alconox detergent and the product became widely distributed by just about every lab or hospital dealer.

Alconox Inc. launches a decade of innovation with some hits and some misses. They created the powdered detergent, ORANOX[®] Rust Inhibitor, that targeted dentists and oral surgeons. It was ultimately not successful and was discontinued in 1954. Recently, one box was recovered from an antique store in Albuquerque, New Mexico.

ALCOTABS[®] Tablet Pipet Detergent, a tablet solution to better clean siphon pipet washers, was developed and hit the market July 12th, 1957. The new, innovative, flotation cleaning, slow dissolving tablet allowed for cleaning over multiple cycles in the pipet washer resulting in better pipet cleaning.

Closing out the decade came another Alconox Inc. powerhouse, in fact our flagship detergent for lab washers. ALCOJET[®] Low Foaming Powdered Detergent was created and put in distribution August 12th, 1959. It was invented to provide a low-foaming detergent effective in automatic dishwasher glassware washing applications.

1960s On Oct. 28th, 1964 LIQUINOX[®] Critical Cleaning Liquid Detergent, was developed in response to customer requests for a phosphate-free detergent that would not interfere with biological oxygen demand (BOD) bottle washing where unrinsed bottles could result in contamination with phosphate essential nutrients causing false high readings in BOD testing.

1970s In order to improve removal of protein residues of blood, body fluids, and tissue for cleaning medical instruments, TERGAZYME[®] Enzyme-Active Powdered Detergent was introduced on November 21st, 1971.

In order to improve removal of protein residues of blood, body fluids, and tissue for cleaning medical instruments, TERGAZYME[®] Enzyme-Active Powdered Detergent was introduced on November 21st, 1971.

1980s In response to requests for a nonionic and ion-free detergent that does not leave conductive residues on electronic components, DETERGENT 8[®] Low-Foaming Ion-Free Detergent was introduced on July 14th, 1983.

For improved inorganic salts, oxides and acid labile residue cleaning, CITRANOX® Liquid Acid Cleaner and Detergent was introduced on December 8th, 1987.

1990s To help replace hazardous ozone depleting solvents that were being restricted by the Montreal Protocol, LUMINOX[®] Low-Foaming Neutral pH Liquid Detergent was first sold on April 21st, 1997.

2000s Per the need for a low foaming acid detergent and neutralizing rinse for automatic lab washers, CITRAJET[®] Low-Foam Liquid Acid Cleaner/Rinse was released on March 13th, 2001.

To address requests for an automatic lab washer phosphate free detergent for use in cleaning biological oxygen bottles (BOD), SOLUJET[®] Low-Foaming Phosphate-Free Liquid, went on sale July 2004.

Concurrently, TERGAJET[®] Low-Foaming Phosphate-Free Detergent was also released at the same time in order to have a powdered product for use in automated washer BOD bottle cleaning.

TERGAZYME makes a cameo on Bones Season 10 Episode 4.

Working with customers with difficult cosmetic polymer and sticky botanical extract residues we developed DETONOX[®] Ultimate Precision Cleaner, introduced in April 2015.

To match the manual cleaning power of DETONOX for cosmetic polymers and sticky botanical residues in an automated washer cleaning, KEYLAJET[®] Low-foaming Chelating High Alkaline Liquid was released on August 18th, 2016. Alconox Inc. celebrates 75 years of solving critical cleaning challenges.



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