

# Nanotechnology Critical Cleaning for Quality & Safety

Malcolm McLaughlin, Vice President, Product & Business Development, Alconox, Inc.

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## ABSTRACT

*Nanotechnology is currently employed across a wide range of industrial, research, and academic applications. Stringent cleaning protocols are essential to the successful fabrication of nanotechnology particles, structures, and systems. Additionally, environmental health and safety (EHS) concerns have resulted in the development of a new sensitivity to the protection of researchers and workers. Aqueous cleaners have played a significant role in many nanotechnology fabrication processes, with different chemistries designed for different methods and materials. Matching the correct aqueous cleaner to the preferred method yields appropriate results in terms of both fabrication quality and EHS guideline compliance.*

## LESS IS MORE

A nanometer is a billionth of a meter. Yet from particles of such infinitesimal size may come the greatest scientific advances of the new century. As medicine, biotechnology, industry, and physics explore the potential application of nano systems, quantum phenomena, and even new matter, fabrication techniques are being stretched beyond existing boundaries.

Integral to the success of these new explorations is the development of reliable cleaning techniques to meet stringent quality standards as well as new health protocols. Contamination can prove ruinous to nano level manufacturing and exposure to nano particles remains a source of concern for employee health.

Numerous cleaning protocols have been developed to meet these challenges and aqueous cleaning solutions have proven to be appropriate choices in many cases.

## TOP DOWN OR BOTTOM UP

There are two essential methods for creating nano systems. Lithography involves the deposition or removal of a specific material from a surface resulting in a top down approach to construction. Alternatively, chemical, crystal, or biologic agents can be used to grow nano scale components from the bottom up. Both methods have application across a wide range of industries and research initiatives but each requires strict adherence to cleaning guidelines for achieving quality and safety standards

Numerous common nano fabrication techniques are employed today including optical mask generation, electron beam lithography; physical, chemical, and plasma enhanced chemical vapor deposition; etching and embossing. One national laboratory has even bonded metal oxide titanium dioxide with DNA to produce a bio-inorganic hybrid.

But regardless of industry or technique, the goals of nanotechnology fabrication are the same – achieving impeccable levels of purity while minimizing human exposure to nanoparticles during the process.

## NANO AND NIOSH

As recently as February of 2009, The National Institute for Occupational Safety and Health (NIOSH) issued guidance for medical screening and hazard surveillance for workers potentially exposed to engineered nanoparticles. The recommendations reflect NIOSH's desire to determine whether engineered nanomaterials pose risks for adverse occupational health effects.

As stated in *Approaches to Safe Nanotechnology* published the Department of Health and Human Services, the Centers for Disease Control and Prevention, and the National Institute for Occupational Safety and Health:

“Nanomaterials present new challenges to understanding, predicting, and managing potential health risks to workers. As with any material being developed, scientific data on the health effects in exposed workers are largely unavailable. **In the case of nanomaterials, the uncertainties are great because the characteristics of nanoparticles may be different from those of larger particles with the same chemical composition.**”

In response, leading laboratories, academic research centers, and manufacturers have established safety guidelines to minimize or eliminate worker exposure to nanoparticles. Many have followed the advice provided by NIOSH for the cleanup and disposal of nanomaterials. Standard approaches for cleaning powder spills include using HEPA-filtered vacuum cleaners, or wiping up the powder using damp cloths or wetting the powder prior to dry wiping. According to NIOSH, damp cleaning methods are preferred while energetic cleaning methods such as dry sweeping or the using of compressed air should be avoided.

## ULTRASONIC CLEANING

In addition to the significant attention focused on worker safety, cleaning plays a critical role in nanotechnology fabrication. Certain manufacturing protocols require clean room technology and the attendant processes associated with maintaining the highest air and surface standards of decontamination. Other manufacturing and research environments involve simple bench hoods.

Regardless of the environment itself, nanotechnology cleaning involves both the substrates upon which a nanotechnology coating or process will be deposited as well as cleaning the equipment and surrounding surfaces employed during fabrication. In both cases, hard surfaces must be clean and free of any interfering residues and particles.

Often the size of the equipment or surface to be cleaned is fairly small and these can be effectively batch processed. Where nanotechnology cleaning is small and batch scale, ultrasonic cleaning tends to be the cleaning method of choice. For small batch scale cleaning, ultrasonic cleaning offers the advantage of being able to select the appropriate cleaning chemistry tailored to the residues and substrates being cleaned. Ultrasonic cleaning also allows for the choice of ultrasonic frequency which can be optimized for the sizes of particles that need to be removed (higher frequency ultrasonics are typically best for smaller particles). Lastly, ultrasonic cleaning delivers highly reproducible and reliable cleaning with a high level of local mechanical energy for very efficient batch cleaning.

## DETERGENTS

A review of American Chemical Society literature reveals dozens of recent references to the accepted use of ALCONOX powdered detergent in a wide range of methodologies employed in nanotechnology research and manufacturing. The most typical uses involve the cleaning of glass or metal substrates prior to the performance of a deposition process.

Just a few examples of applications where ALCONOX was employed include *Nanoindentation of Silver Nanowires*, *Hydrothermal Treatment of Nanoparticle Thin Films for Enhanced Mechanical Durability*, *Free-Standing Silica Colloidal Nanoporous Membranes*, and *Electrochemical Tuning of Silver Nanoparticles Fabricated by Nanosphere Lithography*

Researchers and manufacturers have relied on ALCONOX powdered detergent due to its proven performance over years of extensive use by laboratory, cleanroom, semiconductor, vacuum processing, and GMP manufacturing customers.

Two other commonly used cleaners for ultrasonic cleaning in the field of nanotechnology include LIQUINOX and CITRANOX. Both of these cleaners contain excellent emulsifiers and wetting agents capable of removing a broad range of oily organic residues. They also contain dispersants that can remove a broad range of insoluble particles. LIQUINOX is an alkaline cleaner. Alkaline cleaners are the most commonly used general-purpose, broad spectrum cleaners that are effective on most oily and particulate residues. CITRANOX is an acid cleaner that is used for special cleaning requirements such as removing metal oxides, salts and complexes that are more easily cleaned in acids.

## ENLISTING ELECTRICAL CHARGE

In unusual circumstances, certain substrate/residue combinations can be more readily cleaned at an acid or alkaline pH where both the substrate and residue have a pH mediated isoelectric point which can be manipulated to make them they repel each other. This is particularly relevant for addressing the cleanup of nanoparticles which often carry an electrical charge.

In aqueous critical cleaning there are numerous well-understood factors in detergency affected by pH. Far less well known, however, is the role pH can play in harnessing electrostatic effects to improve cleaning efficiency. Since like charges repel, choosing a cleaner of appropriate pH relative to the isoelectric point of the surface and the pKa (inverse log of the acid dissociation constant) of the residue makes cleaning far more efficient—especially when cleaning residues such as acids, bases, and amphoteric proteins, all of which can have their electrical charges manipulated by pH.

The isoelectric point of a surface is the pH at which the surface's electric charge is neutral with regard to its acid/base and electron donor-acceptor reactions. Moving to a higher or lower in pH will shift the effective surface charge or electron density in a negative or positive direction.

Here are two examples involving common substrate materials:

**Steel**—typically has an isoelectric point of 8.5 associated with the reactivity of the oxygen in the oxides Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, and Cr<sub>2</sub>O<sub>3</sub> on the surface of the metal and the hydrates and hydroxides formed in aqueous solutions.

**Glass**—has an isoelectric point of 2.5 associated with the SiO<sub>2</sub>. Raising the cleaner solution pH (past the isoelectric point), causes the surface to take on a more negatively charged character. If the residue to be removed also has a negative charge at that pH, then the negative surface will repel the negatively charged residue.

In addition to material surfaces, many residues can also undergo a change in electrical charge due to a simple change in their pH. For most acids, the pK<sub>a</sub> indicates the pH at which the hydronium ions and conjugate base are present in equal concentrations. Moving higher in pH shifts the equilibrium toward the right, thereby increasing the concentration of the negative conjugate base. Thus, when cleaning acids it is desirable to use a cleaning solution with a pH above the isoelectric point and the pK<sub>a</sub> of the acid. This results in an increase in the concentration of the negative conjugate base, with a pH above the isoelectric point of the surface where the surface will take on a repelling negative character.

For any cleaning, however, it is important to also consider the corrosive effect of pH on the surface being cleaned. Typically, it is desirable to choose a cleaner with a pH that will not etch or corrode the surface—for stainless steel, within the limits of passivation, and for glass, within the limits of etching.

## RINSING

As a generalization, deionized water is lower in ionic content than distilled water, and so deionized water is better for inorganic nanotechnology applications. Distilled water is typically lower in organic content than deionized water, and so it is better for final rinsing

in organic sensitive applications. Reverse osmosis water is typically as good or better than either distilled or deionized water, and so it can be used for most rinsing applications. WFI is typically water that has been additionally treated and filtered for pyrogens beyond ionic and organic trace contaminate removal by deionizing, distilling or reverse osmosis filtering.

## DISPOSAL

Matching the optimal critical cleaning product to the application and cleaning methodology can positively impact both production and performance and meet safety protocols. ALCONOX, LIQUINOX, and CITRANOX can play significant roles in the preparation of necessary labware as well as the preparation of substrates employed in the manufacture of nanomaterials.

Additionally, to prevent accumulation of nanomaterials on work area surfaces and reduce the risk of worker exposure, routine cleaning is necessary. Bench surfaces and all exposed work areas should be periodically damp-wiped and all residual nanomaterials and cleaning wipes should be disposed of as hazardous waste.

## ABOUT THE AUTHOR

*Malcolm McLaughlin is Vice President of Product & Business Development at Alconox, Inc., a leading developer and manufacturer of critical cleaning detergents. He has over 25 years of detergent formulation and application experience, including consulting on projects to clean semiconductors, photovoltaics and electrical substrates in manufacturing. He earned his M.A. in chemistry from Columbia University. He can be reached at the White Plains, NY, office of Alconox, Inc. at +914-948-4040 or [mmclaughlin@alconox.com](mailto:mmclaughlin@alconox.com).*

## STANDARD OPERATING PROCEDURES FOR CLEANING

A large part of successful cleaning relies on having a sound, reproducible procedure. In general, a good SOP should present a list of materials and people involved, the surface being cleaned should be identified, and the eight key variables for cleaning effectiveness should be defined:

- 1) precleaning handling
- 2) cleaning chemistry/concentration
- 3) time
- 4) temperature
- 5) type of agitation
- 6) rinsing conditions
- 7) drying conditions
- 8) postcleaning handling

Where cleaning solutions are re-used in baths or sumps, the control parameters and equipment used should be defined (such as conductivity or pH) the limits should be defined, the person responsible for monitoring the baths should be defined, the type of report or logbook entry should be defined, the trigger points and alert levels should be defined, actions taken in response to these levels and finally the conditions under which the bath is dumped should be defined.

**The following is an example of a standard operating procedure (SOP) for cleaning a glass substrate:**

To clean glass substrates: Make a 1% solution of Alconox detergent (10 g/L) in hot (50 deg C) deionized water in an ultrasonic tank. Remove glass from supplier packaging. Place the glass in a rack and immerse for 5 minutes. Rinse for 1 minute under running deionized water making sure to contact all parts of the glass for at least 10 seconds. Dry for 2 hours in a drying oven with HEPA air filtration. Allow cooling to ambient temperature for 20 minutes in a clean bench before use.

Email: [cleaning@alconox.com](mailto:cleaning@alconox.com)  
Phone: 914-948-4040  
Fax: 914-948-4088  
Website: [www.alconox.com](http://www.alconox.com)

To read more about critical cleaning, request your FREE copy of The Aqueous Cleaning Handbook or Critical Cleaning Guide by clicking [here](#).



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