Workplace design solutions

NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH

Protecting Workers during Nanomaterial Reactor Operations

Summary

Engineered nanomaterials (ENMs) are materials that are intentionally produced to have at least one primary dimension less than 100 nanometers (nm). These materials have new or unique properties different from those of larger forms of the same material, making them desirable for specific product applications. The health effects associated with nanomaterials are not yet clearly understood, so it is important for producers and users of ENMs to reduce employee exposure and manage risks appropriately. In 2013, the National Institute for Occupational Safety and Health (NIOSH) published a compendium of control approaches for nanomaterial production and use processes entitled *Current Strategies for Engineering Controls in Nanomaterial Production and Downstream Handling Processes.* This Workplace Design Solutions document provides guidance on exposure control approaches for protecting workers during nanomaterial reactor operations.

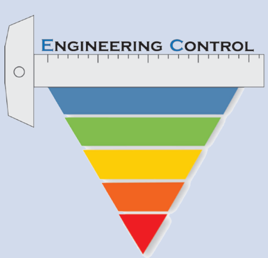
Background

The toxicity of many nanomaterials is presently unknown, but initial research indicates that there may be health concerns related to occupational inhalation exposures. Only a few types of ENMs have undergone extensive toxicological evaluation by NIOSH, e.g., titanium dioxide (TiO_2) and carbon nanotubes (CNTs). Results from animal studies with TiO_2 and other poorly-soluble, low-toxicity particles of fine and ultrafine (nanoscale) sizes have shown adverse pulmonary responses in exposed rats, including persistent pulmonary inflammation and lung tumors [NIOSH 2011; Oberdörster 2002; Donaldson 2009; Poland et al. 2012]. Similar toxicological responses have also been observed in rats and mice exposed to CNTs and carbon nanofibers (CNFs) [NIOSH 2013]. Because of the potential for adverse human health effects, it is important to control worker exposure and to manage risks appropriately throughout the lifecycle of ENM production.

PtD Prevention through Design™

Prevention through Design (PtD)

Prevention through Design (PtD) can be defined as designing out or eliminating safety and health hazards associated with processes, structures, equipment, tools, or work organization. The National Institute for Occupational Safety and Health (NIOSH) launched a PtD initiative in 2007. The mission is to reduce or prevent occupational injuries, illnesses, and fatalities by considering hazard prevention in the design, re-design, and retrofit of new and existing workplaces, tools, equipment, and work processes [NIOSH 2008a,b].



Centers for Disease Control and Prevention
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Description of Exposure

ENMs are often produced from aerosolized precursor materials in a variety of enclosed reactors using methods such as furnace flow (hot wall), laser, plasma/discharge, and flame reactors [Buesser and Pratsinis 2012]. In these processes, vapor/aerosol phase synthesis techniques are effective in producing a wide range of ENMs with different compositions and shapes, including metal and metal oxide nanoparticles, nanotubes and nanowires including CNTs and fibers [Virji and Stefaniak 2014].

Harvesting nanomaterials from reactors results in potentially high exposures [Demou et al. 2008; Lee et al. 2010, 2011; Methner 2008; Yeganeh et al. 2008]. In addition, cleanout of reactors contributes to increased facility concentrations and exposures among operation and maintenance workers. Leakage from pressurized reactors can also contribute to background concentrations and result in exposure to employees throughout the facility. Emission sources related to reactor operations, harvesting, and maintenance can be categorized as fugitive or task–based. The approaches to control both fugitive and task-based emissions from the reactor have primarily been ventilated enclosures.

NIOSH recommends that manufacturers and downstream users of nanomaterials develop PtD strategies to protect workers during the production and handling of engineered nanomaterials. Engineering controls protect workers by removing or designing out hazardous conditions or by placing a barrier between the worker and the hazard, and along with good work practices, they are likely to be the most effective control strategy for nanomaterials. The identification and adoption of effective control technologies is an important first step in reducing the risks associated with worker exposure to ENMs and ENM-associated byproducts.

Harvesting of Product Nanomaterials

The opening of a reactor and collection of nanomaterials has been shown to be a source of emissions to the workplace in a variety of studies. Methner et al. [2010] reported that opening a sealed reactor resulted in elevation of both fine and ultrafine particle concentrations above background in two facilities. One of these facilities showed a dramatic decrease in emissions when using local exhaust ventilation (LEV). Lee et al. [2010] reported that the opening of the reactor for harvesting was the task most often associated with emission of nano-scale and fine particles at seven multi-walled carbon nanotube facilities. Because of the potential for release of primary nanoparticles, manual harvesting of product materials may be better controlled by higher-level enclosures such as a glove box or a specially designed enclosure to provide good capture while minimizing loss of product materials.

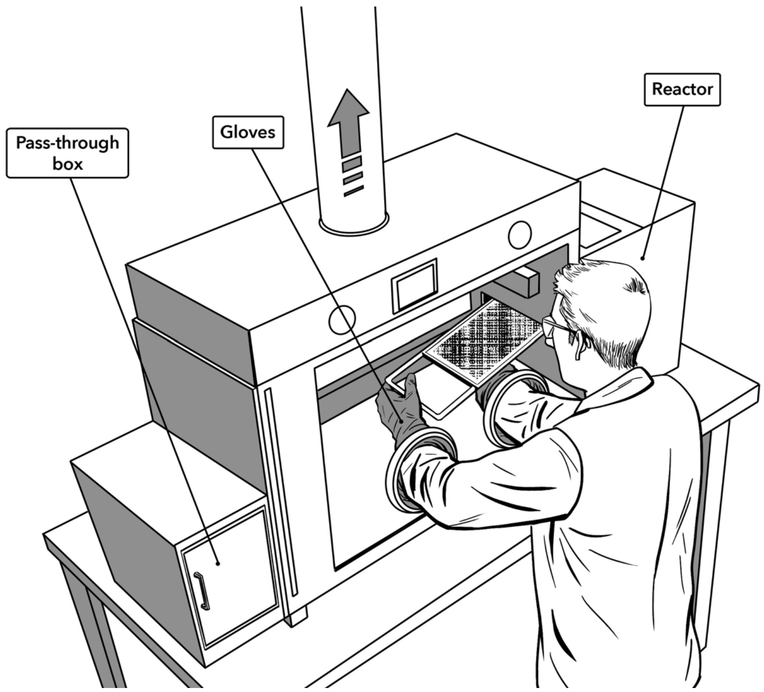
Small Reactors

Laboratory fume hoods, enclosures, and glove boxes can be used when the reactor is small (less than approximately 3 feet in length and 2–3 feet in width), such as in R&D operations. Two studies have shown that when the reactor is housed in a well-designed and operating fume hood, particle loss to the work environment is low [Tsai et al. 2009; Yeganeh et al. 2008]. NIOSH has published information about protecting workers during the handling of nanomaterials using chemical fume hoods and glove boxes as well as other ventilated enclosures [NIOSH 2018]. The figure (small reactor harvest enclosure) below provides an example of a glovebox unit fitted to the outlet of a small reactor which could be used to harvest products from an enclosure.

Medium and Large Reactors

Where the production reactors are larger, custom-fabricated enclosures (often constructed from a polycarbonate, transparent thermoplastic material) or vinyl curtains can be used to reduce fugitive emissions. Since production reactors typically house hot processes, the required exhaust flow calculations should consider the buoyant thermal plume from the reactor [McKernan and Ellenbecker 2007]. A canopy-type hood can be used to collect materials emitted when the reactor is opened for product harvesting (see large reactor harvest enclosure figure below). Side baffles or plastic curtains can be used to improve collection efficiency by minimizing the adverse effects of drafts. The size of the canopy hood (especially depth) should be sufficient to contain reactor emissions while allowing access for the operator.

The bullet points listed with the figure below offer important design and operational considerations for these enclosures.

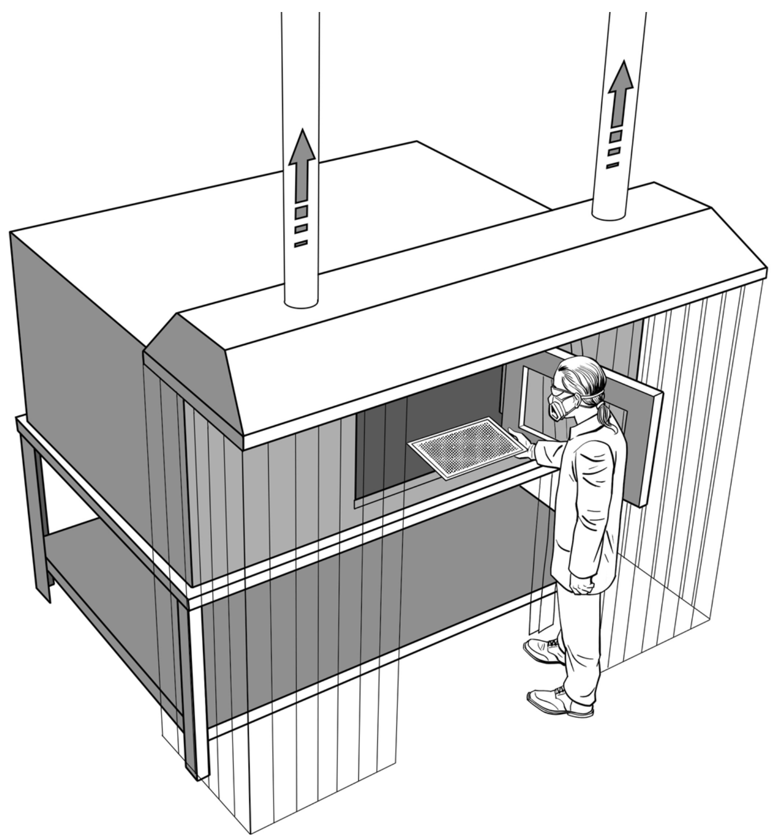


Small Reactor Harvest Enclosure

- Ventilated enclosure for capturing emissions during the harvesting of ENMs from a reactor.
- Enclosure design must account for operator access needs and process visibility to be effective.
- A low exhaust flowrate should be sufficient to maintain negative pressure in the enclosure and contain emissions.
- After ENMs are harvested, they should be placed in a sealed container to minimize contamination during removal from the enclosure.
- A pass through box allows for the removal of nanomaterials from the enclosure with minimal potential for release of materials to the workplace.

Large Reactor Harvest Enclosure

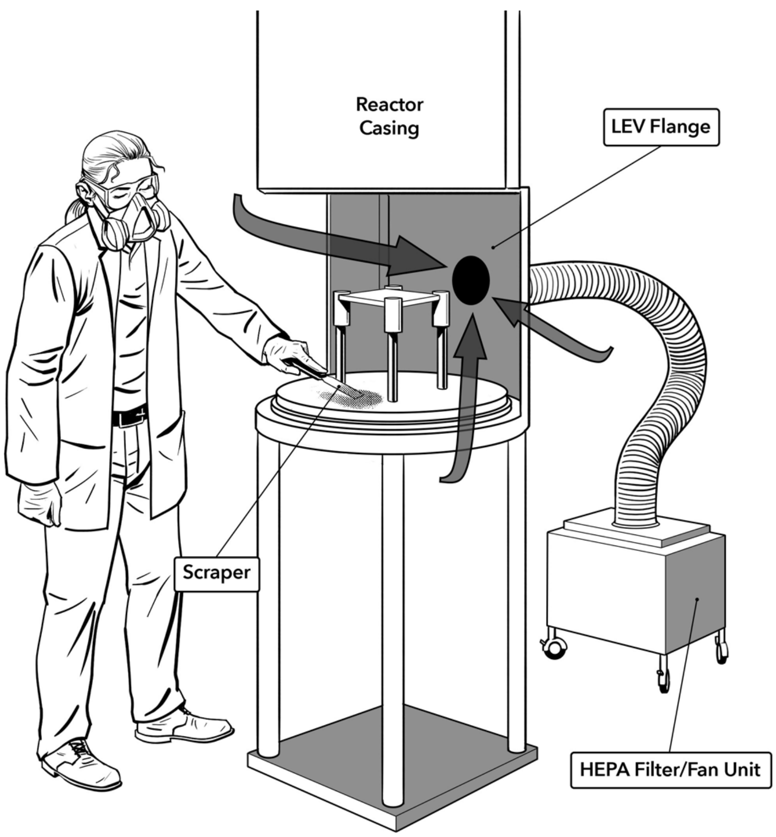
- Ventilated enclosure for capturing reactor emissions during the harvesting of ENMs.
- Exhaust flowrate should be designed to maintain an inward air velocity between 80–100 fpm at the face of the enclosure (curtains).
- A hard enclosure made of a suitable plastic such as polycarbonate or acrylic or a soft enclosure constructed with vinyl curtains can be used to enclose the reactor.
- Ensure that enclosure materials are compatible with the process (i.e. high temperature or anti-static).
- Check performance using a visual indicator such as a smoke tube/source to confirm that air flows move away from the worker breathing zone and toward the exhaust.



Routine Cleaning of the Reactor

Following the completion of production, unwanted byproducts frequently coat the walls of the reactor requiring periodic maintenance/cleaning. The cleanout of reactors may involve manual sweeping, brushing, or scraping to remove waste materials. A study of exposures linked to reactor cleanout showed that the potential for emission of nanoparticles exists during cleaning [Zimmermann et al. 2012]. This study looked at a variety of different reactor-based production methods (chemical vapor deposition, physical vapor deposition, pyrosol) and cleaning methods (dry/wet dusting, scraping, scouring pad, sanding, heat gun). The researchers concluded that cleanout of reactors could lead to emissions of nanoparticles regardless of method. Wet methods resulted in generally lower emissions while dry and energetic methods (like scraping, sanding, and use of an air jet) resulted in higher emissions. Demou et al. [2008] showed that the use of a vacuum cleaner, outfitted with a Class M (medium efficiency) filter, was one of the highest particle emission sources when cleaning a reactor.

Yeganeh et al. [2008] evaluated a nanotechnology process that was enclosed in a ventilated fume hood. The reactor was cleaned daily using manual sweeping and vacuuming to remove the waste material. The ventilated fume hood adequately contained the particles generated during the cleaning process. Methner [2008] evaluated the use of a portable LEV unit for controlling exposure during cleanout of a vapor deposition reactor which was used for producing nanoscale metal oxides (see reactor cleaning figure below). Following the automated collection of product materials, an operator cleaned out slag and waste product from the reactor using brushes and scrapers. The use of a commercially available portable fume extractor with HEPA filtration resulted in an average reduction in airborne concentrations of 88%–96% during cleanout procedures.



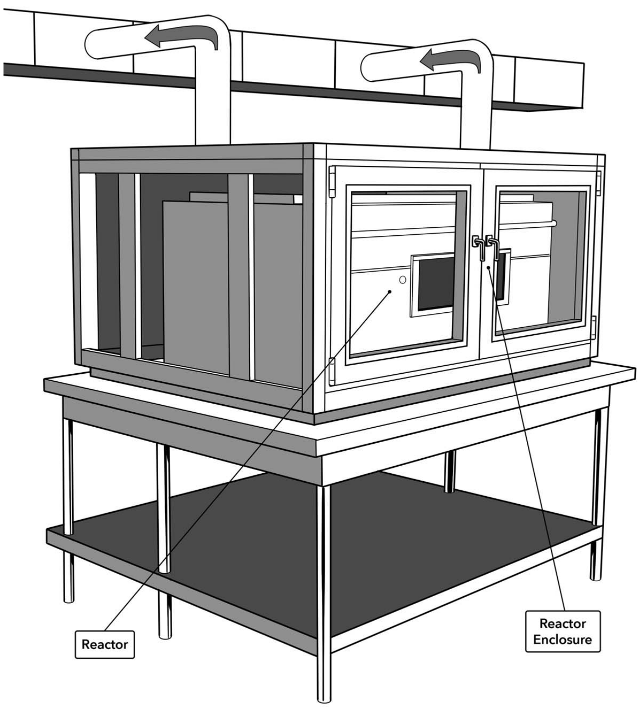
Reactor Cleaning

- Local exhaust ventilation (LEV) can be used to collect emissions during cleaning.
- Place the exhaust pickup as close to the emission source as possible (typically within 6 inches). Velocity decreases rapidly moving away from the exhaust pickup.
- The air velocity at the point where contaminants are emitted should be at least 100 fpm.
- Use baffles and side shields to enclose the process as much as possible. Cross currents and drafts in the workplace can reduce effectiveness.
- Note the direction of the air flow is away from the breathing zone of the worker and towards the exhaust.

Fugitive Emission Control

Leakage of nanoparticles from reactors to the work environment has not been well documented. If the reactor is operated under negative pressure with respect to the environment, emissions are less likely, except when opening the reactor for harvesting or cleaning. However, a study has shown that leakage from reactors can result in the increase in workplace nanoparticles [Demou et al. 2008]. Demou et al. showed a consistent increase in the workplace concentrations over the course of a day as production continued followed by a drop off once production ceased.

The figure below shows an example of a ventilated reactor enclosure (see large reactor enclosure figure). These enclosures should be designed to account for the removal of heat from the process so that the reactor can operate properly when doors are closed. When a process is heated, the use of canopy hoods over the reactor may be another effective alternative as long as the design meets operational and facility exposure control requirements [ACGIH 2016; McKernan and Ellenbecker 2007].



Large Reactor Enclosure

- Ventilated enclosure for capturing fugitive emissions (leaks) from reactor.
- Must account for operator and maintenance access needs and heat dissipation from reactor to be effective.
  - Lack of proper exhaust ventilation for heat loss may require that enclosure doors remain open to maintain the required process temperature.
  - Exhaust ventilation for maintaining a negative pressure in the enclosure will typically not provide adequate capture when doors are open.
- The use of transparent doors and walls allow for visibility of the reactor by the operator.

Design and Operational Considerations

The local exhaust ventilation hood or enclosure should be designed to effectively capture the contaminants released by a process. It should be tailored to the specific process being controlled (especially important for hot processes, processes generating contaminants at high velocities, and processes where other chemicals, such as solvents, may co-occur). Information about the design, operation, and maintenance of engineering controls for industrial processes is available from a variety of sources [ACGIH 2007, 2016; Burton 1999; Burgess et al. 2004]. When designing these types of controls, it is necessary to follow the design and operational considerations below:

- ☐ Consult a qualified industrial ventilation engineer, industrial hygienist, or containment specialist to design the new control system.
- ☐ Consider access requirements when designing the control to ensure that the operator and maintenance personnel can perform required tasks without reducing control effectiveness (e.g. leaving enclosure doors open).
- ☐ Consider heat loads generated by the process when designing the enclosure and determining the airflow. A tight enclosure with inadequate airflow may affect reactor temperature.
- ☐ Determine exhaust airflows capable of maintaining a negative pressure (even during the opening of access doors). Fans that move air through the LEV system need to be adequately sized to ensure the system works properly.
- ☐ Provide an easy way of checking that the control system is working, e.g., manometer, pressure gauge or other visual indicator. Always confirm that the exhaust is turned on and working prior to starting the task.

- ☐ Provide clean make up air to the workroom to replace most of the exhausted air.
- ☐ Discharge exhaust air to a safe place away from doors, windows, supply air intakes, or other points where re-entry of exhausted contaminants into the workplace may occur.
- ☐ Keep exhaust ducts short and simple—avoid flexible duct if possible. The duct material and filters chosen need to be compatible with the ENMs and byproducts generated.
- ☐ Conduct initial performance tests of the controls installed at the facility. These tests should be scheduled as part of a regular preventive maintenance program to ensure adequate containment.
- ☐ If using a vacuum cleaner, consider purchasing an industrial system with HEPA filtration.

Preventive Maintenance and System Checks

- ☐ Develop a written preventive maintenance (PM) plan to check system performance and repair identified deficiencies.
- ☐ Keep equipment in effective and efficient working order.
- ☐ Look for signs of damage to the ducting and ventilation control system. Repair damage immediately.
- ☐ Regularly check that the enclosure system is working properly and that the enclosure has no visible dust leaks.
- ☐ Have a qualified industrial ventilation engineer or industrial hygienist examine the ventilation control system and check its performance at least once every year or if it is modified or relocated.
- ☐ Conduct routine industrial hygiene monitoring to ensure controls are working at design conditions.
- ☐ Keep the information obtained from all engineering control system tests/checks in a PM logbook.

Administrative Controls

The use of engineering controls is likely the most effective control strategy for nanomaterials. Administrative controls and personal protective equipment (PPE) also have a place in PtD strategies and are usually identified as additional safeguards. Work practices, an administrative control, are procedures followed by employers and workers to control hazards in the workplace. These include housekeeping and cleaning, storage and use procedures, labels and postings, hazard training, and procedures for the use of engineering controls, many of which are discussed below. In addition, respirators may be needed and can be used during the implementation of engineering controls and work practices as well as during some short-duration maintenance procedures, when engineering and administrative controls are not feasible, and in emergencies. Therefore, facilities should consider the following administrative and PPE approaches as a part of a comprehensive occupational safety and health management plan for nanomaterial production and use.

Cleaning and Housekeeping

- ☐ Clean the work area and equipment every day. Deal with spills immediately according to written procedures and using appropriate PPE. Standard approaches for cleaning spills can be used for cleaning surfaces contaminated with dry powder nanomaterials. These include using HEPA-filtered vacuum cleaners, wiping up dry powders with damp cloths, or wetting the powder before wiping.
- ☐ Dispose of cleaning wipes and other contaminated materials in a sealed bag to prevent release of the dried nanomaterial. Nanomaterial contaminated waste, including cleaning materials, should be kept in a separate waste stream.
- ☐ Do not use dry methods such as a brush, broom, or compressed air to clean up contaminated work surfaces.
- ☐ Care must be taken when using wet methods for housekeeping activities to make sure that any other safety hazards (e.g., electrical hazards, slips/trips, etc.) are not introduced into the workplace.
- ☐ Cover all containers when not in use. Dispose of empty containers safely.

Training

- ☐ Provide safety and health training to workers, supervisors, and managers including information about proper use, maintenance, and inspection of the control.
- ☐ Provide workers with sufficient information to understand the nature of potential workplace exposures, health risks, routes of exposure, and instructions for reporting health symptoms [OSHA 2012].
- ☐ Ensure that training includes how to keep exposures low; how to check that the ventilation control system is working; how to use and care for PPE, including respirators; and what to do if something goes wrong.

Personal Protective Equipment

Personal Protective Clothing

Because some types of nanoparticles have been found to penetrate the skin, appropriate protective clothing should be worn. PPE should be worn when engineering and/or administrative controls are not feasible or effective in reducing exposures or when controls are not feasible such as maintenance or response to a spill. Follow job hazard assessment procedures for determining the need for and selection of PPE [OSHA 2002; ACS 2015].

- ☐ If appropriate, use nitrile or other chemically impervious gloves during handling and cleanup of nanomaterials. Gloves should be selected based on their effectiveness against the nanomaterial as well as any other chemicals being used. Gloves should be inspected before use and changed at least at the end of each shift and whenever they show visible signs of wear. Used gloves should be kept in a sealed plastic bag in the work area until they can be disposed of properly.

- ☐ Never use compressed air or other high energy techniques such as brushing or shaking to remove dust from clothing.

Respirators

Employers should consult with an occupational safety and health professional to determine the respirator best suited for their specific application. Employers should always follow the Occupational Safety and Health Administration (OSHA) Respiratory Protection Standard (29 CFR 1910.134) if respiratory protection is used (www.osha.gov/SLTC/etools/respiratory/index.html). NIOSH guidance for selecting respirators is found at http://www.cdc.gov/niosh/docs/2005-100/default.html [NIOSH 2004].

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For More Information

NIOSH developed detailed information about comprehensive PtD strategies for nanomaterial use and production [NIOSH 2013b] that can be found in the document *Current Strategies for Engineering Controls in Nanomaterial Production and Downstream Handling Processes* (http://www.cdc.gov/niosh/docs/2014-102/pdfs/2014-102.pdf).

The information in this document is based on research related to Prevention through Design (PtD) initiatives. More information about PtD is available on the NIOSH Website at http://www.cdc.gov/niosh/topics/PtD/

The Nanotechnology Research Center (NTRC) leads the federal government nanotechnology initiative to conduct research and provide guidance on the occupational safety and health implications and applications of nanotechnology. More information about the NTRC is available on the NIOSH Website at https://www.cdc.gov/niosh/topics/nanotech/nanotechnology-research-center.html

Engineering controls protect workers by removing hazardous conditions or by placing a barrier between the worker and the hazard. More information about the Engineering Controls Program is available on the NIOSH Website at https://www.cdc.gov/niosh/engcontrols/

To obtain information about other occupational safety and health topics, contact NIOSH at:

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