Product Safety Assessment

Chemical-Mechanical Planarization (CMP) Slurries

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Names
• ACUPLANE™ Copper barrier removal slurries
• CELEXIS™ Shallow trench isolation (STI) slurries
• KLEBOSOL® Interlayer dielectric (ILD) slurries
• Reactive Liquid (RL) Bulk copper removal slurries
• NANOPURE™ Silicon wafer polishing slurries

Product Overview
• Rohm and Haas Electronic Materials CMP, Inc., a division of Rohm and Haas Company which is a wholly owned subsidiary of The Dow Chemical Company, manufactures and distributes chemical-mechanical planarization (CMP) slurries. These materials are odorless, milky white, stable suspensions of abrasive materials dispersed in water with other chemicals, such as rust inhibitors and bases to provide an alkaline pH (>10). The abrasive materials can include but are not limited to silicon dioxide, cerium oxide, or aluminum oxide.1,2 Conversely, the Reactive Liquid (RL) slurries manufactured and distributed by Rohm and Haas Electronic Materials CMP, Inc. are non-abrasive solutions with an acid pH (<5) which are odorless, water clear solutions of buffered mild organic acids dissolved in water with polymers and a rust inhibitor. For further details, see Product Description.
• CMP slurries manufactured and distributed by Rohm and Haas Electronic Materials CMP, Inc. and its foreign affiliates are used to polish the surface of silicon wafers, which are then used to produce integrated circuits and other microelectronic devices.3,4,5 For further details, see Product Uses.
• Exposure can occur either in a facility that manufactures these slurries or in the various microchip manufacturing facilities that use these products. Such exposures are anticipated to be minimal since current manufacturing processes are automated, even during transfer of raw materials between their original containers and the receiving mix vessels. Those working with CMP slurries in manufacturing operations could be exposed during maintenance, sampling, testing, clean-up, or other procedures. Rohm and Haas Electronic Materials does not sell these slurries for direct or indirect consumer use.6,7 For further details, see Exposure Potential.

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Contact with the slurries may cause slight eye or skin irritation. Inhalation may result in irritation of the nose, throat, and respiratory tract. In some instances, skin sensitization (allergies) is possible. Swallowing may irritate the mouth, throat, and digestive tract. For further details, see Health Information.

The abrasive materials in the slurries are expected to be inert in the environment. They are not likely to accumulate in the food chain (bioaccumulation potential is low) and can be slightly to moderately toxic to aquatic organisms on an acute basis. For further details, see Environmental Information.

The slurries are stable under normal storage and use conditions, but can decompose at elevated temperatures (e.g., at or near temperatures that boil water). The slurries are not readily combustible, but may produce hazardous vapors in a fire. For further details, see Physical Hazard Information.

Manufacture of Product

Locations – CMP slurries are manufactured by Rohm and Haas Electronic Materials CMP, Inc. in Newark, Delaware, USA. Rohm and Haas Electronic Materials CMP, Inc. and its foreign affiliated companies also distribute slurries manufactured by AZ Electronic Materials Corporation and those produced by Nitta Haas Incorporated (a joint venture of The Dow Chemical Company).

Process – Slurry products manufactured by Rohm and Haas Electronic Materials CMP, Inc. are produced in mix tanks by blending purified water with abrasive materials and other chemicals such as alkaline materials and rust inhibitors to form a highly stable and homogeneous suspension. Similar blending steps are used for manufacturing Reactive Liquid (RL) slurries. The blending processes do not involve chemical reactions, only blending occurs.

Product Description

CMP slurries manufactured and distributed by Rohm and Haas Electronic Materials CMP, Inc. and its foreign affiliated companies are odorless, milky white, stable mixtures (see image) of abrasive materials (amorphous non-crystalline inorganic oxides) dispersed in water with other chemicals, such as rust inhibitors and bases to provide an alkaline pH (>10). The abrasive materials can include but are not limited to silicon dioxide (silica, SiO₂), cerium oxide (ceria, CeO₂), aluminum oxide (alumina, Al₂O₃). The abrasive materials have a uniform shape and narrow size distribution, with an average particle size ranging from 10 to 100 nanometers, depending on the product. The particles dispersed in the slurries remain in suspension because negative charges are incorporated on the particle surface, so that the particles repel each other in solution. The products range from about 1-5% abrasives for the ceria slurries to 10 to 25% abrasives for the silica slurries.

Reactive Liquid (RL) slurries marketed by Rohm and Haas Electronic Materials CMP, Inc. are non-abrasive solutions with an acid pH (<5). These products are odorless, water clear solutions of buffered mild organic acids dissolved in water with polymers and a triazole rust inhibitor.

The slurry products are packaged in 20 and 200 liter plastic drums and 1040 liter tote tanks.
Product Uses\textsuperscript{15,16}

The slurries are used with pads in the polishing process of silicon wafers as part of the creation of integrated circuit (microchip). Slurries are a highly engineered chemical formulation – typically comprised of abrasives – that works with the pad to smooth and flatten the wafer surface.

Microchip manufacturing has become so complex and delicate that silicon wafers must be perfectly flat and smooth to prepare them for later steps when circuit patterns are imaged onto the wafer. This is done repeatedly as layer after layer of intricate circuits are created on the surface so the slurries can be dispensed 40 or more separate times as each chip is built.

Immediately before use, customers stir the slurry at more than 250 RPMs (Rotations Per Minute) to make it homogeneous (uniform). Customers often transfer slurries from the original containers to central storage tanks where they may dilute slurries with water and optionally add other additives (e.g., hydrogen peroxide) to suit their particular polishing applications.

The slurries are then pumped to a planarization tool through piping. Operators stand outside the planarization tool and program it to auto-dispense the slurry onto the surface of polishing pad that is within the tool enclosure (pictured below). The rotating pad transports the slurry underneath the wafer and operates to polish and planarize (flatten) the wafer through chemical and mechanical action.

The slurries are used by semiconductor companies to manufacture microprocessors and memory chips found in PCs, mobile phones, music players and other electronic devices.

Exposure Potential\textsuperscript{17,18}

CPM slurries are commercial products for industrial application. Based on this, the public can be exposed through:

- **Workplace exposure** – Employee exposure can occur during slurry production. Such exposures are anticipated to be minimal since current manufacturing processes are automated, even during transfer of raw materials between their original containers and the receiving mix vessels. Employees may have incidental dermal contact during slurry packaging operations in the rare event of spills, overflows, or other unintentional events. Inhalation exposures are not likely because the slurry products are non-volatile and not released as mists or aerosols. Customer use of slurries occurs in a clean room environment of a semiconductor facility where the planarization tools (pictured above) and handling practices are designed to prevent direct worker contact with the chemicals. This environment prevents substantial exposure to chemicals (including slurries) used during routine RHEM CMP process. Incidental skin contact is possible during maintenance, sampling, testing,
clean-up, or other procedures. Even for these potential exposures, inhalation exposure is not probable given the non-volatile and non-aerosolized form of the slurries. Each slurry manufacturing facility and CMP planarization operation should have a thorough training program for employees and appropriate work processes, ventilation, and safety equipment in place to limit exposure. See Health Information.

- **Consumer exposure to CMP slurries** – These products are for industrial use only. Consumer contact is unlikely. See Health Information.

- **Environmental releases** – CMP slurries manufactured and distributed by Rohm and Haas Electronic Materials CMP, Inc. are used under strictly controlled conditions, and inadvertent releases to the environment are uncommon. If released to soil, the solids from these products are likely to adsorb to soil and remain in place. If released to water, the products would disperse and eventually adsorb to sediment. Process wastewaters are discharged to wastewater treatment facilities, and the components of the CMP slurries are expected to be removed by adsorption to biosolids during wastewater treatment. In the event of a spill, the focus is on containing the spill to prevent contamination of soil and surface or ground water. Small spills should be absorbed or contained with sand or soil. See Environmental, Health, and Physical Hazard Information.

- **Large release** – The potential size of release is limited by the size of the containers sold and distributed by Rohm and Haas Electronic Materials CMP, Inc. The largest is 1040 liters. If a large spill does occur, the material should be captured, collected, and reprocessed or disposed of according to applicable governmental requirements. Keep slurries out of sewers and waterways. See Environmental, Health, and Physical Hazard Information.

- **In case of fire** – CMP slurries sold and distributed by Rohm and Haas Electronic Materials CMP, Inc. are over 65% water and not readily combustible. Fight fires in accordance with the material that is burning. During intense fire situations, CMP slurries are not expected to decompose. The slurry particles can be suspended into air as water is vaporizes into the atmosphere. As a precaution deny any unnecessary entry into the area. Firefighters should wear positive pressure, self-contained breathing apparatus (SCBA) with an approved full-face mask and protective firefighting clothing. Follow emergency procedures carefully. See Environmental, Health, and Physical Hazard Information.

For more information, request the Safety Data Sheet from the Dow Customer Information Group.

**Health Information**

Health information for CMP slurries manufactured and distributed by Rohm and Haas Electronic Materials CMP, Inc. is summarized on the relevant Safety Data Sheets. It is important to note that health risks associated with individual products may vary based on their formulation or intended use. These products may contain minor components or additives that have additional health risks. The Safety Data Sheet is the preferred source for specific health information. An overview of health information for CMP slurries appears below.

**Eye contact** – May cause slight eye irritation.

**Skin contact** – May cause slight irritation and/or dermatitis. Skin sensitization may occur from dermal contact with NANOPURE™ Silicon Wafer Polishing Slurries.

**Inhalation** – May result in irritation of the nose, throat, and respiratory tract.

**Ingestion** – Swallowing may irritate the mouth, throat, and digestive tract.
Other – For slurries containing silica abrasives, there is a possibility that the crystalline form of silica may be present in small amounts. The slurries are intended to contain only amorphous (non-crystalline) form of silica. The crystalline form may cause permanent lung damage in persons who are subjected to repeated, prolonged overexposures. For more information, request the Safety Data Sheet from the Dow Customer Information Group.

Environmental Information

Environmental information for CMP slurries manufactured and distributed by Rohm and Haas Electronic Materials CMP, Inc. is summarized on the relevant Safety Data Sheets. It is important to note that environmental properties associated for individual products may vary based on their formulation or intended use. The Safety Data Sheet is the preferred source for specific environmental information. These products may also contain minor components or additives that have additional environmental characteristics. An overview of environmental information for the major component of CMP slurries manufactured and distributed by Rohm and Haas Electronic Materials CMP, Inc. appears below.

Cerium oxide, silicon dioxide, and aluminum oxide occur naturally. If released to soil the solids from the CMP slurries are likely to adsorb to soil and remain in place. If released to water, the products would disperse and eventually adsorb to sediment. Small amounts would be removed by adsorption to biosolids during wastewater treatment.

Cerium oxide, silicon dioxide and aluminum oxide are not likely to accumulate in the food chain (bioaccumulation potential is low) and the components can be slightly to moderately toxic to aquatic organisms on an acute basis.

For more information, request the Safety Data Sheet from the Dow Customer Information Group.

Physical Hazard Information

CMP slurries are stable under normal storage and use conditions. Avoid excess heat or freezing temperatures. Avoid contact with metal nitrates, strong acids, or strong bases.

In case of fire, the slurries are not readily combustible or flammable. Fight fires in accordance with the material that is burning. During intense fire situations, the slurries are not expected to decompose. The slurry particles can be suspended into air as water is vaporizes into the atmosphere. As a precaution deny any unnecessary entry into the area. Firefighters should wear positive pressure, self-contained breathing apparatus (SCBA) with an approved full-face mask and protective firefighting clothing. Follow emergency procedures carefully.

Regulatory Information

Regulations may exist that govern the manufacture, sale, transportation, use, and/or disposal of CMP slurries. These regulations may vary by city, state, country, or geographic region. Information may be found by consulting the relevant Safety Data Sheet or Contact Us.
Additional Information

- Request Safety Data Sheets or product information from the Dow Customer Information Group (www.dow.com/assistance/dowcig.htm)
- Contact Us (www.dow.com/assistance/thoughts.htm)


References

3. CUS\textsuperscript{†} 1300 Family: Barrier Slurries for Cu CMP, Technical Data Sheet, Rohm and Haas Company, Form No. CP07N017, Rev. 0, November 2007, page 1.
4. KLEBOSOL\textsuperscript{®} Slurry Products, Rohm and Haas Company, Form No. CP07N026 Rev. 0, November 2007, page 1.
5. ACUPLANE\textsuperscript{™} LK393c4 Cu Barrier Slurry, Rohm and Haas Company, Form No. CP07N012, Rev. 2, April 2008.
14. NANOPURE\textsuperscript{™} EG1101 Slurry Material Safety Data Sheet, Rohm and Haas Company, July 15, 2010, pages 1, 3 and 4.

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