Methylene Chloride Use in the Production of Ion Exchange Resins

Comments to the Office of Management and Budget

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DuPont Water Solutions

Executive summary

- DuPont Water Solutions is attentive to the world's need for water and is dedicated to innovate and support the application of water separation technologies that enable water to be accessible, adaptive and affordable.
- Ion Exchange Resins play a key role to water management for important growth segments in the United States including but not limited to Microelectronics, Nuclear Power, and Green Hydrogen.
- The use of methylene chloride to produce USA made cation exchange resins is completed in a closed-loop industrial setting and is minimized by using extensive process recycle. This serves to reduce the frequency of off-loading methylene chloride from trucks to storage tanks which is identified is the highest potential for human exposure in the current process.
- The current process operates within the existing regulatory requirements and is amenable to guided improvements under a workplace chemical protection plan (WCPP). **DuPont Recommends: the use of methylene chloride as a process aid in the manufacture of ion exchange resins to be allowed under WCPP and a de minimis value be permitted using a value consistent with the current hazard communication guidelines.**
- Alternatives to the use of methylene chloride are not readily available and will take years to develop. Implementation will require cooperation and ability to accept the new resins by downstream users in sensitive use applications such as ultra pure water generation and nuclear power water management.

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Water is at the heart of the world's most critical needs.

Solving global water challenges helps to unlock the rest of the United Nations' 2030 Sustainable Development Goals.

DuPont Water Solutions Technology Portfolio

The broadest in the industry

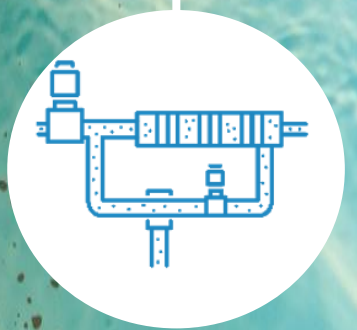
MemPulse™
MBR

Multibore™
Ultrafiltration

DesaliTec™
CCRO

Electrodeionization

Wastewater



Ultrapure Water

OxyMem
MABR

IntegraTec™
Ultrafiltration

FilmTec™
Reverse Osmosis
Nanofiltration

Amber Series
Ion Exchange Resins

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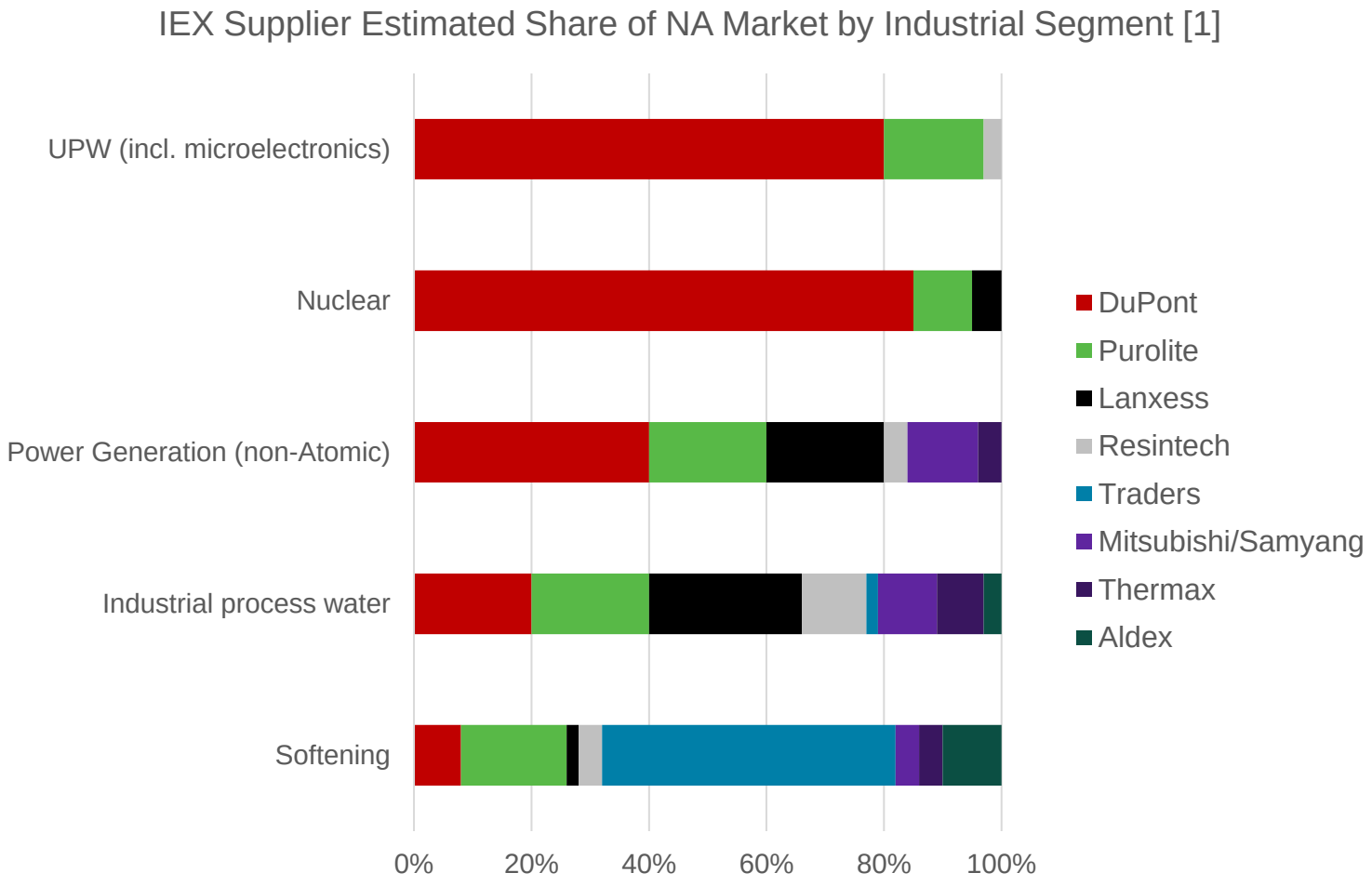
Water Solutions

North America Industrial Ion Exchange Market Segment



- DuPont Ion Exchange Resins are important to North America's Ultra-Pure Water (UPW), Nuclear Power, and General Power applications.
- DuPont is the only Tier 1 supplier (DuPont, Purolite, Lanxess) located in the USA.

[1] BlueTech Insight Report, Ion Exchange Resin Market and Technology Overview, 2018

Micro Electronics – Ultra-pure water

- 20 Fabs operating in the United States with 6 new Fabs announced thanks to the CHIPs Act.[1]
- 2019 annual water withdrawal for US Fabs was 3.12 billion gallons.[2]
- 76% of the water used in a Fab is for process water with stringent ultra-pure water requirements.[3]
- To produce ultra-pure water the water passes by an ion exchange resin 3 times.

[1]SIA (Semiconductor Industry Association): Mar 20, 2024 update (https://www.semiconductors.org)
[2]https://www.semiconductor-digest.com/water-supply-challenges-for-the-semiconductor-industry

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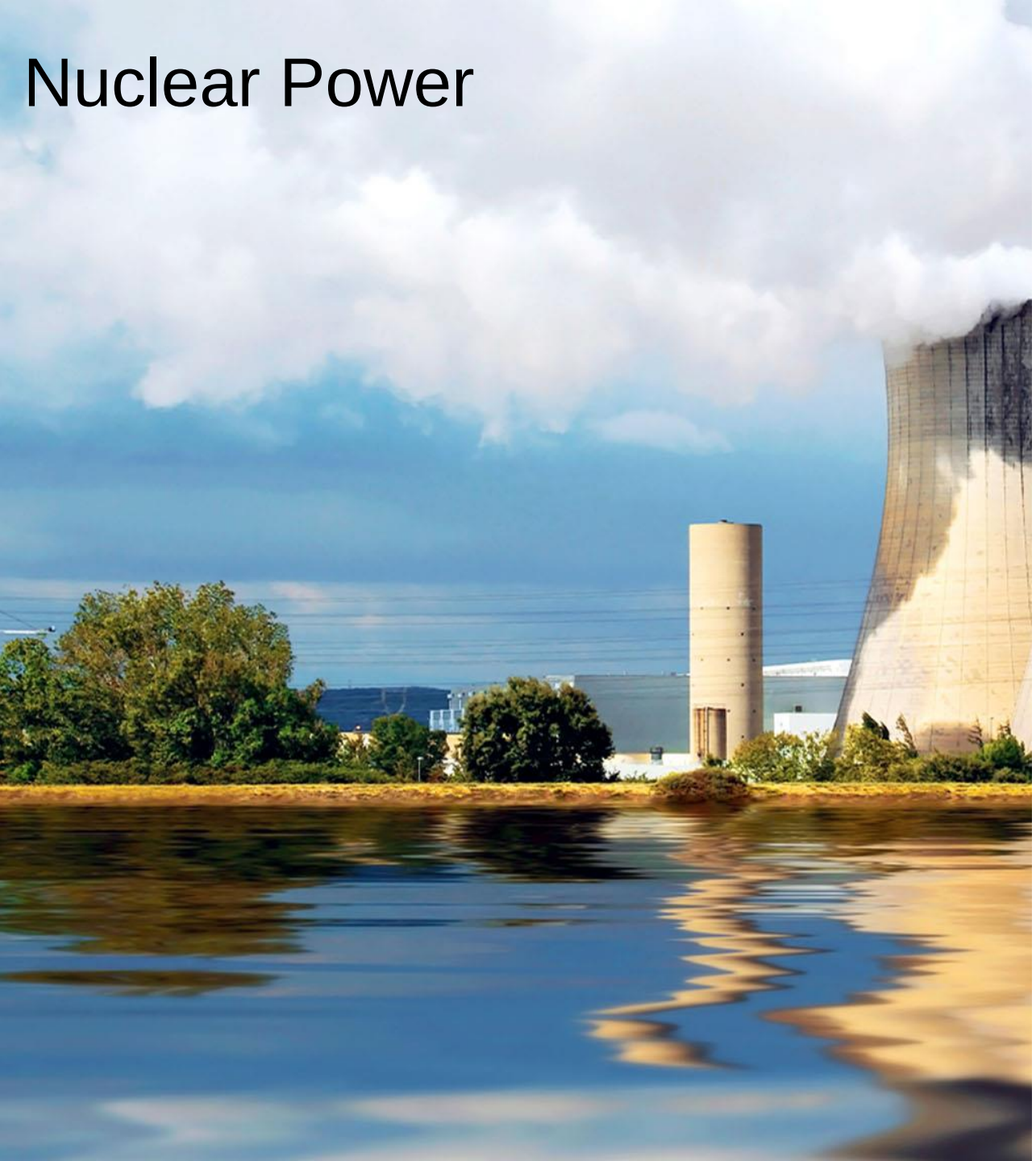
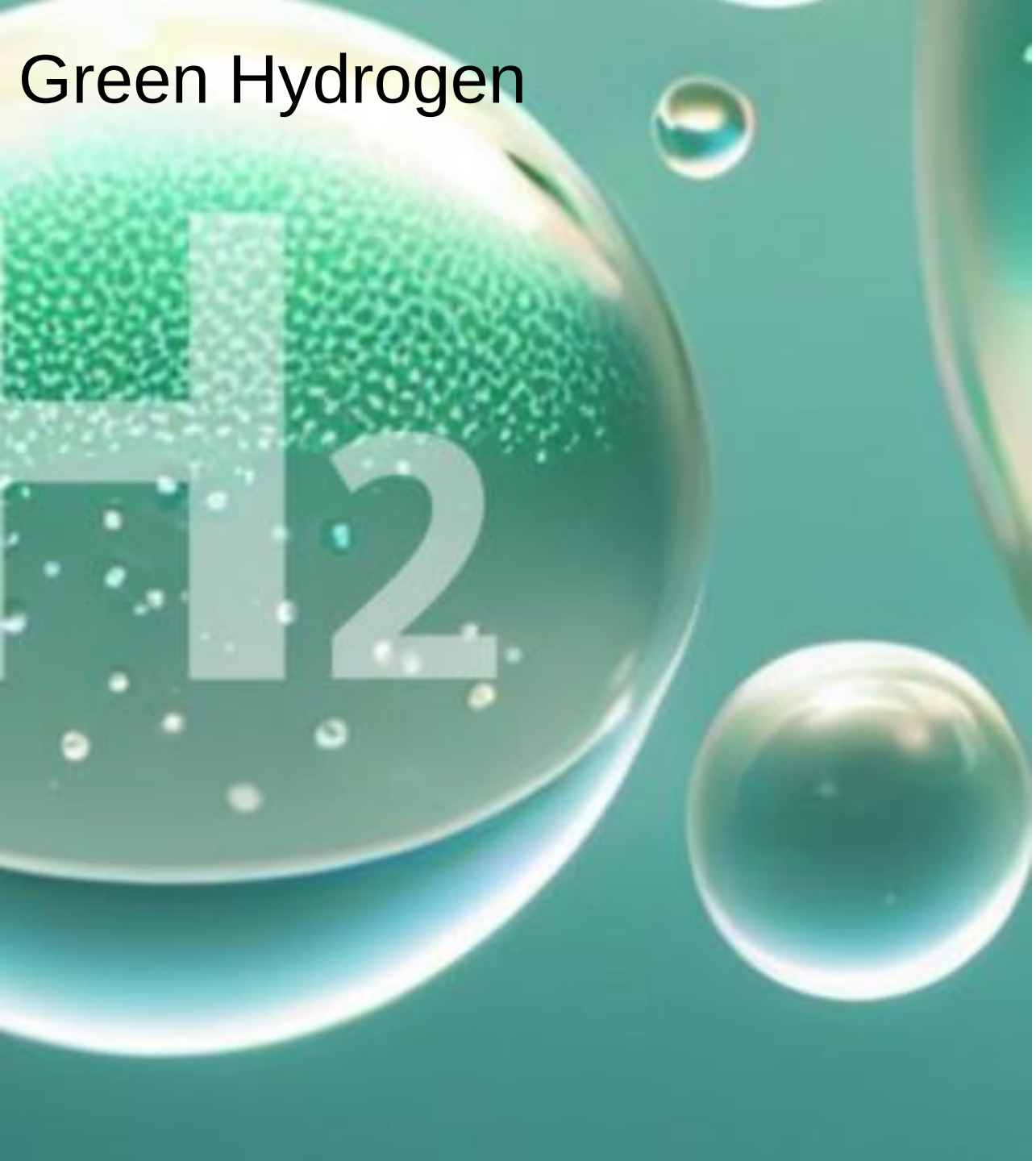
Nuclear Power



- 54 Nuclear Power Plants with 93 active nuclear reactors in the United States.[1]
- Summer electricity generating capacity in 2022 was 94,765 MW in the US.[1]
- Ion Exchange Resins are used in water management throughout the plant including[2]:
  - Cooling tower water,
  - Reactor coolant water,
  - Pressurized water reactor secondary side steam/water circuit,
  - Stator cooling,
  - Spent fuel pool purification,
  - Radioactive wastewater management
- Any water management process change requires extensive qualification due to the regrettable impact of a reactor shutdown in the event of a failure.

1 https://www.eia.gov/energyexplained/nuclear/us-nuclear-industry.php
2 https://www.dupont.com/content/dam/dupont/amer/us/en/water-solutions/public/documents/en/DWS-Nuclear-Power-Plant-Interactive-Map-Br-45-D00724-en.pdf

Green Hydrogen



- In 2022, North America is reported to have 33 Green Hydrogen plants operating and producing 691,000 tons of hydrogen annually.[1]
- By 2027 this capacity is expected to increase 3X to support the decarbonization strategy.[1]
- Based on stoichiometry, in 2027 at least 18 million tons (4.2 billion gallons) of water will be needed to produce this H_2
- High purity demineralized water is needed for the electrolysis.
- Ion exchange resins are used to polish water to the quality required.

[1] https://www.airswift.com/blog/green-hydrogen-projects-usa#:~:text=There%20were%2033%20operational%20Green,tons%20per%20annum%20(MTPA).

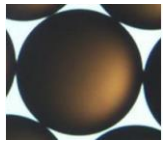
Resin Sulfonation with Methylene Chloride (MDC)

Strong Acid Cation Ion Exchange Resins

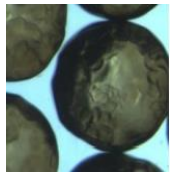
Suspension of monomer droplets | **Polymerization: network of polymer chains** | **Functional groups added to beads**

H. Roth, Industrial & Engineering Chem., **1957***, 49(11), 1820-1822; J. of Polymer Sci.: Part A,* **1965,** 3, 1063-1067*; J. Braz. Chem. Soc.,* **2003**, 14(5), *Macromolecules* **2010**, *43*, 10498-10504; *Macromolecules*, **2006***, 39*, 2373-2379; ECHA public AoA for EDC use in IEX resin production

Current process



Alternative Challenges

a) 

b) 

Critical Process Aid Properties:

- Recyclability
- Swelling efficiency
- Chemical/thermal stability
- Separation from water and H_2SO_4
- Low residuals in final product
- Sulfonation extent, quality
- Environmental regulations

Sulfonation of polystyrene w/ Methylene Chloride

- Sulfonation process is completed in a **closed loop system** with no physical contact with MDC
- **>95%** of MDC loaded in the reactor is **recovered.**
  - Vented to a thermal oxidizing unit with 99.9% efficiency
  - Rest sent through a recovery loop to capture MDS and other raw materials for reuse
- Compliant with OSHA 29 CFR 1910.1952

Alternatives

	1,2,4-trifluorobenzene	Solvent-less Sulfonation
Is the potential alternative technically feasible?	No – residue of fluorine were found in the final product	No – technology exists for limited resin types but may not be suitable for all applications
Is the potential alternative economically feasible	No – residual fluorine removal will increase costs	No – yields are lower and cycle times longer resulting in higher costs
Is the potential alternative (and associated technology/process to implement it) available?	No – process development would be needed	No – more than 15 yrs would be needed to develop and qualify sensitive applications
Does the potential alternative result in a reduction of risk?	No – halogenated solvent management required	Yes – no solvent management required

- Over 600 solvents were screened using literature review, computational evaluation and/or laboratory testing
- No clear alternative is available for immediate replacement
- Significant time is needed to develop, implement and qualify alternatives. Close cooperation of the end user is required.

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Summary

Methylene chloride is a process aid in the industrial manufacture of **Cation - Ion Exchange Resins** made in the USA which are needed to generate pure water for microelectronic, nuclear power, and green hydrogen production as well as many other water applications.

Methylene chloride is used in a controlled manufacturing environment where exposure potential is limited using closed loop engineering and high degree of recycle to reduce the need for material transfer.

Alternatives are not available; therefore, it is recommended that **continued use of methylene chloride as a process aid in the production of ion exchange resins be allowed under a workplace chemical protection plan (WCPP) and a de minimis value be permitted using a value consistent with the current hazard communication guidelines.**

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