

ZMWG Comments to the Minamata Secretariat on Mercury-free Alternative Processes to VCM

31 March 2025

The Zero Mercury Working Group appreciates the opportunity to provide information on technically and economically feasible alternatives to the use of mercury and mercury compounds in vinyl chloride monomer (VCM) production, in accordance with Paragraph 8 of Article 5 and Paragraph 1 of Article 17 of the Convention.

Based on the latest research, it's clear that the mercury-free alternative processes are available, affordable and effective. There are mercury-free catalysts that perform better than mercury-based ones and are commercially available, as already reported at the last COP in 2023.¹

The production of vinyl chloride monomer (VCM) is a manufacturing process that uses a catalyst containing high concentrations of mercury. However, a significant proportion of the mercury on the catalyst can be lost via evaporation, either during VCM production or during reprocessing of the used catalyst. VCM is the building block of polyvinyl chloride, or PVC, which is a type of plastic that is used for everything from water and sewer pipes to plastic toys and clothing.



As a result, there is a significant demand for plastic, with over 40 million tonnes of PVC produced annually. The majority of VCM (around 90%) is used in PVC manufacture.²

Most manufacturing of PVC around the world uses natural gas or petroleum as the "feedstock" or raw material from which the plastic is manufactured. However, there are a few countries that continue to produce vinyl chloride monomer using an older process that starts with coal as the feedstock. This is due to the relative abundance of coal as a resource. About 95% of these plants are in China. The Chinese PVC industry is effectively the world's largest consumer of mercury, responsible for roughly a quarter of global consumption and an annual consumption of mercury in VCM or 670 to 790 metric tons (during 2019-2020), as per the last trade report³.

³https://minamataconvention.org/en/documents/first-effectiveness-evaluation-minamata-convention-mercury-draft-report-mercurytrade

¹ <u>https://minamataconvention.org/sites/default/files/inline-files/Ready%201031B-NRDC.pdf</u>

² https://www.sciencedirect.com/science/article/abs/pii/S1872206716624828

In the coal-based process (technically, the hydrochlorination of acetylene process), mercury chloride is the catalyst that sparks the main chemical reaction. Some of the mercury used in this process is lost and must be continually replenished. Even after years of research, it is poorly understood exactly how some of this mercury is lost and where the lost mercury ends up. For example, a mass balance study in a Chinese PVC plant "...found that the total input and out mass of Hg is not balanced."⁴ As a result, it appears there is approximately 30% of mercury that is lost in the process with unknown destination.⁵ Furthermore, during the recycling of the mercury chloride catalyst, even more mercury is lost.

As the PVC industry represents one of the most significant uses of mercury in the world today, these mercury losses add unnecessarily to the deterioration of human health and the environment, also due to the potential for occupational exposure to mercury and mercury vapors. Given mercury's well-known toxicity, ability to travel long distances and its possibility to bioaccumulate and biomagnify, the potential risk of exposure can be substantial.

Based on research carried out over the last ten years, the following references explain why the VCM industry can now bring itself in line with the objectives of the Convention:

GEF 6921 - Demonstration of Mercury Reduction and Minimization in the Production of Vinyl Chloride Monomer in China , Project Implementation Report (1 July 2023- 30 June 2024),

https://www.thegef.org/projects-operations/projects/6921

The project has already achieved 359.5 tons of mercury reduction which was verified by the mid-term review in 2021. In 2020, China reduced the mercury by 50% compared to 2010 through the technology demonstration, BAT/BEP replication, and capacity building activities. FECO and the Government of China commit to further strengthening efforts in mercury reduction.

The evaluation of mercury-free technologies is progressing well. Preliminary results from participating companies are now available, following a successful phase of laboratory, pilot, and industrial tests. This data provides a strong foundation for the final results and the 10,000 ton-demonstration planned for 2025.

Progress in mercury-free catalysts for acetylene hydrochlorination

https://pubs.rsc.org/en/content/articlelanding/2024/cy/d4cy00549j

This 2024 review systematically summarizes the recent achievements in mercury-free catalysts including noble/non-noble metal-based catalysts and metal-free catalysts in acetylene hydrochlorination with the focus on catalyst design, catalytic performance and the reaction mechanism. Moreover, the advantages and drawbacks of diverse mercury-free catalysts are comprehensively discussed. Eventually, the current challenges and opportunities for the exploration and application of mercury-free catalysts in industrial VCM production are presented.

Vinyl Chloride Monomer Production From Acetylene

https://matthey.com/products-and-markets/chemicals/process-licensing/vinyl-chloride-monomer-production

The Johnson Mattey high yield, long-lasting vinyl chloride monomer production process with JM's PRICAT™ mercury-free catalyst (MFC) is presented. PRICAT MFC is a highly selective gold catalyst that is three times more productive than mercury-based alternatives and achieves high acetylene-to-VCM conversion for significantly longer. The catalyst's long life means high uptime and fewer changeovers to keep OPEX low, while the elimination of mercury from the process enables safer maintenance. 95% of the gold in PRICAT MFC can also be recovered and reused in fresh catalysts. This helps keep gold use low and improves the environmental impact of the overall VCM technology.

⁴ Ren, W.; Duan, L.; Zhu, Z.; Du, W.; An, Z.; Xu, L.; Zhang, C.; Zhuo, Y.; Chen, C., Mercury

Transformation and Distribution Across a Polyvinyl Chloride (PVC) Production Line in China.

Environmental Science & Technology 2014, 48, (4), 2321-2327.

⁵ <u>https://minamataconvention.org/sites/default/files/documents/submission_from_government/compilation_10_processes.pdf</u>

Transform Materials and Johnson Matthey Collaborate

<u>https://www.prnewswire.com/news-releases/transform-materials-and-johnson-matthey-collaborate-to-enable-lower-carbon-and-mercury-free-alternative-routes-for-pvc-manufacturing-302170248.html</u>

In June 2024, <u>**Transform Materials**</u>, a leader in the development of clean and sustainable chemical technologies, has joined forces with <u>Johnson Matthey</u>, a global leader in sustainable technologies. Scientists and engineers at both companies are applying their combined expertise with the aim of revolutionizing VCM production through a novel, lower-carbon-emission, mercury-free process.

[November 2023] VCM without Hg - Johnson-Matthey

https://minamataconvention.org/sites/default/files/inline-files/Ready%201031B-NRDC.pdf

[November 2022] Environmentally friendly high-efficient metal-free catalyst

https://www.sciencedirect.com/science/article/abs/pii/S2468823122006058

Mercuric-free catalysts, especially metal-free catalysts, are quite intriguing in the industrial production of acetylene hydrochlorination. In this work, nitrogen-doped biochar is prepared as green metal-free catalyst for acetylene hydrochlorination with natural walnut shells as starting material, in which the condensation product of dicyandiamide or dicyandiamide-formaldehyde is applied as nitrogen source.

Progress and Challenges of Mercury-Free Catalysis for Acetylene Hydrochlorination

https://www.semanticscholar.org/paper/Progress-and-Challenges-of-Mercury-Free-Catalysis-Liu-Zhao/14531f86198c9044b05cea073eb11b78c0eb398f

This 2020 review summarizes research progress on the design and development of mercury-free catalysts for acetylene hydrochlorination. Three types of catalysts for acetylene hydrochlorination in the chlor-alkali chemical industry are discussed. These catalysts are a noble metal catalyst, non-noble metal catalyst, and non-metallic catalyst. This review serves as a guide in terms of the catalyst design, properties, and catalytic mechanism of mercury-free catalyst for the acetylene hydrochlorination of VCM. The key problems and issues are discussed, and future trends are envisioned.

[April 2022] Facile synthesis of precious-metal single-site catalysts using organic solvents https://www.nature.com/articles/s41557-020-0446-z

Single-site Au/C catalysts have previously been validated commercially to produce vinyl chloride, and here they show that this facile synthesis method can produce effective catalysts for acetylene hydrochlorination in the absence of the highly oxidizing acidic solvents previously used.

[2018] High Performance Non-Mercury Catalysts for VCM Production

<u>https://proceedings.aiche.org/conferences/aiche-annual-meeting/2018/proceeding/paper/31f-high-performance-non-mercury-catalysts-vcm-production-theoretical-study-industrialization</u>

Gold is widely considered as the most active metal for acetylene hydrochlorination reaction and copper is the most common metal with cost-effective advantage. The combination of two metals shows the best potential as the active component for environmentally friendly non-mercury catalysts. In this study, the performance of Au/Cu catalyst was enhanced dramatically by the introduction of organic ion ligands. Several ligands including trichloroisocyanuric acid (TCCA), cyanuric acid (CA) and melamine (M) were studied and TCCA was proved to be the best ligand for preventing Au³⁺ from reduction by acetylene, leading to longer catalyst lifetime. The findings were successfully verified by over 18000 hours industrial plant-trial evaluation, and the VCM productivity reached about 4.2 times comparing to industrial mercury catalyst.

The Convention enabled Parties to continue to produce PVC, but required the use of a mercury free process as soon as possible. In summary and as per above, mercury-free alternatives are readily available. Therefore, the COP has sufficient evidence to establish that mercury-free catalysts based on existing processes have become technically and economically feasible, requesting the phase out of this process in the next five years.