A Novel Purifier for Acid-Sensitive Applications:

Suppressing Dimerization and Metal Impurities in Solvent System

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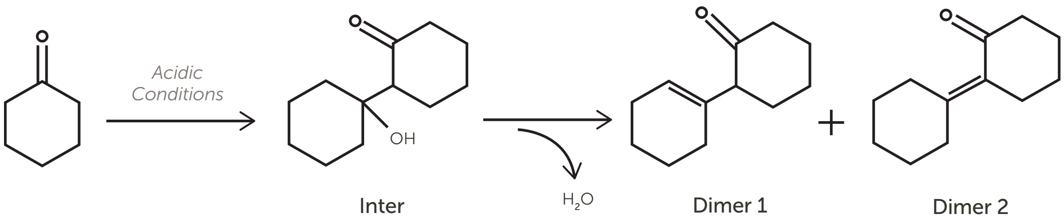
BACKGROUND

Cyclohexanone (CHN) is commonly used in semiconductor manufacturing, particularly in photoresist formulations and cleaning processes. In advanced process nodes, metal contamination originating from CHN can directly contribute to increase on-wafer defectivity, impacting yield and reliability. In addition, CHN is prone to self-aldol condensation under acidic conditions. An intermediate, 1-hydroxy-[1,1-bicyclohexyl]-2-one, is first formed, but in the presence of strong Brønsted acid sites, it is rapidly dehydrated to yield the isomeric mixture, including 2-(1-cyclohexen-1-yl)-cyclohexanone and 2-cyclohexylidene-cyclohexanone. These dimers have been associated with surface contamination and film irregularities in semiconductor manufacturing process. Therefore, a purification solution is needed that can effectively reduce both metal and dimer levels to ensure process integrity and minimize defect formation.

INTRODUCTION

EUV lithography continues to push device scaling, exposing limitations in resist performance and process integration. A key challenge arises from the inherent trade-off among resolution, line-width roughness (LWR), and sensitivity, which becomes more severe as feature sizes shrink. The need for thinner resist films to avoid pattern collapse reduces pattern transfer margin and increases susceptibility to edge placement errors. In addition, substrate interactions and thin-film confinement effects can distort resist profiles, leading to bending, footing, or undercutting during development. These phenomena are further intensified by the high absorption and photon energy of EUV radiation, as well as the intrinsic constraints of chemically amplified resists (CARs). While EUV processes do not require anti-reflective coatings, the integration of optimized underlayer (UL) materials has become essential for improving pattern verticality, suppressing resist deformation, and maintaining sensitivity. However, UL processing introduces its own complexity: even sub-micron particles introduced upstream can generate printing defects, making filtration performance a critical and often overlooked component of process stability. This creates a growing need for filtration media that combine exceptional cleanliness with microstructural efficiency tailored for EUV UL applications.



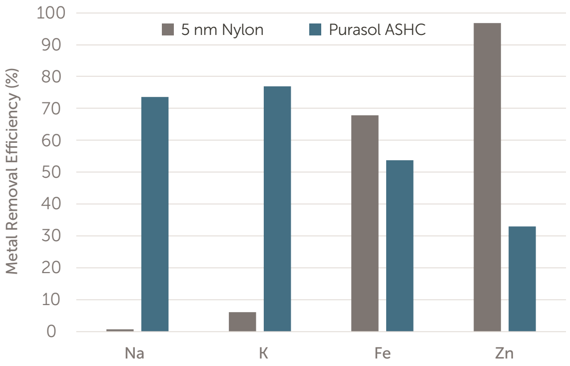
Acid-catalyzed dimerization mechanism of cyclohexanone.

METAL CONTAMINATION CONTROL

Metal Removal Efficiency

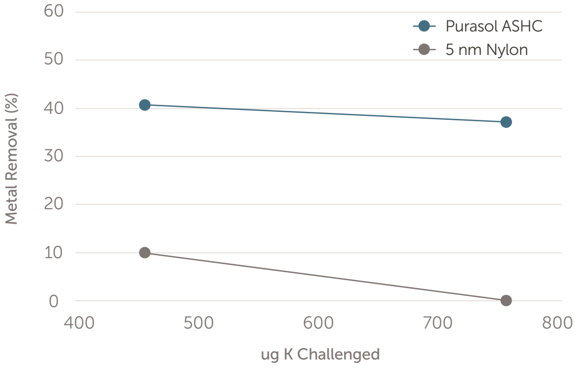
A metal challenge solution was prepared by spiking cyclohexanone with 2 ppb of a metal analytical standard. The filtration was conducted at a constant flow rate of 10 mL/min for each experiment. Metal concentrations in the solution were quantified using ICP-MS. For each test, 47 mm coupons of Entegris 5 nm-rated Nylon membrane and Purasol® AS-HC, were used.

The results show that Purasol AS-HC delivers superior removal efficiency for alkali metals such as Na and K, while Nylon demonstrates higher efficiency for Fe and Zn.



Metal Removal Efficiency (CHN) 200 mL Throughput
Feed: 2 ppb each metal

Metal removal efficiency for common contaminants in CHN at 200 mL throughput with 2 ppb initial concentration of each metal.



Metal Removal Capacity in CHN
Feed: 500 ppb K

Comparison of capacity performance between Entegris 5 nm Nylon and Purasol AS-HC under 500 ppb K feed in CHN.

Metal Removal Capacity

A metal challenge solution was prepared by spiking cyclohexanone with 500 ppb of potassium. The total amount of potassium introduced for each filtration test was calculated based on the solution volume and reported as µg K. Each test utilized a 47 mm coupon of Entegris 5 nm rated Nylon membrane and Purasol® AS-HC.

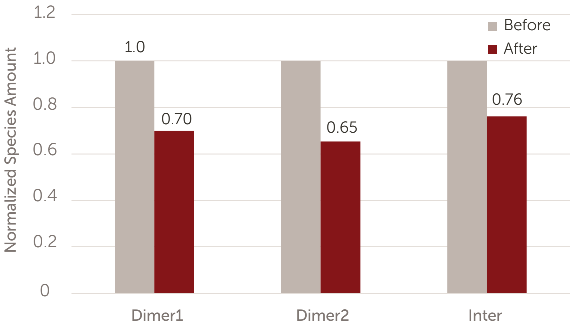
Purasol AS-HC maintains a relatively stable removal efficiency (approximately 35 – 45%) even as the potassium challenge increases up to 800 µg, highlighting its high metal removal capacity. In contrast, Entegris 5 nm rated nylon shows a downward trend in removal efficiency, suggesting a more limited capacity.

VALIDATION FOR ACID-SENSITIVE APPLICATION

Cyclohexanone Dimerization Test

A 10" Purasol AS-HC device was fully immersed in CHN and soaked at ambient temperature for 24 hours. Dimer and intermediate concentrations were analyzed pre- and post-soaking via GC-MS.

The Purasol AS-HC device was soaked in CHN, and the relative amounts of CHN dimer-related species before and after soaking were compared. No significant increase in the signals of these species was observed after soaking, indicating that residual protons in the device were insufficient to induce CHN dimerization. Interestingly, a slight decrease in these species was observed, suggesting that the purifier's functionalized surface may adsorb pre-existing dimers from CHN.



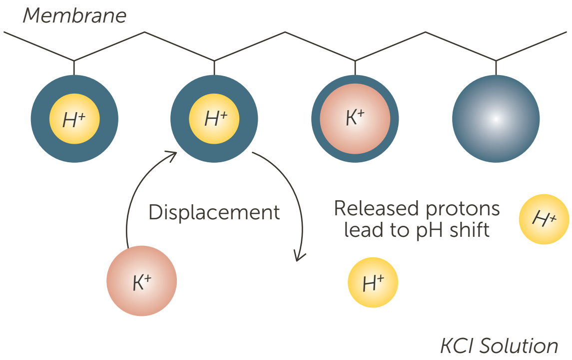
Cyclohexanone Dimerization Test
Relative species amounts before and after soaking

Relative amounts of the CHN dimers and the intermediate before and after soaking Purasol AS-HC device in CHN.

Proton Residue Assessment

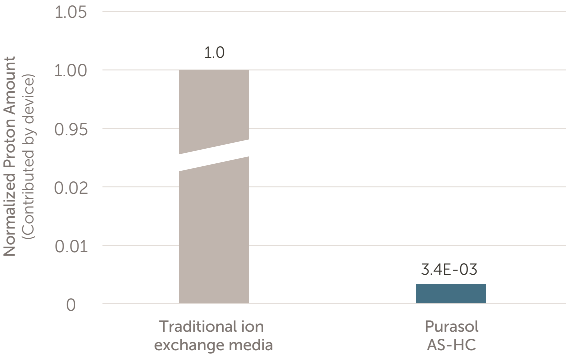
The proton residue of Purasol AS-HC was compared to a traditional ion-exchange filter. 10" cartridges were soaked in a 1 M aqueous KCl solution for 24 hours. During soaking in a KCl solution, potassium ions displace residual protons from the functionalized membrane surface into the solution, and the displaced proton concentration [H+] was calculated from the change in the solution's pH.

It is known that traditional ion-exchange filters are not fully compatible with CHN, primarily due to the strong acidic functional groups. The results revealed that Purasol AS-HC contained nearly 300 times fewer protons than a traditional ion-exchange filter. This finding provides definitive validation for the dimerization test results, confirming that the residual protons in Purasol AS-HC are insufficient to induce dimerization of CHN.



Schematic illustration of the proton displacement mechanism underlying the proton residue assessment.

Proton Residue Assessment
1M KCl Solution, 24h, Ambient Temperature



Normalized proton amounts for traditional ion-exchange filter and Purasol AS-HC after 24-hour immersion in 1 M KCl solution at ambient temperature.

DISCUSSION

Modern photoresist systems include highly acid-sensitive components – PAGs, non-imide quenchers, and photo-decomposable quenchers. Excess protons in such applications can protonate quencher functionalities, hydrolyze acid-labile protecting groups, and disrupt the delicate acid-base equilibrium essential for precise lithographic performance. These effects may lead to uncontrolled deprotection and ultimately compromise imaging accuracy during the lithography process. Given the low residual proton level demonstrated by Purasol AS-HC, this purifier effectively minimizes the risk of proton-induced side reactions, making it highly compatible with the acid-sensitive components mentioned above. Furthermore, its high metal removal capacity ensures suitability for raw materials with elevated metal impurity levels, where stringent ionic control is critical for advanced photoresist formulations across leading-edge lithographic processes.

CONCLUSION

The newly developed Purasol AS-HC purifier effectively addresses two major challenges in acid-sensitive solvent systems: metal contamination and acid-catalyzed dimerization. Experimental evaluation demonstrated its superior metal removal efficiency and capacity, particularly for alkali metals, while maintaining exceptionally low proton residue. This significant reduction in residual protons minimizes the risk of dimer formation in cyclohexanone. These combined attributes position Purasol AS-HC as a robust and scalable solution for acid-sensitive applications, including Cyclohexanone and raw materials in photoresist formulations, where stringent control of both metal impurities and proton contamination is essential to ensure lithographic accuracy and yield across leading-edge semiconductor processes.

This paper was first presented at the 2026 SPIE Advanced Lithography + Patterning conference.

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