# Targeted Removal of Metallic Contamination from Lithography Solvents Using Membrane Purifiers

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## INTRODUCTION

Metal ions in photoresists and solvents pose an ever greater contamination problem in photolithography's advanced applications. The reduction of metal contaminants is critical in the entire photochemical supply chain. In this paper we demonstrate two novel membrane purifiers Purasol™ SP and SN that dramatically reduce the metal contents in a range of organic solvents. These solvents are used for photoresist manufacturing and for wafer surface and dispense line rinse in track tools. The chemical compatibility of new purifier media with lithography solvents was experimentally proven Furthermore, a study to determine the dominant mechanism of metal reduction in solvents is proposed.

## EXPERIMENTAL

### Metal Removal Efficiency in Various Lithography Solvents

The 47 mm diameter discs of the purifier membrane were used to evaluate the metal removal efficiency in a small scale environment. The testing membrane discs were installed in a clean PFA (Perfluoroalkoxy) membrane holder. The solvents were pumped from a PFA reservoir into the membrane holder. The test solvents were prepared by spiking Conostan® Oil Analysis Standard S-21 (SCP Science) into solvents at a target concentration of 5 ppb of each metal (19 metals total). The feed and the filtrate samples were then analyzed by an Agilent Model 8800 ICP-MS (Inductively Coupled Plasma-Mass Spectroscopy) to determine the membrane's ability to remove metal ion from the solvents.

### Metal Removal Capacity Testing

OK73 thinner was strongly spiked to demonstrate the metal removal capacity of a 47 mm diameter disk of the Purasol SP purifier as compared to a 10 nm rated nylon membrane. Iron (Fe) was added at a 110 ppb level. Samples of filtrate were collected as a function of time and analyzed for Fe by ICP-MS.

### Metal Removal Mechanism Investigation

Purasol membranes were loaded with a traceable surrogate ion, equilibrated in metal free challenge solvent (100% DIW or 99% hexane/1% IPA), recirculated in solution containing 100 ppb of Na and Fe, re-equilibrated in metal free challenge solvent and IPA, and eluted with diluted Nitric acid. The level of challenge in this testing was much higher than expected in lithography solvents and was designed to induce detectable competition and displacement of ions when possible. The experiment was also conducted using a system known to operate by ion-exchange where the non-polar solvent mixture was replaced with 100% deionized water spiked with Na and Fe. The metal removal efficiency for each membrane during recirculation was calculated along with the recovery of the surrogate ion in dilute Nitric acid.

### Compatibility of Purasol Purifiers with Various Lithography Solvents

The compatibility of Purasol SN and SP purifiers with lithography solvents was examined by soaking the membrane samples into OK73 thinner, GBL, and CHN respectively over a four-week period. The membrane samples were then tested for performance at certain soaking time period to determine if the membrane surface modification chemically degraded as a function of exposure time in solvents.

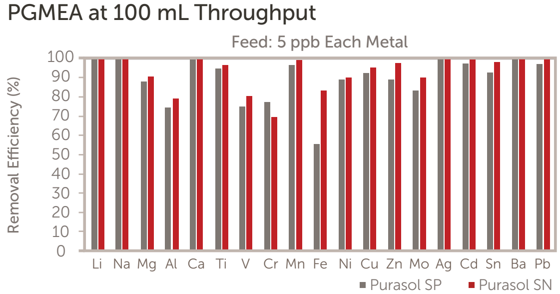
## RESULTS AND DISCUSSIONS

### Metal Removal Efficiency in Various Lithography Solvents

Figures 1 and 2 demonstrate the metal removal efficiency testing results for Purasol purifiers in PGMEA and OK73 thinner respectively. Both SP and SN purifiers demonstrated a high removal efficiency of >90% for total metal ion contamination in PGMEA. SN showed slightly higher removal efficiency than SP. In contrast, Purasol SP was significantly more effective in removing metals than SN in OK thinner. Also, SP and SN demonstrated complimentary metal removal behavior in OK73. SP showed higher selectivity towards lightweight metals than SN while SN is more effective to remove some heavyweight metals such as Silver (Ag) and Cadmium (Cd). A combination of SP and SN purifiers demonstrated the enhanced total metal removal efficiency in OK73.

The results of metal removal efficiency testing of Purasol purifiers in various solvents are summarized in Table 1. The results indicate that two different types of Purasol purification media have different affinity to various metals and are highly effective to remove metallic contamination in a range of lithography solvents.

Metal Removal Efficiency of Purifiers in PGMEA at 100 mL Throughput




Total Metal Removal of Purifiers in PGMEA

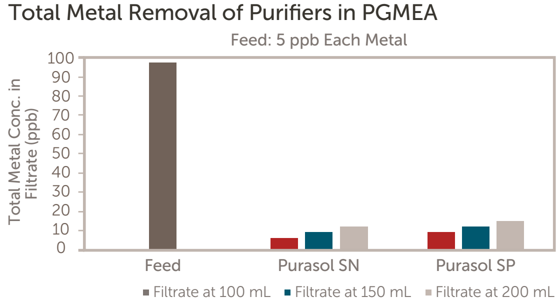
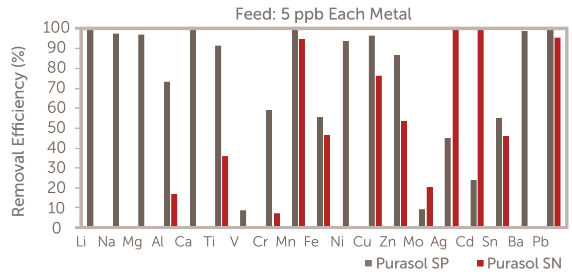



*Figure 1. Multi-metal removal efficiency of Purasol SP and SN in PGMEA solvent.*

Metal Removal Efficiency of Purifiers in OK73 at 100 mL Throughput




Total Metal Removal of Purifiers in OK73

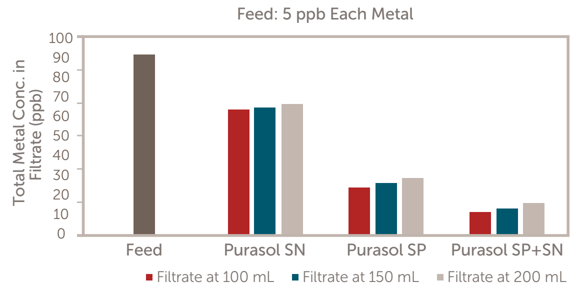



*Figure 2. Multi-metal removal efficiency of Purasol SP and SN in OK73 thinner.*

### Table 1. Comparison of metal removal efficiency of Purasol purifiers in various solvents

| | **TOTAL METAL REMOVAL EFFICIENCY** | | |
|---|---|---|---|
| **Solvent** | **SP** | **SN** | **Remark** |
| PGMEA | 90% | 94% | |
| Cyclohexanone | 79% | 95% | |
| PGME | 66% | 36% | Complimentary removal |
| OK73 | 74% | 31% | Complimentary removal |
| GBL | 12% | 96% | |
| ArF thinner (PGMEA 45-55%, HBM 35-45%, EL 5-15%) | 86% | 44% | Complimentary removal |

## Metal Removal Capacity Testing Results

The level of challenge in this testing was much higher than expected in lithography solvents but was performed to demonstrate capacity of the purifier membrane and the gradual breakthrough of contaminants after capacity has been reached. The active adsorption sites on the membrane eventually become occupied and the reduced Fe removal efficiency was observed at the breakthrough. The profiles of Purasol SP and 10 nm Nylon membranes for 110 ppb Fe challenge in OK73 are shown in Figure 3. The results indicate a 200 microgram capacity for Fe removal for the Purasol SP membrane area in the membrane holder, which is significantly higher than that of a 10 nm Nylon membrane with the same area.

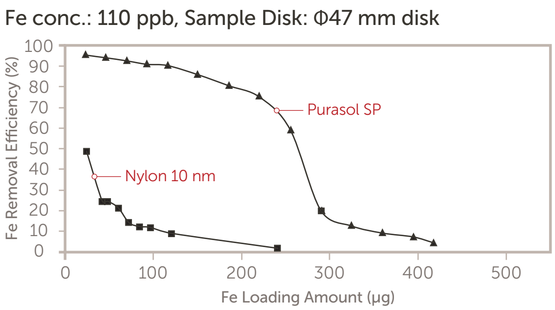



*Figure 3. Profiles of Purasol SP and 10 nm Nylon membranes for 110 ppb Fe Challenge in OK73.*

## Metal Removal Mechanism Investigation

Figure 4 shows the removal of Na and Fe achieved during recirculation in an aqueous system and in an organic solvent system.

After the membranes were challenged with a high level of Na and Fe they were equilibrated and eluted with dilute Nitric acid. The amount of the surrogate ion that remained on the membrane was compared to the native capacity of the membrane for the surrogate ion. The results are expressed in percentage of surrogate ion recovered relative to native capacity and are depicted in Figure 5. In the cases where Na and Fe were loaded in an aqueous system, results show only 20.2 to 18.2% recovery of the surrogate ion, which suggests that the dominate mechanism involves the exchange of ions. Alternatively, in the cases where the metals were loaded via organic solvent, the majority of the surrogate ion was recovered, thus indicating that ion-exchange is not the dominate mechanism.

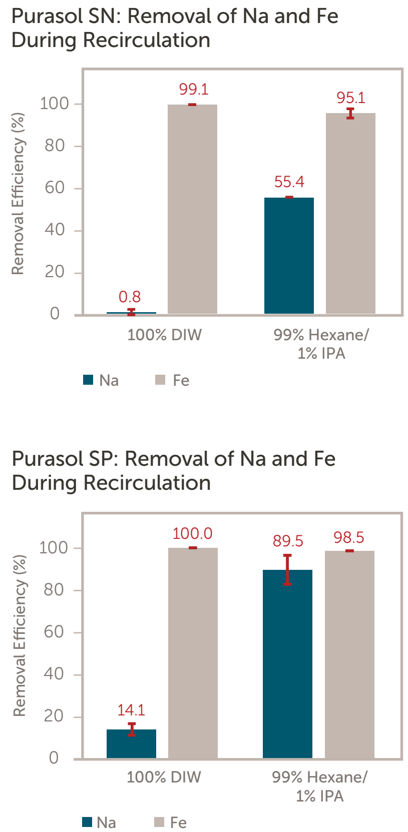



*Figure 4. Metal removal efficiency of Purasol SN and SP with high metal loading in DI and 99% Hexane.*

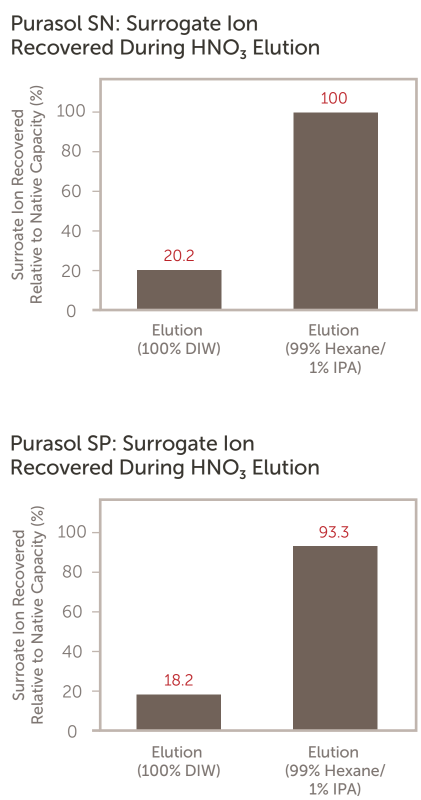
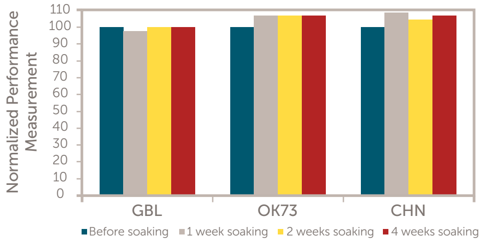



*Figure 5. Percent recovery of surrogate ion relative to native surrogate ion capacity for Purasol SN and SP with high metal loading in DIW and 99% Hexane.*

### Compatibility of Purasol Purifiers with Various Lithography Solvents

Purasol SP and SN membrane samples were removed from the solvents after 1 week, 2 weeks, and 4 weeks soaking and were measured for the performance of membranes. The results of this experiment are shown in Figure 6. There was no measurable change on the membrane performance of both Purasol SP and SN membranes after 4 weeks of soaking in various lithography solvents. The results experimentally proved that Purasol media is chemically stable with common lithography solvents.

Compatibility Test of Purasol SP Membrane with Solvents




Compatibility Test of Purasol SN Membrane with Solvents

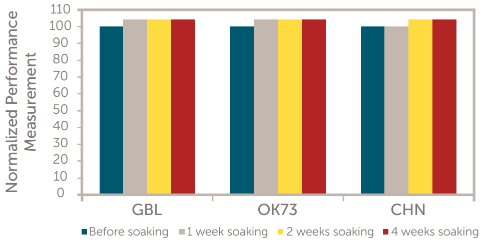



*Figure 6. Effect of solvent exposure on the performance of Purasol SP and SN purifier membranes.*

## CONCLUSION

The specially developed membrane based Purasol purifiers remove metallic contamination with high efficiency and capacity from a broad range of lithography solvents. Two types of Purasol purifiers demonstrated complimentary metal removal behavior in some solvents, suggesting that a combination of two types of purifiers would provide enhanced total metal removal efficiency in these solvents. The chemical compatibility of Purasol media with lithography solvents was experimentally proven. Experiments designed to elucidate the mechanism of metal ion removal demonstrated that exchange of ions is not the dominate mechanism of Purasol when used in a model organic solvent.

*This paper was originally presented at a 2018 SPIE Advanced Lithography poster session.*

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