Iron (Fe) removal from cyclohexanone thinner used in lithography process using nylon 6,6 membrane filtration. – Toru Umeda

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Introduction The requirement for metal cleanliness within lithography process fluids has become increasingly critical.[1)] Within photoresist coating processes, organic solvents are used in applications such as edge bead removal (EBR), backside rinse (BSR), and reduce resist consumption (RRC). The RRC process is especially critical, as it introduces process fluid to the wafer surface prior to the introduction of resist or other ancillary layers. Cyclohexanone was found to be one of the most suitable organic solvents for RRC,[2)] and is commonly used in commercial lithography processes. In the present work, filtration with nylon 6,6 membrane is evaluated for the reduction of iron (Fe) ions both in commercial, electronics-grade cyclohexanone and in Fe-spiked cyclohexanone. Conclusions are drawn based on an assumed filtration mechanism.

Fe removal in cyclohexanone and mechanism investigation The removal of metal-nucleated gels from a photoresist polymer solution using nylon 6,6 membrane filtration has been reported.[3)] The present work proceeds from this, and postulates a mechanism whereby Fe removed from cyclohexanone existed as complex ions, bound to some tiny amount of ligand, such as adipic acid or caproic acid, which can be formed by exposure to ambient environmental elements like oxygen, water, and light.[4)] Figure 2 illustrates an experiment that was designed to validate the removal of complexed Fe (coordinated ion) via filtration with nylon 6,6 membrane. Initially, Fe-spiked cyclohexanone (Fig. 2a) was filtered across a nylon 6,6 membrane (Fig. 2b) using an applied upstream static pressure of 200 kPa. Then, additional Fe was added to the resulting effluent (Fig. 2c), which was then filtered across a new nylon 6,6 membrane (Fig. 2d). Total Fe concentrations in the initial spiked solution (Fig. 2a) and spiked effluent were 1.4 ppb and 1.6 ppb, respectively. Fe concentration in filtered effluents was measured using ICP-MS. Results are plotted in Figure 3. The 1st filtration step (initial solution spiked to 1.4 ppb Fe) removed Fe with 86% efficiency, and the 2nd filtration step (effluent from 1st filtration spiked to 1.6 ppb Fe) achieved 52% efficiency. Assuming removal of complexed Fe is the dominant mechanism (vs. removal of free Fe ions), results indicate that a greater amount of complex ions were present in the initial solution. Since the 1st filtration step consumes some portion of ligands that were present in the initial solution, fewer ligands were available to form complex ions when the effluent was again spiked (prior to the 2nd filtration step). Thus, removal efficiency of the 2nd filtration step is less than the 1st filtration step.

Commercial results Metal ion removal from electronics-grade cyclohexanone using the Pall Ultipleat® Asymmetric P-Nylon filter (0.15 µm rating) was measured, and results are given in Table 1. A significant reduction of metals was realized, even with variable influent concentration, and a high-purity effluent (0.1 ppb, each metal) was generated.

Conclusion Iron (Fe) contamination in cyclohexanone can be reduced using nylon 6,6 filtration, likely driven by removal of complexed Fe ions. Reduction of metal contamination from commercial, electronics-grade cyclohexanone using nylon 6,6 filtration was confirmed, and a very high purity of cyclohexanone achieved. Applying nylon 6,6 filtration for cyclohexanone, both in chemical manufacturing and device manufacturing processes at point-of-use should contribute to improved device quality and yield.

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References

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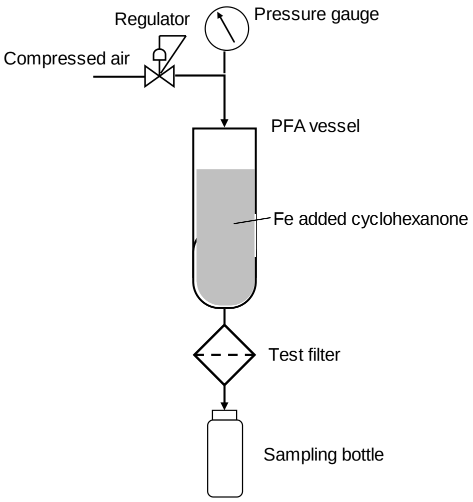

Figure 1. Filtration test setup for Fe removal efficiency evaluation.

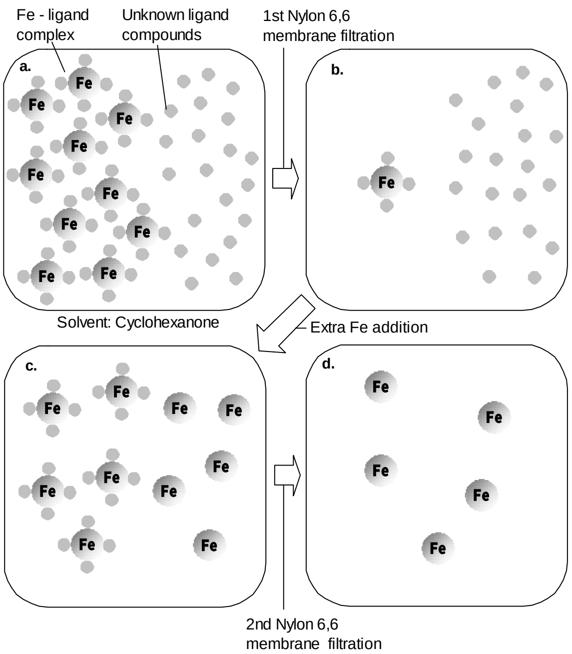

Figure 2. Schematic of experiment to investigate Fe removal mechanisms in nylon 6,6, filtration. a) Fe is added to cyclohexanone to form complex with unknown ligand compounds. b) Fe complex ions and ligands are removed by nylon 6,6 filtration, similar to the mechanism postulated in previous work.[3)] c) Fe is added to the effluent of 1st filtration step. d) Fe remains (as free ions) after a 2nd nylon 6,6 filtration step.

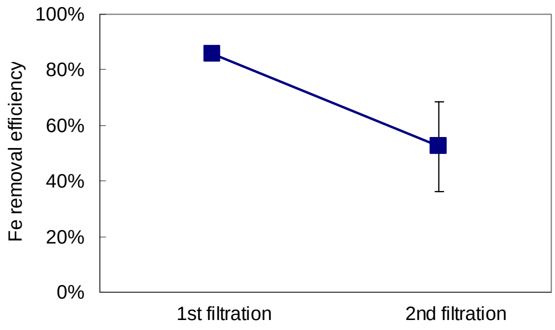

Figure 3. Fe removal efficiency via nylon 6,6 filtration. Each test run was repeated twice to observe repeatability. Data points represent mean values. Error bars indicate efficiency range (max – min).

Table 1. Metal contaminant reduction in electronics-grade cyclohexanone using nylon 6,6 filtration.

unit: ppb

	Test 1, Filter lot A		Test 2, Filter lot A	
	Influent	Effluent	Influent	Effluent
Fe	0.1	< 0.1	0.6	< 0.1
Zn	0.4	< 0.1	1.1	< 0.1
Ca	0.7	< 0.1	0.1	< 0.1
Mg	0.2	< 0.1	< 0.1	< 0.1
Cr	< 0.1	< 0.1	0.2	< 0.1
Ni	0.1	< 0.1	< 0.1	< 0.1

	Test 3, Filter lot B		Test 4, Filter lot B	
	Influent	Effluent	Influent	Effluent
Fe	0.1	< 0.1	0.6	< 0.1
Zn	0.4	< 0.1	1.2	< 0.1
Ca	0.7	< 0.1	0.2	< 0.1
Mg	0.2	< 0.1	< 0.1	< 0.1
Cr	< 0.1	< 0.1	0.1	< 0.1
Ni	< 0.1	< 0.1	< 0.1	< 0.1