



## BREAKTHROUGH CHEMICAL ANALYSIS OF HMDS REVEALS A SOLUTION FOR THE PREVENTION OF LENS HAZING

DONALDSON PROVES THAT ADVANCED LAYERING TECHNOLOGY AND BSMMAX FILTERS MOST EFFECTIVELY REMOVE TMS, NH<sub>3</sub> AND HMDSO

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### OBJECTIVE

**To identify the most effective solution for lens hazing by gaining the industry's most in-depth understanding of the HMDS to TMS/HMDSO chemistry process in ambient air.**

### CONCLUSION

**It is necessary to focus on the hydrolysis products of HMDS to ensure adequate removal of volatile siloxane compounds. We have shown that the hydrolysis of HMDS predominantly creates TMS and ammonia, and layered adsorbents can effectively remove these compounds. Activated carbon or carbon impregnated with a base for the removal of acids are very effective at removing hydrocarbons and siloxanes such as TMS or HMDSO. Furthermore, acid impregnated carbons are effective at removing ammonia and also catalyzing the dimerization of TMS to the less volatile, and easily removed HMDSO.**

In recent years as the industry has moved from 248 nm lithography tools to higher powered 193 nm tools, a new and costly problem emerged for semiconductor processors: molecular contamination on the optics (lens hazing). Because progress in one area almost always prompts new concerns in another, Donaldson has applied its more than 90 years of filtration expertise to learn more about this problem and discover the breakthrough solution. With so much at stake—costly lens replacement along with lost time and productivity—Donaldson's network of engineers delved into the problem to gain a clear understanding of the undefined chemistry issues involved with both ammonia and organics.

While previous studies<sup>1</sup> have attempted to unlock the mystery behind lens hazing, this definitive Donaldson study is the first of its kind to reveal in-depth analysis of the adsorption of HMDS, HMDSO and TMS in semiconductor facilities. Through greater understanding of the chemistry involved, Donaldson creates superior processing environments with its advanced, cost-effective filtration solution: BSMmax filters.

## FOCUSING ON HMDS

Lens hazing is caused by salt deposition and by siloxane contamination, which causes severe and sometimes irreversible damage.

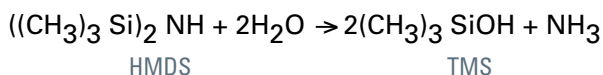
To date, the concern in lens hazing has focused on siloxane contamination from hexamethyldisilazane (HMDS). HMDS is commonly used as a wafer treatment to improve adhesion of the photoresist on to the wafer, and the presence of HMDS has been linked to lens hazing in the 193 nm lithography tools.<sup>2</sup> Once the lens has become contaminated with haze it must be cleaned or removed and replaced. This type of repair requires the adjustment of the optical axis and involves extensive downtime. The detrimental effects of siloxane contamination are not limited to lenses on lithography tools, but also reticles and masks, inspection tools, and other critical surfaces. Small amounts of siloxanes normally found in indoor air are enough to cause problems, so these and additional siloxanes must be eliminated.

## CHALLENGES OF REMOVING AMMONIA AND SILOXANES

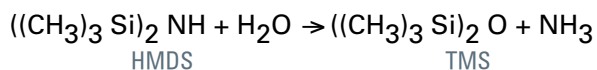
Historically, filtration in the lithography area has concentrated on ammonia removal via acid impregnated carbon or cation exchange resins. These methods, however, are not effective in removing siloxanes (organics) such as HMDS or HMDSO. Donaldson enlisted its industry leading expertise in organics removal to take a more critical look at this issue. Typically, activated carbon would be used to remove organic compounds like HMDS and HMDSO, however, ammonia is not removed without acid impregnation.

To better understand the most effective removal strategy, Donaldson worked collaboratively with out semiconductor customers who provided filter media for testing from their fabs after use. Donaldson studied the mechanism of reactions of HMDS in the air and on the filter media. The analysis showed that these fabs' filter media contain both TMS and HMDSO. However none of these filters were found to contain HMDS indicating the instability of HMDS in air and on the surfaces of these filter adsorbents.

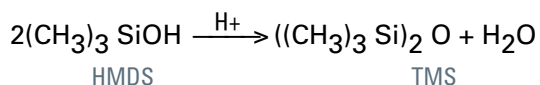
Equation 1



Equation 2



Equation 3



## HOW HMDS CONVERTS TO TMS/HMDSO

Drawing on its filtration expertise and R&D resources, Donaldson set out to analyze HMDS by running it through an acid catalyst to generate TMS in the lab. HMDS has been shown to hydrolyze in aqueous solution to trimethylsilanol (TMS) plus ammonia as shown in Equation 1, or directly to hexamethyldisiloxane (HMDSO) and ammonia as shown in Equation 2.<sup>3</sup>

Through its lab tests and analysis, Donaldson subsequently discovered the new breakthrough that TMS undergoes acid catalyzed dimerization into HMDSO as shown in Equation 3.

In order to protect expensive optics, it is essential to effectively control not only HMDS, but equally importantly, its decomposition by-products—both ammonia and siloxanes (organics). As shown in equations 1-3, TMS, NH<sub>3</sub> and HMDSO can readily be found in the environment of these lens systems.

Figure 1: HMDS in air at 25°C and 50% relative humidity yields TMS and NH<sub>3</sub>.

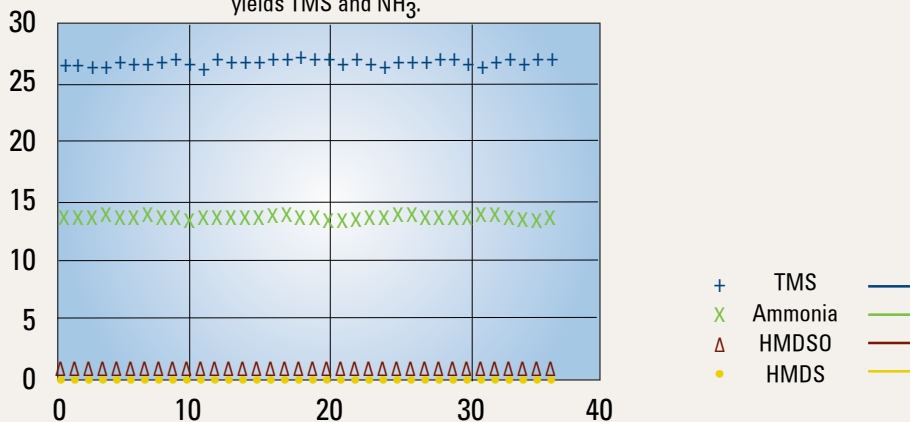


Figure 2: TMS and NH<sub>3</sub>, from HDMS, removal with activated carbon

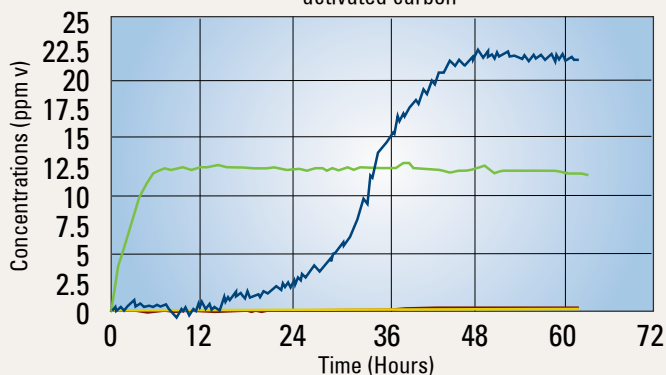
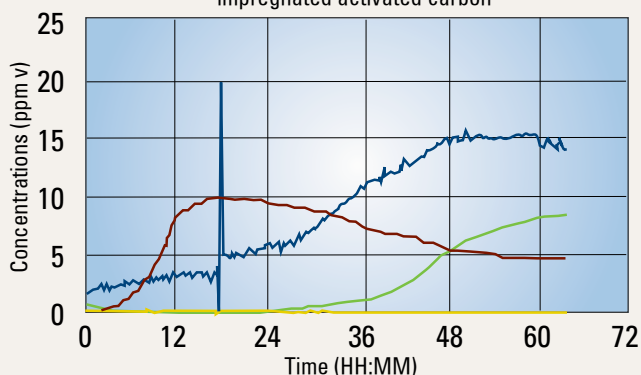


Figure 3: TMS and NH<sub>3</sub>, from HDMS, removal with acid impregnated activated carbon



## FILTRATION KNOWLEDGE REVEALS THE ANSWER

Donaldson conducted experiments using a typical breakthrough test bench design. The test bench consisted of an ultrahigh purity air line connected to a Miller-Nelson model HCS-401 Controller System. The Miller-Nelson controlled the flow rate as well as humidity and temperature of the air supplied to the test bench. A contaminant vapor was added at a specific rate and diluted with the air stream to achieve the desired concentration. The air then passed through a media sample holder. Most of the air was then directed to a fume hood but a portion was passed to an On-Line Technologies model 2010 Fourier transform infrared spectrophotometer (FTIR).

The temperature and humidity in semiconductor manufacturing facilities is tightly controlled at about 25°C and 45% relative humidity. We added HMDS vapor to an air stream in our test bench and found

that under these conditions HMDS can hydrolyze in air to form TMS and ammonia as shown in Figure 1.

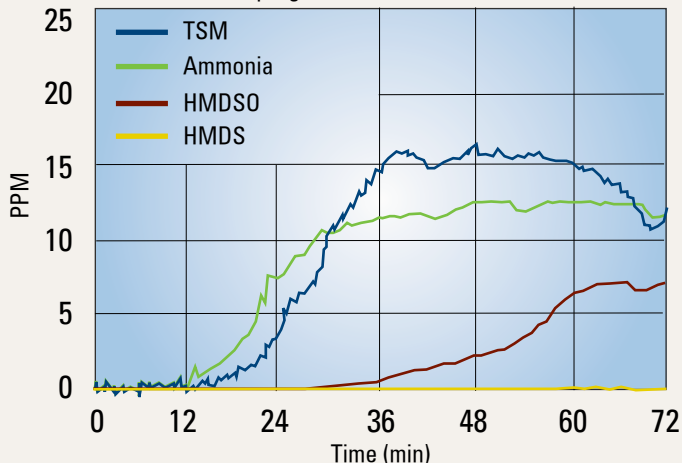
Figure 2 shows the concentration of TMS, NH<sub>3</sub>, HMDSO downstream of a sample of activated carbon when exposed to HMDS as described above. As expected, activated carbon alone removes TMS very well, despite its volatility, and does little to remove ammonia.

Also as expected, Figure 3 shows that acid impregnated carbon alone removes ammonia very well, but does little to remove TMS. It is also apparent that HMDSO is generated through the acid catalyzed dimerization of TMS.

## THE LENS HAZING SOLUTION

Through testing and analysis, Donaldson proves that layering acid-impregnated carbon with a non-impregnated activated carbon or base-impregnated carbon effectively removes ammonia, TMS and HMDSO. The benefits of this combined adsorbent system are evident in Figure 4. This shows that the acidic adsorbent, such as acid-impregnated carbon can effectively remove NH<sub>3</sub>, and activated carbon is effective at removing TMS and HMDSO. These observations show that the optimized filtration solution, BSMmax filters with layering technology, is most effective at removing the two primary culprits of lens hazing—ammonia and siloxanes.

Figure 4: Breakthrough curves with HMDS at 50% humidity using layers of base impregnated and acid impregnated activated carbon.



## CREATING SUPERIOR PROCESSING ENVIRONMENTS

Thanks to in-depth understanding of the chemistry of HMDS breakdown in cleanroom conditions, and thanks to efficiency testing of layered media combinations, Donaldson shows that our BSMmax technology provides the best solution for cleaner air and more productive work environments. Our proprietary V-bed design combined with BSMmax technology removes both ammonia and siloxanes that can lead to lens hazing. Acid gas filtration and the effective removal of SO<sub>2</sub> at low challenge concentrations has already been addressed in SPIE papers 2005.<sup>4,5</sup> Available for Donaldson's Lithoguard chemical filtration cabinets, point of use filters and replacement filters for other manufacturers' cabinets, BSMmax filters provide tangible benefits of ownership: maximum protection and longer filter life. Along with longer filter life and lower maintenance, BSMmax filter inserts are refillable which substantially lowers the cost of ownership and offers environmental benefits.

When it comes to lens hazing, engineers trust Donaldson. We stand behind our filters. With more than 90 years of filtration expertise and the most extensive worldwide network of filtration engineers, manufacturing facilities and technical centers, Donaldson is committed to driving innovation that solves the most complex filtration problems.

## REFERENCES

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