

# AIRBORNE MOLECULAR CONTAMINATION CONTROL AND THE EFFECT OF FILTER MEDIA TECHNICAL PARAMETERS

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## Biography

Matthew C. Middlebrooks is Senior Research Engineer at AQF Technologies LLC, where he has been employed for two years developing custom products and exploring product fundamentals for the filtration industry. He has worked in Research and Development for 16 years in the fields of filtration, specialty products, and melt-spun fibers. Mr. Middlebrooks earned BS and MS degrees in Chemical Engineering from Clemson University. He has been married 18 years and has a 13-year-old daughter.

## Abstract

This paper will review the SEMI F21-95 classification system, propose representative gases within each category to use as markers, and provide comparative testing results based on these markers. The comparative testing will demonstrate the impact of the following parameters on filter media performance:

- Adsorbent Type
- Adsorbent Modification (Impregnation, etc.)
- Adsorbent Particle Size
- Adsorbent Technology/Configuration

In addition, this paper will explain the differences between adsorption and chemisorption and the effects of the type of contaminant, contaminant concentration level, and media velocity/residence time.

However, the final decision on filter format depends on the specific application and the technologies available. Therefore, several current formats will be reviewed with respect to the parameters listed above. Typical filter properties such as efficiency, pressure drop, and life will be compared as they relate to various applications.

Keywords: Airborne Molecular Contamination, Air Filtration, Adsorption, Chemisorption, Impregnation, Breakthrough, Pressure Drop, Capacity.

## Introduction

The semiconductor industry has traditionally focused on controlling particle contamination and its impact on

processing, yields, and quality. However, as more and more sites gain control over their particle contamination issues and circuit geometries continue to shrink, emphasis is shifting to airborne molecular contamination as the next target for improving productivity. Semiconductor manufacturing processes and products are sensitive to a variety of contaminants including acid gases, volatile organics, dopants, and amines. Corrosion and buildup lead to increased maintenance cycles. Unknown odors can cause unnecessary shutdowns or evacuations even when there is no risk to the equipment, operator, or product. For all of these reasons, the semiconductor industry is incorporating gas phase filters in both make-up and recirculation air units to control gaseous contaminants.

A variety of filtration technologies are available to choose from, but these can generally be divided into three configurations. Adsorbent powder slurry-coated nonwovens are inexpensive and have low pressure drop, but have poor adsorption performance due to the small amount of adsorbent present and the fact that much of it is covered with adhesive. This type is not typically appropriate for cleanroom applications. Bulk granular packed beds and panels are perhaps the best known, and are available in a wide range of price and performance combinations. These are typically large, heavy systems requiring significant labor for changeout, but are especially effective for applications with relatively high contaminant levels. However, performance can be quite variable depending on how the filters are manufactured and installed. Dusting, bypass, and high pressure drop are also concerns with this type of filter. Adsorbent loaded nonwovens are a relatively new “hybrid” product typically applied in pleated form. With the proper construction and application, these products can offer extremely high value in terms of high efficiency and service life, as well as low pressure drop and ease of handling.

Within and common to each of these methods of presenting an adsorbent to an air stream are other technical parameters. These include the type of adsorbent, the size of the adsorbent particles, chemical modification of the adsorbent, and velocity of the air stream past the particles. Each of the filter technologies

has limitations with respect to these parameters that affect its performance in different applications.

In addition, the characteristics of the air stream must be considered with regards to the types of contaminants and the concentrations of those contaminants. This analysis may lead to a combination of adsorbents or even a combination of filtration technologies to most effectively control contamination in a given application.

### **Cleanroom Classifications and Requirements**

With respect to airborne molecular contamination the most widely known classification system for cleanrooms is SEMI F21-95<sup>1</sup>. This standard, approved in 1996, classifies contaminants into four categories and establishes a means to communicate acceptable levels of these contaminants in the specification of an environment. The four contaminant categories are:

- **Acids** – corrosive materials whose chemical reaction characteristics are those of an electron acceptor.
- **Bases** – corrosive materials whose chemical reaction characteristics are those of an electron donor.
- **Condensables** – substances (other than water) typically having boiling points above room temperature at atmospheric pressure, capable of condensation on a clean surface.
- **Dopants** – chemical elements which modify the electrical properties of a semiconductive material.

The classification number is determined by the maximum allowable concentration of a category expressed in parts per trillion molar. The classification is written as MX-###, where the X represents the first letter of the contaminant category (A, B, C, or D) and ### represents an order of magnitude for the concentration allowed. For instance, MA-100 specifies an environment that allows no more than 100 pptM of all acids combined.

Though not an official part of the standard, SEMI F21 also includes a list of contaminants in each category that are recommended for monitoring to determine classification. These are:

- **Acids** – Hydrofluoric, Sulfuric, Hydrochloric, Nitric, Phosphoric, Hydrobromic.
- **Bases** – Ammonia (ammonium hydroxide), NMP, Tetramethylammonium hydroxide, Trimethylamine, Triethylamine, Methylamine, Trimethyldisilazane, Cyclohexylamine, Morpholine, Diethylaminoethanol, Dimethylamine, Ethanolamine.
- **Condensables** – Silicone (BP $\geq$ 150°C), Hydrocarbon (BP $\geq$ 150°C).

- **Dopants** – Boron (as boric acid), Phosphorous (as organophosphates), Arsenic (as arsenates).

As circuit dimensions continue to shrink, SEMATECH estimates allowable levels for these contaminants ranging from 100,000 pptM for condensables in the DUV Photolithography process to 0.1 pptM for dopants in Pre-Gate Oxidation<sup>2</sup>. While these levels might be argued depending on each facility's experience and some are even beyond current monitoring capability, it is apparent that the need for gas phase filtration will continue to grow.

### **Testing Program**

For this study, dynamic adsorption testing was performed at two different labs under simulated end-use conditions. Tests were performed using both standard marker gases for various contaminant categories and specific gases taken from the SEMI F21-95 recommended list. The standard marker gases for indoor applications are toluene for volatile organic compounds, sulfur dioxide for reactive gases, and ammonia. Tests on higher concentration, standard contaminants (toluene, sulfur dioxide, and ammonia) were conducted at AQF Technologies LLC in the application labs. Tests on low concentrations or nonstandard contaminants (NMP, nitrogen dioxide, nonane, trimethylphosphate, hydrochloric acid) as well as confirmation tests were conducted at AJE Testing and Research, an independent lab located in Pittsburgh, PA. All tests were conducted under "accelerated" conditions; i.e. concentrations were elevated to produce results within a practical and economic timeframe.

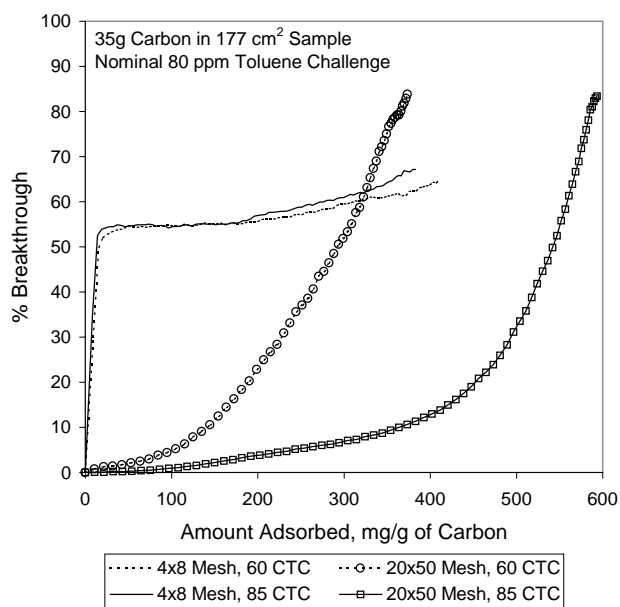
Various filtration components, media, and filters were challenged under a range of conditions to determine the effects of the various technical parameters on the adsorption of AMC's (airborne molecular contaminants). Except on loose adsorbent testing, volumetric flows were set to match media and face velocities of actual filter constructions and application conditions.

### **Results**

By definition, adsorption is a surface phenomenon. A compound (in this case, a gas) is attracted to the surface of another material (a solid) and held there by physical forces. In a related process, chemisorption, the compound is adsorbed onto the surface and then is chemically bound or changed, either by reacting with the adsorbing material or through a catalyzed reaction. For both processes, the higher surface area per unit mass or volume that a material possesses the higher its adsorption capacity will be. Activated carbon is the most common material used

for this purpose, with estimated surface areas of 1000-1500 m<sup>2</sup> per gram or more within the pore structure in the particles. Surface areas are typically measured indirectly with the use of “activity” levels. The activity level of a carbon is defined as its percent adsorption by weight of a reference compound (typically carbon tetrachloride). Other high surface area materials include activated alumina and zeolite. These materials are also used as support matrices for chemical reagents and additives (impregnation) used to modify air streams.

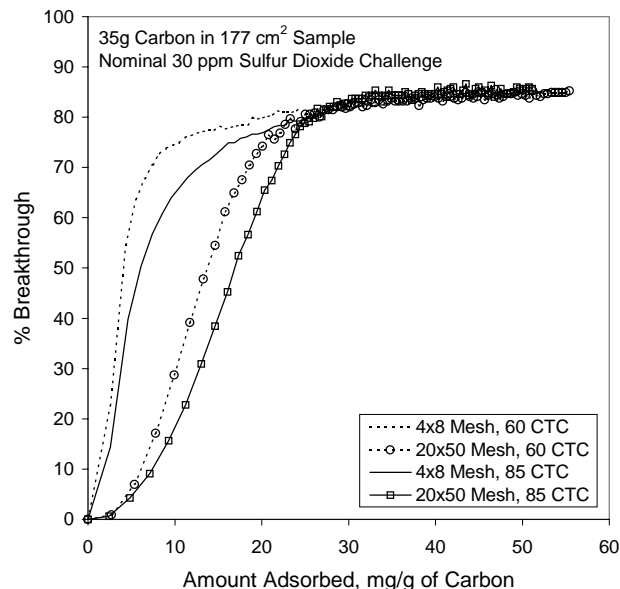
In order for a contaminant to adsorb on a surface, however, it must be able to reach that surface. For a high surface area particle this requires diffusing from the main air stream into the particle’s pores. Thus, particle size can have a significant impact on the rate at which adsorption can occur. Figures 1 and 2 show the combined effects of the activity level of an activated carbon and the particle size on adsorption of toluene and sulfur dioxide.



**Figure 1. Toluene Breakthrough vs. Carbon Particle Size and Activity Level.**

The smaller particles (represented by the higher mesh sizes) for both carbon activity levels have much better efficiencies during the early part of the dynamic adsorption process. Note, however, that the curves for the 60% active carbon eventually cross. This is because the particle size does not effectively change the total surface area per gram of carbon. The majority of the adsorption area is inside the pores, not on the surface of the particle. Thus, the total capacity of the carbon is not changed unless the activity increases. This can be seen by comparing the curves for the 60% and 85% active

carbons. The higher activity carbon has better performance throughout the test. Also note that the effect of particle size is larger than the effect of activity level.



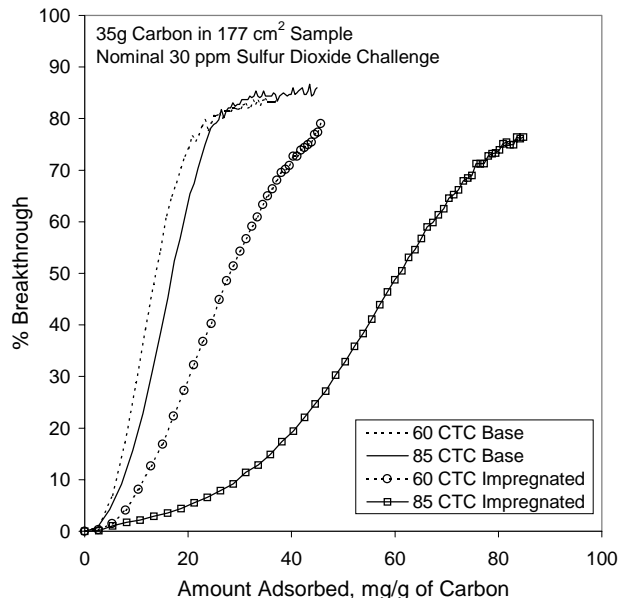
**Figure 2. Sulfur Dioxide Breakthrough vs. Carbon Particle Size and Activity Level.**

The other result that is obvious from the preceding graphs is how much worse plain carbon is at adsorbing sulfur dioxide than toluene. Impregnation can be used to increase the capacity for a compound that carbon does not otherwise have a high capacity for. Figure 3 shows the 20x50-mesh adsorption curves for sulfur dioxide plus adsorption curves for the same carbons impregnated with a base. The adsorption efficiency and capacity are increased for both carbon activity levels, but there is a synergistic effect between carbon activity and impregnation which gives a much larger improvement with impregnation on the high activity carbon.

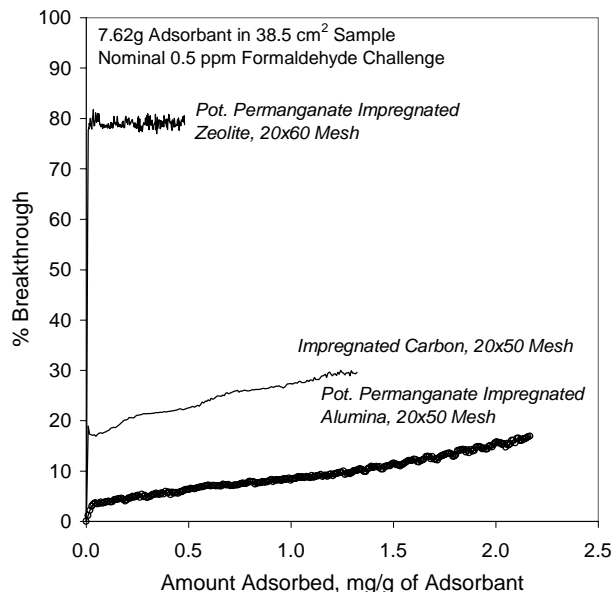
Impregnations are also available for other types of compounds including formaldehyde (Figure 4) and ammonia (Figure 5). Figure 4 shows impregnated carbon, potassium permanganate-impregnated zeolite, and potassium permanganate-impregnated alumina of the same particle size against a 500-ppb formaldehyde challenge. Note that not all potassium permanganate is the same.

Figure 5 shows the use of several acids as impregnants against ammonia. Notice that the acid strength has a large impact on the effectiveness of the removal. The moderate acid is most commonly used as the impregnant for ammonia as a balance between effectiveness and

handling. While the strong acid would be somewhat more effective it would introduce a range of complications from equipment corrosion to operator safety that would increase its cost as well.

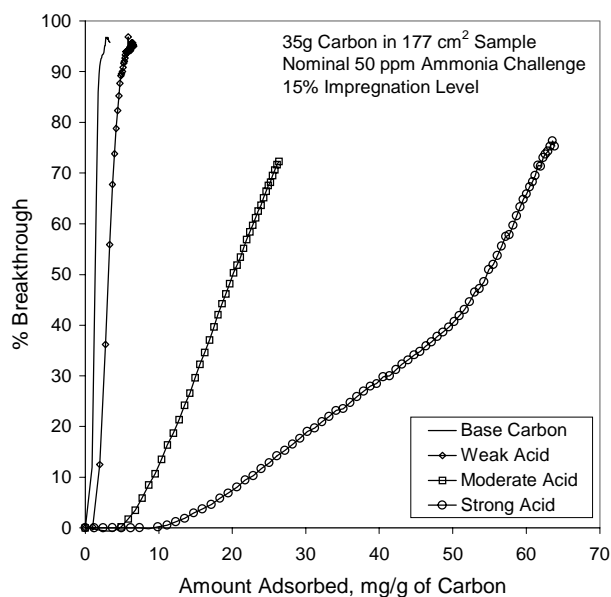


**Figure 3. Sulfur Dioxide Breakthrough vs. Carbon Activity and Impregnation.**



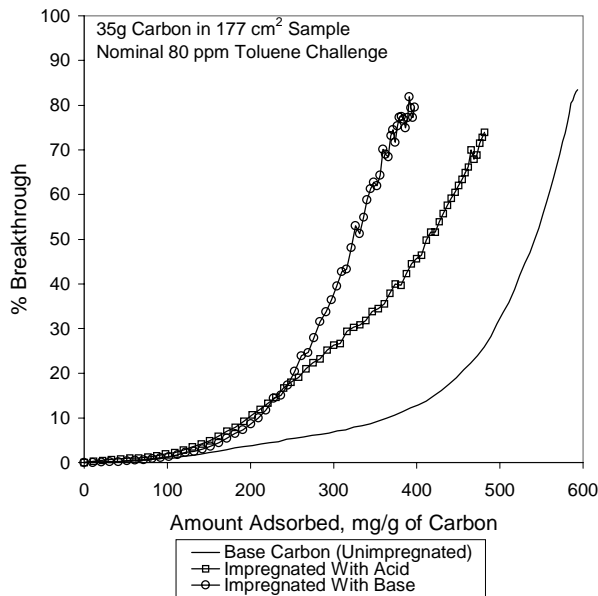
**Figure 4. Formaldehyde Breakthrough vs. Various Impregnants.**

Impregnation does not lead just to improvements, however. When a carbon is impregnated to target a specific compound, it often loses performance against others. This is most apparent with toluene performance, as shown in Figure 6. Notice how the toluene breakthrough increases when the carbons are impregnated with a base (to target sulfur dioxide) or an acid (to target ammonia). This is because the impregnant covers adsorption sites that toluene would normally adhere to without reacting significantly with toluene. Since most air streams have a mixture of contaminants this requires either prioritization of the contaminants or the use of combinations of adsorbents.

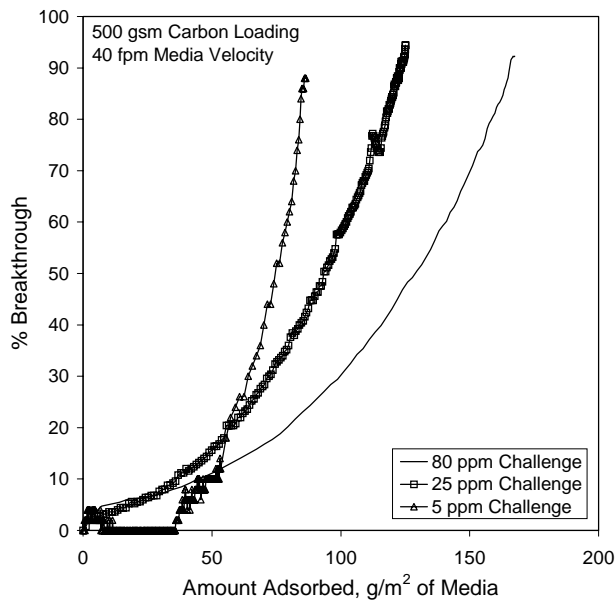


**Figure 5. Ammonia Breakthrough vs. Various Impregnants.**

Physical adsorption also depends on the concentration of the contaminant. This comes from two effects: equilibrium and concentration gradient. Physical adsorption is an equilibrium process with adsorption and desorption occurring simultaneously. The local concentration of contaminant in the air near the surface and the amount of contaminant already on the surface determine which process is prevailing. A high concentration of contaminant in the air stream will favor adsorption, increasing the amount of contaminant on the surface. Likewise, lowering the concentration in the air stream will favor desorption, resulting in lower amounts on the surface. This is shown for toluene in Figure 7. This equilibrium condition is not as important in the case of chemisorption since the process is essentially an irreversible reaction. The plot of sulfur dioxide breakthrough vs. concentration in Figure 8 confirms this.



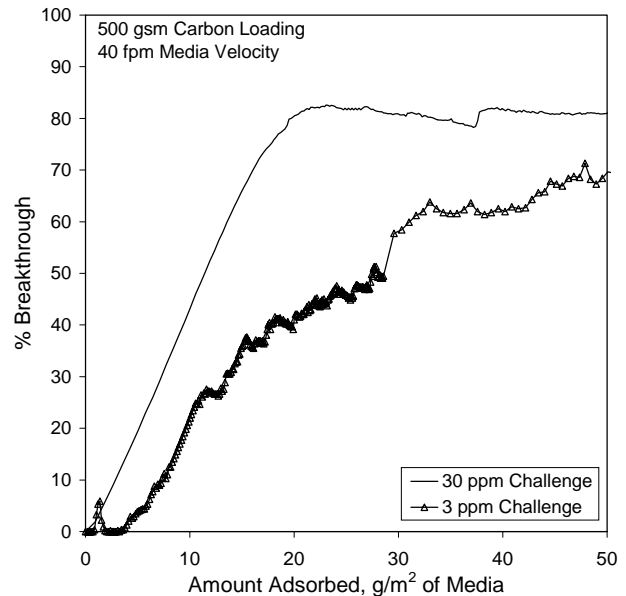
**Figure 6. Toluene Breakthrough vs. Impregnation for Other Compounds.**



**Figure 7. Toluene Breakthrough vs. Challenge Concentration.**

The concentration gradient affects how quickly the contaminant will reach the innermost surfaces of the carbon particles. When adsorption first begins the concentration of contaminant in the air inside the carbon particle is zero. Diffusion drives the contaminant into the particle in proportion to the difference in concentration from the main air stream. At high concentrations this

driving force is large, but at low concentrations the contaminant may not reach the innermost pores before the filter reaches terminal breakthrough. Thus, the particle size is even more critical to achieve high efficiency at low concentrations as seen in cleanroom environments.

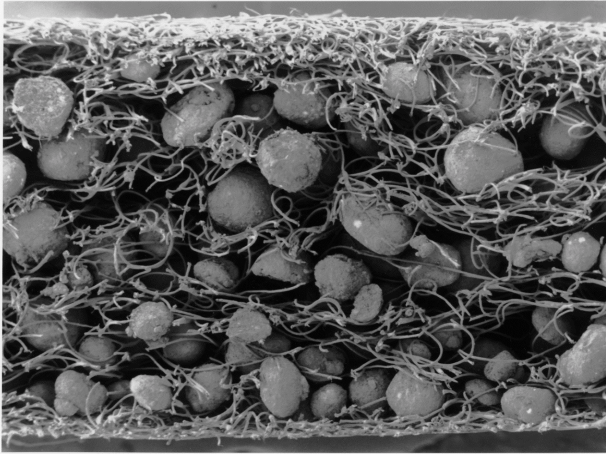


**Figure 8. Sulfur Dioxide Breakthrough vs. Challenge Concentration.**

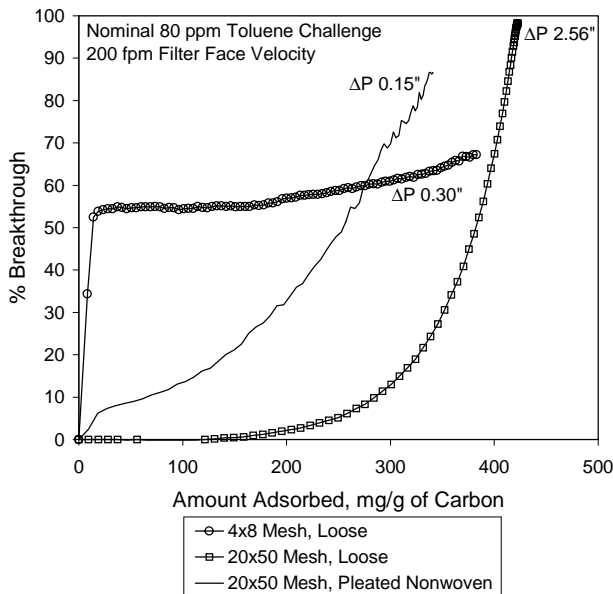
All of the parameters discussed so far can be applied to any of the filter formats discussed so far – within limits. Both packed beds and carbon-loaded nonwovens can use various adsorbents, high and low activity carbons, impregnants, and are subject to concentration impacts. However, loose carbon trays typically use particles that are 4x8 mesh due to pressure drop concerns as opposed to 20x50 mesh (or finer) particles in some carbon-loaded nonwovens. When particles are packed together, as in loose carbon trays, there is little space between the particles for airflow. Thus, the resistance or pressure drop is high. The smaller the particles are the higher the pressure drop is at a given airflow. In addition, there is the increased flow resistance from the screens or plates used to keep the carbon in place. This restricts the size that packed beds or panels can use.

But carbon-loaded nonwoven media can be pleated, dramatically increasing the area for airflow and reducing the media velocity. Therefore, this product can use much smaller particles (20x50 mesh or finer) while still maintaining low pressure drop. In addition, a newer version of these materials (Figure 9) creates a controlled and permanent space between the particles, further reducing the pressure drop. The particles are anchored in

place using bicomponent fibers to create a 3-dimensional matrix with even lower air resistance. Figure 10 shows a comparison of the performance of the two filter formats.



**Figure 9. Cross-section of New Carbon-Loaded Nonwoven.**



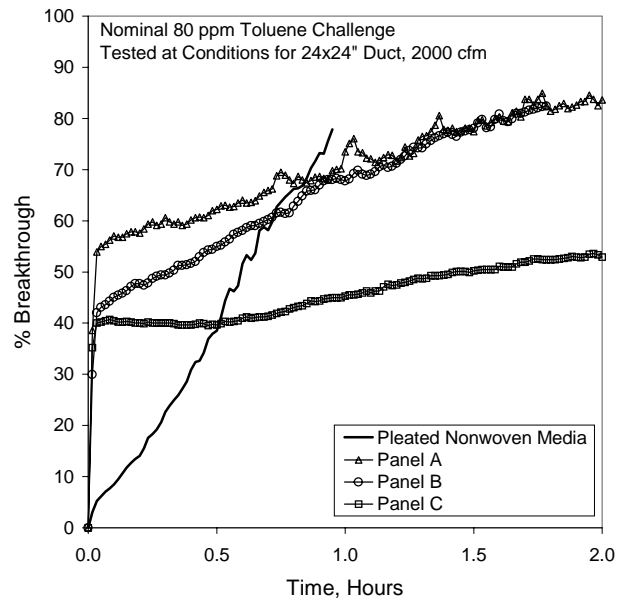
**Figure 10. Toluene Breakthrough vs. Filter Format (All With 35g Carbon).**

First, look at the two loose adsorbent curves. This is the comparison we had earlier due to particle size with the pressure drops added for comparison. The 20x50-mesh carbon shows much better performance, but has a pressure drop of 2.56" H<sub>2</sub>O. The larger particle size lowers the pressure drop to 0.3" H<sub>2</sub>O, but sacrifices the performance as we have seen earlier. If we use the same 20x50 mesh carbon to create a 500-gsm nonwoven of the new type, form a 1" pleated filter with the same weight of

carbon, and use the same filter face velocity the resistance drops to 0.15" H<sub>2</sub>O while maintaining the high early efficiency of the small particles. The early breakthrough of the loose carbon format can be addressed by using additional layers of carbon (deeper beds), but the penalty is further increases in pressure drop.

**Application Comparisons**

The first comparison is in 12" deep V-bank filters for a 24"x24" duct using eight 24x12x1" panels at 2000 cfm. A comparison of the new carbon-loaded nonwoven pleated filters to loose carbon panels for a toluene challenge is shown in Figure 11. Notice the initial breakthroughs ranging from 40 to 60% for the carbon panels versus <10% for the carbon-loaded nonwoven. This is despite the fact that there are only 3 kilograms of carbon in the AQF filter construction and anywhere from 4.1-11.8 kilograms in the carbon panel formats. The pressure drops are also dramatically different: 0.15" of H<sub>2</sub>O for the AQF filter system and 0.28-0.55" of H<sub>2</sub>O for the carbon panel constructions.



**Figure 11. Toluene Breakthrough of Loose Carbon Panels and Carbon-Loaded Nonwoven.**

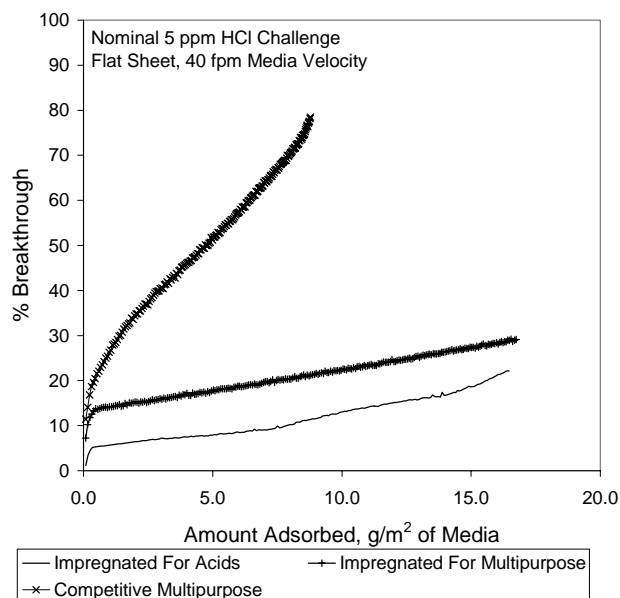
The determination of which filter format is best for a given application is heavily dependent on the effective life of that filter. The life is determined by three parameters: acceptable downstream concentration, actual challenge concentration, and performance of the filter system. The challenge concentration and acceptable downstream concentration define the acceptable or "terminal" breakthrough concentration. When applied to

the breakthrough curve a useful life of the filter system can be projected.

For instance, if the application requires a concentration of condensables less than 10 ppb for acceptable yield rates and the actual concentration is 50 ppb, then a breakthrough of <20% is required from the filter system. In the above comparison between loose carbon panels and carbon-loaded nonwoven the panels would fail immediately because they let at least 40% of the contaminant through from the very beginning. However, if the acceptable concentration was 25 ppb (or conversely the actual concentration was only 20 ppb), then the required breakthrough is <50%. Under these circumstances the loose carbon panel C lasts almost three times as long as the pleated carbon-loaded nonwoven. At this point it would be necessary to calculate the additional energy costs from the fans due to the higher pressure drop as well as the costs for changing out both systems to decide on the most appropriate solution.

The second application comparison is between two types of pleat media, the newer carbon-loaded nonwoven described earlier and another commercially available medium intended for multipurpose use. The new carbon-loaded nonwoven that has been described is available in several grades specifically targeted for certain contaminants through the use of impregnated carbons. Four of these were tested for this comparison: the base carbon and impregnations for acids, bases, and multipurpose contaminants. Only the multipurpose version of the competitive pleat medium was available at the time of these studies. The multipurpose variants are generally intended for acids, nitrogen dioxide, and formaldehyde (not shown in these graphs) while still retaining some effectiveness against condensables.

Both types of media were tested as flat sheets against contaminants chosen from each of the SEMI F21-95 categories. We chose hydrochloric acid from the acids group because of repeated inquiries we have had. To represent the bases we used ammonia and NMP, again because of repeated inquiries, but also because they represent extremes in terms of molecular weight and boiling point for the group. From the condensables we chose nonane as being the lowest hydrocarbon with a boiling point above 150°C (as specified). This should be a conservative test, since the higher the boiling point for condensables, the easier they adsorb on activated carbon. From the dopants we tested trimethylphosphate to represent the organophosphate group and boron trifluoride to represent boron compounds. We also looked at nitrogen dioxide as a potential contaminant from ambient fresh air. Each of the tests was approximately four hours long. The plots are shown in Figures 12-16.



**Figure 12. Acid Adsorption of Various Carbon-Loaded Nonwoven Media.**

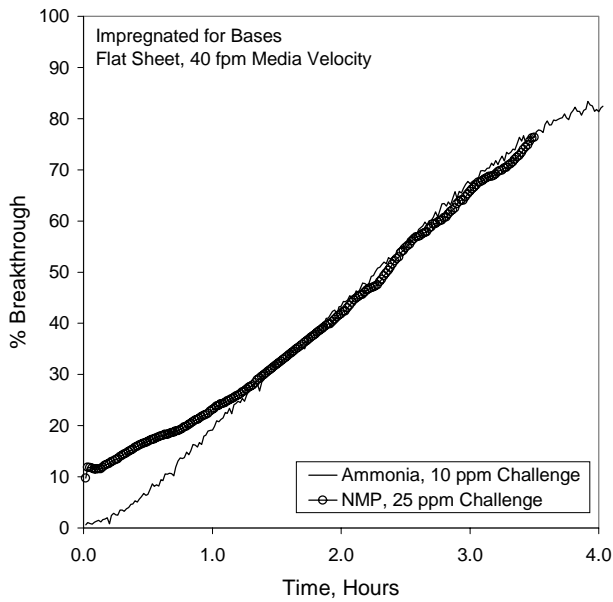
The graphs are shown in two formats. For acids, condensables, and nitrogen dioxide the breakthrough results are displayed versus the grams of contaminant adsorbed per square meter of media. This normalized curve allows a better comparison of different materials as it eliminates other factors such as filter construction and concentrations that affect the results. For bases and dopants, however, only the new carbon-loaded nonwoven medium was tested. The results are displayed versus time because different contaminants at different concentrations are shown on the same graph.

Against acids (hydrochloric) the acid impregnation works best followed closely by the multipurpose impregnation in the new carbon-loaded nonwoven. The competitive multipurpose medium quickly reaches breakthroughs of 50% and greater. Since particle sizes are comparable for these media, the difference is thought to be due to the choice of impregnation.

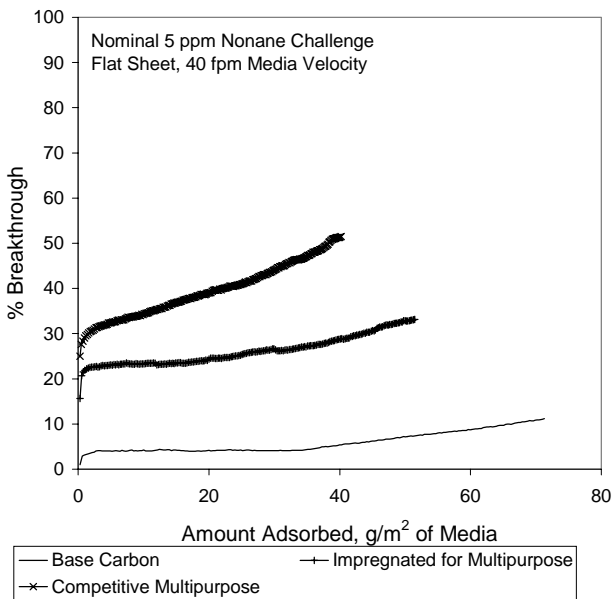
For bases we see that the impregnation in the new carbon-loaded nonwoven works equally well with both ammonia and NMP despite the low molecular weight and boiling point of ammonia.

With condensables, the unimpregnated base carbon performs best. Impregnation interferes with the purely physical adsorption that occurs with these contaminants. Note that of the multipurpose media the new carbon-loaded nonwoven outperforms the competitive product.

Again, the type or level of impregnation would explain the difference.



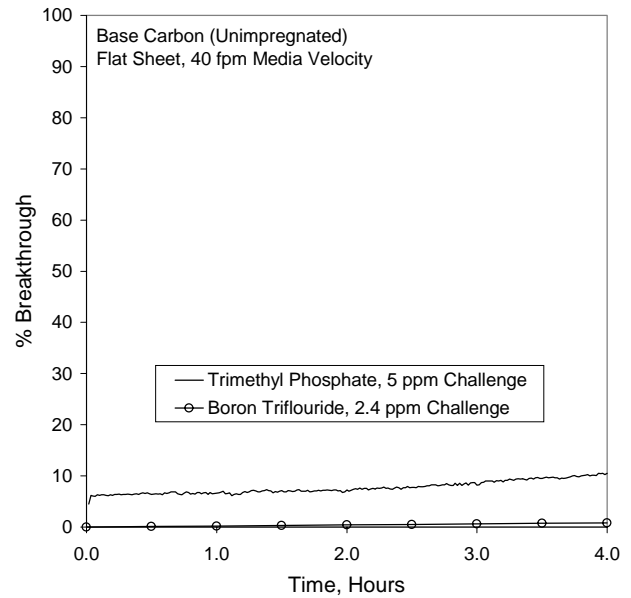
**Figure 13. Adsorption of Bases by New Carbon-Loaded Nonwoven Medium.**



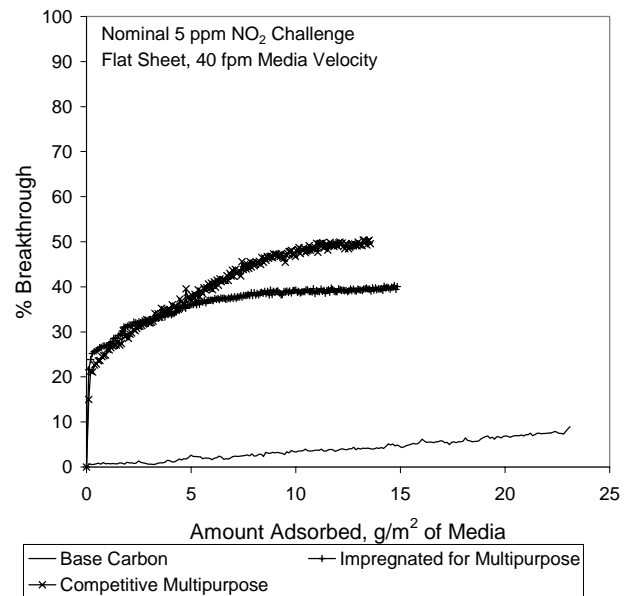
**Figure 14. Condensable Adsorption of Various Carbon-Loaded Nonwoven Media.**

Finally, for dopants, the unimpregnated base carbon performs best, showing excellent results against both phosphate and boron compounds. It also performs well against nitrogen dioxide, in all three cases reaching at most 10% breakthrough by the end of the test. The

multipurpose impregnation has some impact against nitrogen dioxide, leveling off at about 40% breakthrough and outperforming the competitive multipurpose medium.



**Figure 15. Adsorption of Dopants by New Carbon-Loaded Nonwoven Medium.**



**Figure 16. Nitrogen Dioxide Adsorption of Various Carbon-Loaded Nonwovens.**

Once again, the choice of systems depends greatly on the actual conditions in the application. The mix of contaminants in the air stream and their relative importance to the process performance or product quality

will determine which medium or combination of media will be required. It may be possible to compartmentalize the filter systems to control specific compounds for each of the sensitive process steps. Otherwise, it may become necessary to use two media in series or in a checkerboard arrangement to control several contaminants. In some cases a multipurpose impregnation may be sufficient to control all of the key contaminants. Here, the choice of impregnants can become critical, as can be seen by comparing the new carbon-loaded nonwoven and competitive media above.

### **Summary**

The data presented in this paper show the importance of specifying multiple technical parameters of a gas filtration system for cleanroom applications rather than simply targeting the pounds of adsorbent. Particle size has a tremendous impact on the early efficiency of a system as well as on pressure drop (operating cost) of different filter formats. Higher activity levels of carbon greatly increase its capacity for physical adsorption if the particle size is small, but at a large raw material cost penalty. The choice of impregnation has an even greater effect than activity on chemisorption of certain targeted compounds while increasing cost and sacrificing physical adsorption capacity. Lower contamination levels decrease the capacity of the carbon for physical adsorption, but have the opposite effect on chemisorption.

It has also been shown that the new carbon-loaded nonwoven media offer a unique combination of

performance benefits and are highly effective against the types of contaminants that are critical to the semiconductor cleanroom environment. The ability to use small particle size, maintain access to the adsorbent surface, and achieve low pressure drop lead to a filter system with high adsorption efficiency at low challenge concentration and little additional load on fan systems. Products have been developed to deal with all four of the SEMI contaminant categories: acids, bases, condensables, and dopants.

### **Acknowledgements**

The author wishes to thank the following for their contribution: Mr. Nick Wolcheck and Mr. Jerry Gillespie for their help in the AQF Technologies test lab; Mr. Jay Forcucci, Market Manager, Indoor Air Products, AQF Technologies; and Ms. Eve Henderson, Proprietor of AJE Testing and Research, for specialized testing.

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