Photoresist & Ancillary Chemicals Manufacturing

Introduction

Photoresists are photosensitive chemicals that are responsible for laying down and forming the circuitry of electronic devices. In the manufacturing of integrated circuits (IC), a thin layer of photoresist is applied to the surface of the device. Light, in the pattern of the desired circuitry, is then applied to the resist and the exposed chemicals polymerize creating the circuitry on the device. Undeveloped photoresist is removed, and after some further processing, additional layers are applied until the device is completed. As the trend towards smaller line-widths continues, so has the importance of contamination control for every step of the fabrication process. The electronics industry has traditionally focused on the removal of hard particles. However, reduction of other kinds of contaminants such as gel particles, micro-bubbles, and trace metals are just as important.

Critical specifications have been set by manufacturers at less than 15 particles/ml @ > 0.3 micron (µm) and soluble trace metals concentrations at less than 5 parts per billion (ppb) for ancillary chemicals and less than 25 ppb for fully formulated photoresists. This application brief describes a cost-effective approach that will meet particle specifications and maximize throughput for photoresist and ancillary chemical manufacturers.

The Process

Photoresist chemicals are manufactured by blending a Resin with a desired Solvent and a Photo Active Generator (PAG) Compound. Purification and filtration steps are critical in achieving the necessary particle and metal ion specifications. The typical clarification process can be described as follows:

First, the ancillary chemical (resin/solvent) is passed through an ion exchange column in order to remove trace metals to a concentration of less than 5 ppb. Re-circulation continues until the specified concentration, as measured by inductively coupled plasma mass spectrometer (ICP-MS) or a graphite furnace atomic absorption (GF-AA) spectrometer, is obtained. Once the metals specification is met, the resin is then filtered by high efficiency membrane filters in order to meet the required particle count specifications of less than 15 particles/ml @ ≥ 0.3 µm. Typically, two filters are used in series with the first stage being a 0.2 µm or 0.1 µm pre-filter and the second stage being a 0.04 µm final filter. The recirculation of the ancillary chemicals through the ion exchange column and absolute rated membrane filters may extend over several hours before the required specifications are achieved. After the specification is met, the ancillary chemicals are bottled and shipped to the photoresist manufacturer for further processing. Figure 1 shows the typical manufacturing process for preparing the ancillary chemicals.

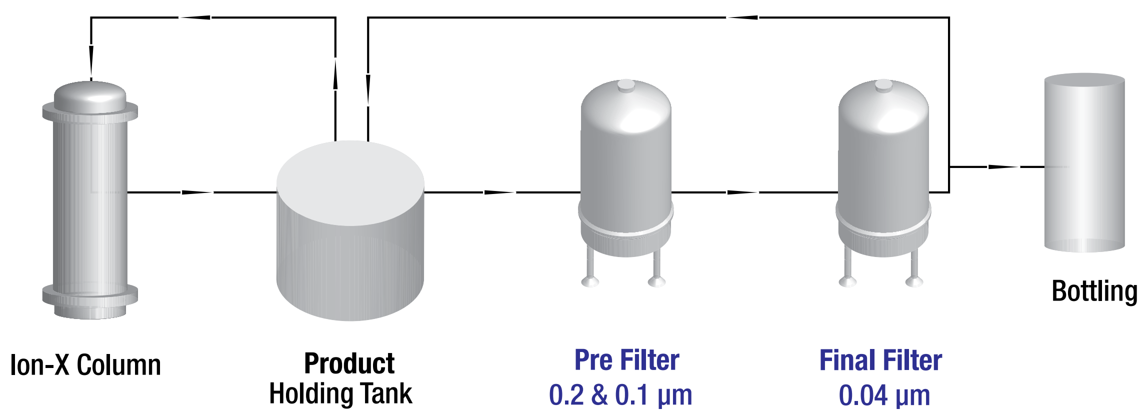

Figure 1 — **Typical Manufacturing Process for Ancillary Chemicals**

The photoresist manufacturer then blends the ancillary chemicals (resin/solvent) together with the desired PAG compound forming the photoresist. During the blending process, contaminants such as soft gels and hard particles are formed and for that reason the photoresist is filtered once more before bottling. Figure 2 shows the typical manufacturing process for preparing photoresist.

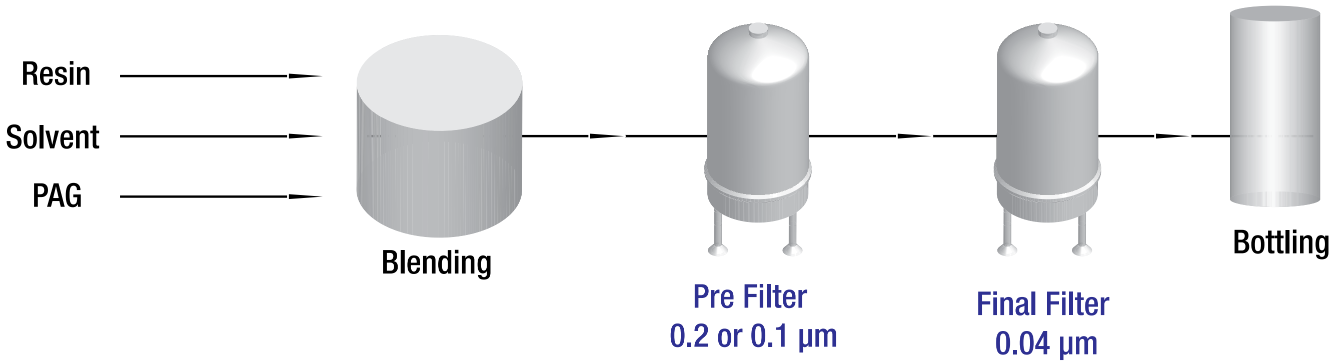

Figure 2 — Typical Manufacturing Process for Photoresist

Factors Which Limit Product Quality and Throughput

Manufacturers of photoresist and ancillary chemicals are challenged with reducing the production cycle to minimize costs and meet production schedules. Ion exchange columns, a process step commonly used to reduce trace metal ions are often the limiting factor in reducing the manufacturing process cycle. Ion exchange columns are comprised of resin beads, which typically have a particle size distribution ranging between 0.3 mm and 1.2 mm in diameter, and are packed into a column.

Channeling and Residence Time

When resin beads are packed into a column they cause a high differential pressure as the highly viscous fluid flows down through the column. Because a finite space exists between ion exchange resin beads, void or interstitial volume is formed. When a photoresist or ancillary chemical is introduced to the ion exchange column, the fluid will take the path of least resistance through the column, which is commonly referred to as “channeling”. To minimize the channeling effect, the ion exchange column is operated at a very low flow rate which in turn increases the contact or “residence time” with the fluid. Residence is described as the period of time when the fluid and functional sites of the ion exchange resin are in contact. It is often necessary to run the ion exchange column in re-circulation mode until the required parts-per-billion levels for trace metals is achieved. This is particularly true with high viscosity chemicals.

Contamination Control

The goal of photoresist and ancillary chemical manufacturers is to reduce contaminants while maximizing production. The four common forms of contaminants which have a significant impact on the quality of photoresist and ancillary chemicals are hard particles, soft gel particles, micro-bubbles, and trace metals. These contaminants can be introduced through the raw materials and the components in the manufacturing system such as pumps, fittings, valves, piping, and transfer drums.

Trace Metals — Soluble trace metals in the photoresist at concentrations greater than 25 ppb will impact the quality of the electronic device. The presence of common metals such as Na, Ca and Fe, have proven to cause shifts in capacitance/voltage curves which can interfere with the conductive properties of the device resulting in product failure.

Hard Particles — Particles greater than 0.3 µm in the photoresist can create non-uniform coating on the semiconductor device. As each new metal layer is added it magnifies the layer just below it. If an oversized particle is present, then it will be compounded by each additional layer that is deposited, potentially creating a defect. Furthermore, particles can also “short-out” a device when they land between the features. Defective ICs resulting from “shorts” cannot be sold and must be scrapped, thereby impacting the profitability of the manufacturing facility. The scrapping of an entire 300 mm wafer can cost as much as $150,000.

Soft Gel Particles — Gels are typically formed during the manufacturing and storage of photoresists. Their reduction from photoresists is highly dependent on differential pressure across the filtration system. Since these gels are soft and deformable, they can extrude through a filter at high differential pressures. At low differential pressures, the forces that would deform gels are correspondingly lower and the gels are retained by the filter membrane.

Micro-Bubbles — Tighter filtration (≤ 0.05 m) and higher flow rates results in higher pressure drops across the filter membrane which causes micro-bubbles to form. Anti-Reflective coatings (ARC, BARC, TARC) containing surfactants are susceptible to "foaming" which will also form micro-bubbles. Furthermore, a significant amount of dissolved gas may be present in photoresists and ancillary chemicals when they pass through the filter. If these chemicals experience a substantial pressure drop across the membrane, cavitation will occur and micro-bubbles will be formed within the membrane. The formation of these micro-bubbles can partially plug pores in hydrophobic membranes, eventually leading to the de-wetting of the membrane pores. The moment the membrane pores de-wet, flow gets restricted because the higher surface tension fluid will no longer wet the pores. If this scenario goes unchecked the pressure drop across the filter increases because a segment of the membrane becomes plugged by air and does not allow flow.

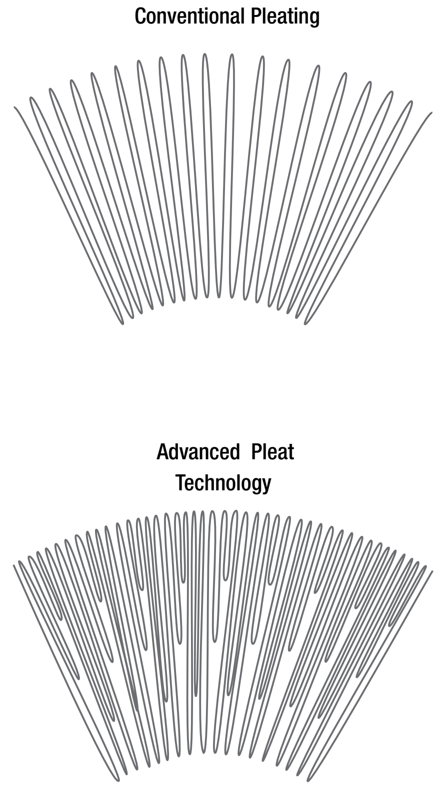

Figure 3 — Comparison of Pleat Configurations

The Solution

3M Purification has been able to maximize filtration surface area, which assures both a low operating pressure to the pump and low differential pressure across the filtration system, which is optimal for gel reduction. The increase in filtration surface area is achieved by utilizing our Advanced Pleat Technology construction.

Advanced Pleat Technology Construction

The accessible surface area often dictates the lifetime of a pleated cartridge filter. Conventional pleated filters may offer a large gross surface area, but when the media is packed into the cartridge, only part of the surface area is used resulting in both flow restrictions and limited contaminant holding capacity. The "blind" or unused area commonly occurs near the inside diameter (Figure 3) where the pleats are most tightly compressed. The LifeASSURE™ PSN series cartridge filter is manufactured using staggered and stepped pleat (Figure 3) configuration, which reduces open space between the outside pleats. This novel technology maximizes capacity by increasing the open area which allows for greater particle loading at the inside diameter, while the shorter stepped pleats take advantage of existing open space closer to the outside diameter of the cartridge. The result is a fully used surface area that provides superior filter life.

Membrane Structure and Its Impact on Soft Gel Retention

PTFE membrane is made by sintering PTFE powder, forming it into a thin sheet, and then stretching it in two directions. The stretching process delivers a dendritic pattern (Figure 4) also known as a string and node structure. While this type of structure exhibits good flow characteristics, soft gel particles are able to pass through it more readily.

3M Purification utilizes a unique manufacturing process for LifeASSURE PSN series Nylon 6,6 membranes.

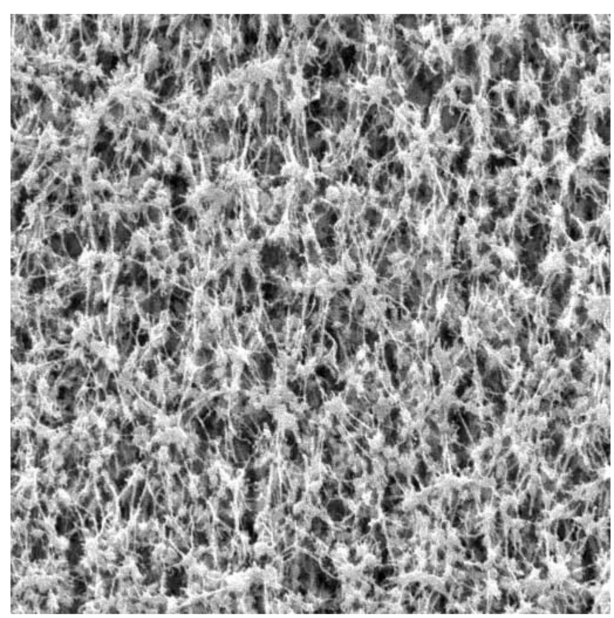

Figure 4 — SEM of PTFE Membrane

This process produces a more rigid, sponge-like structure (Figure 5) which has as much as twice the thickness of PTFE membranes. The combination of the sponge-like structure and increased depth of filtration provides a tortuous downstream path capable of retaining soft gel particles more efficiently, even under high differential pressures.

Hard and Soft Gel Particle Reduction

Effective reduction of contaminants must be accomplished in order to meet the specifications required by IC manufacturers. The mechanisms for reducing particulate and soluble metal contaminants are very different and therefore different types of filtration technologies must be utilized. To cost effectively reduce contaminants to less than 15 particles per ml @ > 0.3 µm, a two stage membrane filtration system may be required. LifeASSURE™ PSN series filters are ideally suited for this application.

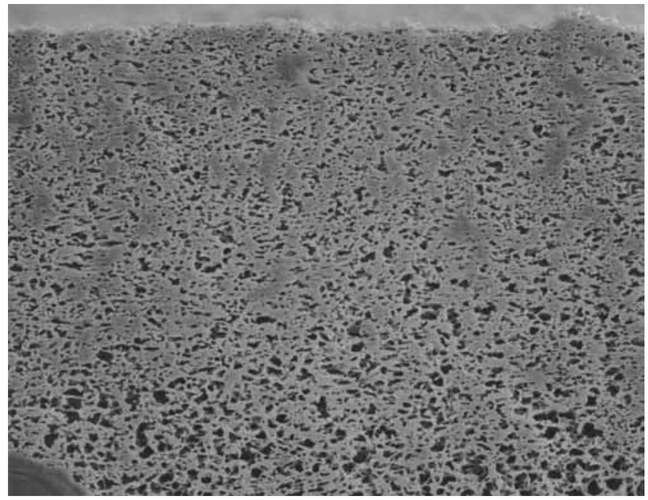

Figure 5 — SEM of Nylon 6,6 Membrane

Pre Filter — The purpose of the first stage, or pre filter, is to provide gross particulate reduction, in order to minimize the load on the more expensive final polishing filter. The pre filter should be constructed of high area, pleated nylon membrane and have a pore size reduction rating of 0.2 µm or 0.1 µm. This pore size has been demonstrated to provide excellent protection for the final polishing filter while preventing premature plugging. A large pleated membrane surface area is required to provide a low differential pressure, particularly with high viscosity photoresists, as well as long filter life. This will allow for the proper size filtration system to economically process an entire batch of photoresist with out having to replace filters. This results in greater throughput while minimizing hold-up volume and waste of expensive photoresists and ancillary chemicals.

Particulate contaminants are most effectively pre-filtered from the photoresist through the use of 0.2 µm or 0.1 µm LifeASSURE PSN series filter cartridges. LifeASSURE PSN series filter cartridges are manufactured using Advanced Pleat Technology (APT). Benefits of APT include:

- Maximum flow in a compact design reduces the number of required filter elements
- Provides both lower operating and differential pressure to minimize outgassing and micro-bubble formation
- A lower pressure drop increases the rate of recirculation which allows particle counts to be achieved more rapidly while reducing energy and wear on the pumps
- Superior reduction of gel particles for reduced defectivity
- Increased throughput and filter lifetime which lowers cost-of-ownership

Final Filter — The final membrane filter in the photoresist process should also be of high surface area pleated construction in order to minimize operating differential pressures. Low filter differential pressure is important to ensure that deformable soft gels are trapped in or on the filter media and not forced through the membrane, thereby contaminating the finished product. The membrane must have an excellent particle reduction efficiency to effectively reduce the number of particles to less than 15 counts per ml @ > 0.3 µm in the shortest amount of processing time.

LifeASSURE PSN series filter cartridges are constructed of high efficiency, naturally hydrophilic, Nylon 6,6 membrane. Benefits of a naturally hydrophilic Nylon 6,6 membrane include:

- No IPA pre-wetting and system flushing required – reduces a potential source of contamination and chemical interaction, while reducing hazardous waste disposal
- Reduces potential for micro-bubble formation by not de-wetting in outgassing fluids unlike naturally hydrophobic membranes such as polypropylene, UPE, and PTFE
- Reduces installation downtime and increases overall equipment effectiveness

Nylon 6,6, has a broad chemical compatibility and is well suited to filter photoresist and ancillary chemicals. The filter's outer cage, inner core, end cap adapters, and membrane support layers are made of high density polyethylene (HDPE), which has low extractables. No adhesives, binders, or surfactants are used in the manufacturing process and all cartridges are double-bagged in a clean environment ensuring superior downstream cleanliness out of the package.

Ionic, organic, and metallic contaminants can extract from other filter materials, which may change the photo speed, viscosity, or molecular weight of the chemical. Table 1 shows metals analysis of extractable levels of LifeASSURE™ PSN series filter cartridges in propylene glycol monoethyl acetate (PGMEA) a common chemical used in photoresist manufacturing.

Table 1. Typcial Metals Analysis for a 10" LifeASSURE™ PSN Series Cartridge

Metal	Detection Limit (ppb)	24 Hour Extraction	120 Hour Extraction
Ca	0.9	< D.L.	< D.L.
Cr	0.3	< D.L.	< D.L.
Cu	0.9	< D.L.	< D.L.
Fe	0.9	< D.L.	< D.L.
K	0.9	< D.L.	< D.L.
Na	3.0	< D.L.	< D.L.

* Analysis using Graphite Furnace Atomic Absorption, extraction using PGMEA

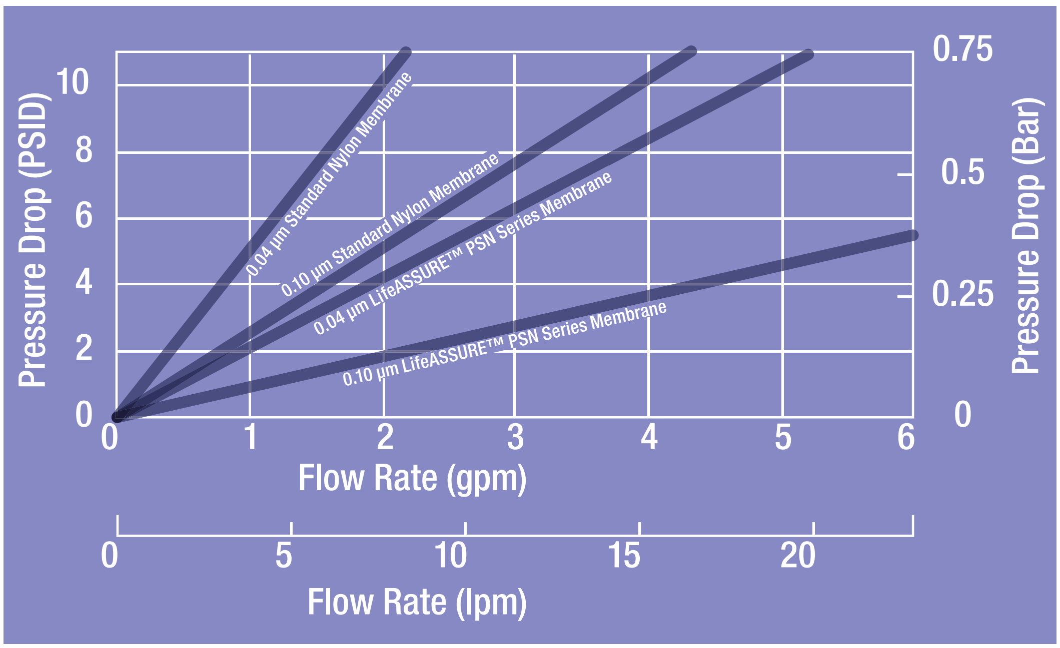

Figure 6 — Comparative Flow Rates: Standard Nylon Membrane vs. LifeASSURE™ PSN Series Filters

Figure 6 compares the flow characteristics of LifeASSURE PSN series and conventional nylon membrane filters.

The large surface area of the LifeASSURE PSN series cartridge also allows for a low differential pressure and extremely high contaminant holding capacity for extended filter lifetime. The enhanced particle reduction efficiency allows photoresist and ancillary chemical manufacturers to meet particle count specifications quickly, thereby increasing throughput and overall equipment effectiveness.

The Solution for Trace Metals Reduction

Ion exchange columns are a proven technique for reducing metal ions from process chemicals to acceptable levels. The key to success is maximizing the accessibility of the adsorptive sites of the ion exchange resin in a way to minimize pressure drop as the photoresist or chemical flows through the purification matrix.

Zeta Plus™ technology is gaining wide acceptance in these applications because of its high capacity and efficiency in removing trace metals, while providing superior flow rates and pressure drop as compared to ion exchange columns. The Zeta Plus 40Q purifier is produced by immobilizing ion exchange resin in a media of purified cellulose fibers and filter aids. These three components are then bound into a matrix that exhibits both dry and wet strength through the use of a binder resin selected specifically for the functionality required. When installed in photoresist and ancillary chemical applications, the Zeta Plus 40Q purifier has demonstrated its ability to reduce trace metals consistently to less than 10 ppb while providing improved throughputs.

Table 2 demonstrates the ability of Zeta Plus 40Q purifier media to reduce the concentration of specific trace metals from the photoresist solvent, PGMEA.

Table 2. Reduction of Trace Metals with Zeta Plus™ 40Q Purifiers in PGMEA Based Photoresist

Sample ID	Effluent Metal Content (ppb) 24 Hour Extraction		
	Na	Ca	Fe
Influent to Zeta Plus™ 40Q Purifier	858	1090	711
Effluent from Zeta Plus™ 40Q Purifier	< 10	< 10	< 10
Detection Limits	10	10	10

Production

During the manufacturing process, photoresist and ancillary chemicals must often be re-circulated through the ion exchange column several times before meeting the metals concentration specification. The high reduction efficiency of the Zeta Plus 40Q purifier allows trace metals specifications to be met in a single pass, reducing the processing time of the photoresist. Figure 7 depicts a modified process schematic showing the replacement of the ion exchange column by Zeta Plus 40Q purifier.

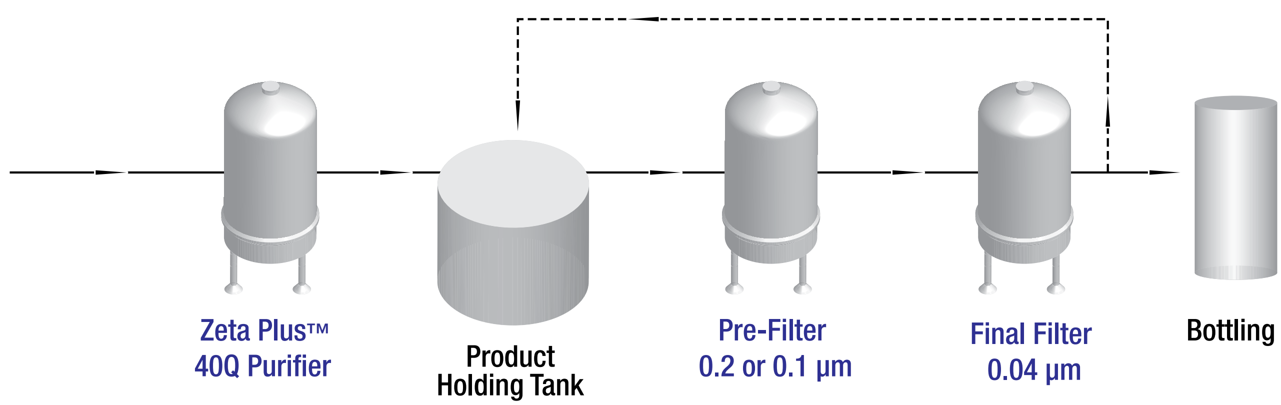

Figure 7 — Process Flow Diagram with Zeta Plus™ 40Q Purifiers

Conclusion And Recommendation

Proper selection of a matched filtration system will allow manufacturers to achieve higher production throughputs while maintaining particle reduction specifications. The following changes will lower the cost-of-ownership:

- Zeta Plus™ 40Q purifiers will replace flow rate limited Ion Exchange Columns with a filtration system that improves both throughput and quality yet has the added benefit of providing an additional particle pre-filtration step.
- LifeASSURE™ PSN series filters provide efficient pre-filtration to the final membrane filter while providing enhanced surface area for longer filter lifetime.
- LifeASSURE PSN series filters provide a lower pressure drop which increases the rate of re-circulation allowing particle counts to be achieved more rapidly while reducing energy and wear on the pumps.
- LifeASSURE PSN series Nylon 6,6 filters are naturally hydrophilic which reduces the potential for micro-bubble formation by not de-wetting in outgassing fluids unlike naturally hydrophobic membranes such as Polypropylene, UPE, and PTFE.
- LifeASSURE PSN series Nylon 6,6 filters provide a more rigid, sponge-like structure with enhanced surface area that is capable of retaining soft gel particles more efficiently than PTFE filters.

The Solution for Laboratory, Pilot Scale, and Full Scale Production

3M Purification offers a wide breadth of electronics grade products that have been specifically designed to meet the exacting requirements of materials suppliers from laboratory scale testing through full scale production.

For laboratory scale and pilot scale testing, 3M Purification offers low hold-up volume disk filters, capsules, and housings to allow end users to assess parameters such as material compatibility, photo-speed, trace metals reduction, and particle retention testing in a rapid and cost effective manner. The compact size also allows for easy replacement and installation of filtration and purification media while reducing the waste of expensive chemicals. 3M Purification filter/purification disks and capsules contain the same filter media as full size cartridges, ensuring a consistent level of quality throughout laboratory, pilot, and full-scale production testing. This makes the scale-up process simple, linear, and predictable.

Scientific Applications Support Services

The cornerstone of our philosophy is service to customers, not only in product quality and prompt service, but also in problem solving, application support and in the sharing of scientific information. 3M Purification Inc. Electronics performs in-house and on-site filtration studies worldwide through its **Scientific Applications Support Services** (SASS) group using the most advanced particle counting technologies to solve difficult separation problems while aiding in the selection of the most effective and economical filtration systems.

Reference Material and Related Product Information

Electronics Chemical Filtration Compatibility Guide

This listing is intended as a guide for selecting the appropriate 3M Purification Inc. filter based on chemical compatibility with most common chemicals. This information is based on technical publications, laboratory experiments, data from material suppliers, and field tests. It is recommended that compatibility of these chemicals be established in the specific application because actual performance may differ as a result of variations in temperature, concentration, exposure time, or other factors. Consideration must also be given in selection of a suitable o-ring material to assure complete compatibility.

LifeASSURE™ PSN Series Nylon Filter Cartridges and Capsules

LifeASSURE™ PSN series Nylon filter cartridges and capsules are highly retentive membrane filter elements designed to meet the exacting requirements of photoresists and ancillary chemical applications. Utilizing Advanced Pleat Technology (APT), LifeASSURE PSN series filters provide superior flow characteristics with minimal pressure drop. Increasing flow while maintaining filter efficiency results in particle specifications being achieved in less time. This decrease in processing time results in lower filtration costs – reduced energy consumption, pump wear, and labor. The naturally hydrophilic Nylon 6, 6 pleated membranes in an all high density polyethylene (HDPE) construction, provides low extractables, increased filter life, and superior reduction of gels and hard particles when compared to other membrane cartridges.

Zeta Plus™ 40Q Purifiers

Zeta Plus™ 40Q purifiers are high capacity purifiers designed to remove metallic ion contaminants from photoresists and ancillary chemicals in a single pass. The purifier contains ion exchange groups that have been bonded to a high density media. This construction improves surface area for the Ion Exchange Groups assuring metallic contaminant reduction to single digit ppb levels.

This listing is intended as a guide for selecting the appropriate 3M Purification filter based on chemical compatibility with most common chemicals. This information is based on technical publications, laboratory experiments, data from material suppliers, and field tests. It is recommended that compatibility of these chemicals be established in the specific application because actual performance may differ as a result of variations in temperature, concentration, exposure time, or other factors. Consideration must also be given in selection of a suitable O-ring material to assure complete compatibility.

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