Mixed-Bed Resin Stability in Semiconductor Applications

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Studies in the stability of mixed bed resins when stored dry prior to use show a slow, but inexorable deterioration in quality, both TOC leachables and rinse up to 18+ megohms. These undesirable changes in the resin properties can be delayed by storage in gas barrier liners that prevent oxygen and carbon dioxide from reacting with the resin. Test work done by ResinTech's laboratory show that with traditional polyethylene plastic drum liners, even carefully packaged mixed bed resin may show some changes during the first year of storage and may no longer be suitable for use in ultrapure water systems after one to two years of storage. However, mixed bed resins stored in gas barrier lined drums lasts three years or longer.

Many semiconductor plants maintain an inventory of spare resin stored in drums waiting to be used in case of unexpected need for change out. In some cases this resin may rest in storage for extended periods of time. What happens to mixed resin as it ages? What changes occur and over what time period? There is little published data regarding optimum storage conditions and changes that eventually make the resin unusable.

Before discussing mixed beds, let's review how the separate components of cation and anion resin age. Here, there is fairly good data published from experiences at nuclear power plants with regenerated resins used in condensate polishing.

Cation resins are generally considered stable, yet there is a slow reaction where bits of the polymer containing sulfonate exchange groups leach out of the polymer or break away from the styrene backbone and become water soluble. The sulfonates can be complex organic fragments of the styrene backbone or simple sulfuric acid. Almost all degradation products from cation resin are acidic (anionic). The molecular weight distribution depends on crosslinking and on how the resin was originally made. When cation resins are stored separately from anion resin the concentration of sulfonate leachables gradually increase over time. The "standard" 16-hour leach test (@160° F) typically reports TOC leachables from below 50 ppm (for a really clean freshly made resin) to over 1000 ppm for a resin that has been stored for several years.

If these leachables are washed into an anion resin during initial use of the resin, the anion resin surface becomes poisoned by the organic anions and the resin kinetics (ability to rapidly exchange ions) is impaired.

Anion resins are considered far less stable than cation resins, particularly when in the hydroxide form. Degradation in the absence of oxygen is primarily the loss of the functional group trimethylamine (TMA). When oxygen is present, particularly at high temperatures, there is a secondary degradation of the amine with methanol released into the water. TMA is a weakly ionized cation and is removed by cation exchange resins; methanol is polar but not ionized and therefore is not removed by ion exchange.

When the two components are mixed together, the anion resin adsorbs the organic and inorganic sulfonates that come out of cation resin. The cation resin adsorbs the trimethylamine that comes out of anion resin. Since most of the organic leachables are removed within the mixed bed itself, the rate of increase in TOC from a mixed resin is much slower than the increase from the separate components. Of course, the leachables do exhaust the counter resin to some extent and eventually cause unacceptably high leakage when the mixed resin is placed into service. However, the rate of exhaustion is quite slow at room temperature and it takes years before the change in the resins capacity is large enough to measure.

Organic leachables from the resins themselves are not the only ionic contaminants the resin is exposed to during storage. Of particular importance are gasses from the atmosphere, notably oxygen, carbon dioxide, and water vapor. No container is 100% gas tight, even metal containers have slow diffusion rates. The typical fiber drums with polyethylene liners used by the resin manufacturing industry have rather high diffusion rates. This leads to a gradual exhaustion of the anion resin with carbon dioxide, a slow loss of moisture, and slow oxidation of both resins. When the carbon dioxide content of the resin reaches about 10% of exchange sites it becomes increasingly difficult for the mixed resin to produce 18 megohm water. As oxidation occurs, the leachable TOC increases, some TOC rinses out easily but a portion slowly increases the lowest TOC possible from the mixed resin.

If a mixed bed resin is left completely open to air (say the drum lid is removed and the liner opened), the top quarter inch of resin exhausts into the carbon dioxide form within a few hours. Then the exchange slows and it takes a week or two for the top inch to become exhausted. The exchange for carbon dioxide is accompanied by evaporation of moisture from the resin; the surface of the resin dries out. A typical seven cubic foot drum is about 36 inches tall, one-quarter inch is less than 1% of the total volume, and even a full inch is only around 3 or 4% of the total. If a small amount of dry (exhausted) resin is blended into the rest of the drum, the effect on performance is minimal, since the fraction of the drum represented by the damaged resin is minimal.

If the drum is left open for several weeks, the average composition deteriorates to where the mixed resin may no longer be capable of 18 megohms. In addition, there is some risk that the dry resin will break into fragments when re-wetted, thus increasing the chance of particulate shedding from the mixed resin. Good housekeeping prevents this type of problem during storage. However, a drum that is breached during handling should not be left "as is" for longer than necessary to repair the damage, otherwise the resin will degrade and in a few months might not be suitable for use in an 18 megohm application.

Even if a drum has a tightly sealed polyethylene liner, there is still an exchange of gasses through the liner. The anion resin in a sealed drum of mixed bed resin will pick up around 10% (or more) carbon dioxide over a two-year period. At the same time, enough oxygen gets in through the liner to begin to produce some noticeable differences in the TOC produced by the mixed resin when it is placed into service.

Anion resin preference for carbon dioxide is significantly lower than for ions, such as chloride and sulfate. Carbon dioxide, along with silica and boron are generally the first anions to appear in a mixed bed effluent. However, since new resins do not normally contain any silica or boron. The presence of a high fraction of carbon dioxide on the resin leads to premature leakage of carbon dioxide into the mixed bed effluent. CO^2 is generally compatible with wafer manufacturing; the leakage of CO^2 from an ultrapure mixed bed is not by itself a concern. However, even though carbon dioxide is weakly ionized, its presence does reduce resistivity and pH. Lower pH changes the conditions inside the mixed bed and causes an increase in sodium leakage from the cation resin. Resistivity drops, eventually the mixed bed will no longer rinse up over 18 megohms.

All mixed resins throw some TOC when first placed into service. No matter how well rinsed a mixed resin is, by the time it is packaged, shipped and loaded, the initial TOC out of the resin will be relatively high. Fortunately, most of this TOC is completely water soluble and rinses out rapidly from well made mixed beds. Although the initial TOC increases, the rinse time to reach low TOC probably doesn't increase much, if at all. What is low TOC for a USP application is considered unacceptably high for a high pressure steam generator and impossibly high to a second tier wafer fabricator. If the need is for USP grade (under 500 ppb TOC) even a mixed bed that has been stored for two years under careless conditions will probably produce low enough TOC and high enough resistivity that the resin will be considered acceptable.

When the requirements are more stringent, it becomes necessary to have a pre-service rinse to purge the TOC that has built up and to rinse out any other contaminants that might be present. Here, the conditions of storage become increasingly important. Boiler water resistivity specs are seldom higher than 10 megohms resistivity or lower than 50 ppb TOC. A short rinse (of 5 to 10 bed volumes) is generally sufficient to meet boiler feed requirements.

For electronics grade water, particularly the highest grades, extended rinses are necessary to reach acceptable TOC levels, usually much longer than the rinses required to reach low levels of ionic leakage and 18 plus megohms resistivity. Here, a mixed resin stored in a sealed polyethylene liner probably won't be suitable after two years of storage even under ideal storage conditions. After about 6 to 9 months, there is a noticeable increase in both initial TOC and in the final base line TOC after the resin rinses down. In addition, the rinse down time increases from less than one hundred bed volumes (for really clean freshly made mixed bed) to more than 200 bed volumes. Resistivity usually doesn't change much during this period, although the carbon dioxide content of the anion resin does gradually increase.

After somewhere between one and two years of storage in polyethylene liners, a mixed bed will have picked up enough carbon dioxide and TOC leachables that it probably won't be suitable for the highest purity applications. The carbon dioxide content may reach 10% or higher and the resin won't quite rinse up to 18 megohms. The higher CO_2 content of the resin can also affect leakage of other anions, notably silica and boron. This is because anion resin has lower preference for both silica and boron than for carbon dioxide. These contaminants are not always present in the mixed bed feed water but if they are this can be an added concern when trying to use a mixed resin that has been stored for a long time.

A partial answer to the storage problem is to use drum liners that are not gas permeable. Mylar plastic has much lower gas permeation rates than does polyethylene. Two part (foil/PPE) liners are even better at offering very low gas permeation rates. In extreme cases, the drums can be nitrogen purged to reduce the initial oxygen surrounding the resin. Under these conditions, the rate of deterioration slows dramatically. Carbon dioxide pick up is virtually non detectable even after five or more years of storage. The TOC leachables in the resin do increase, but at a much slower rate. The anion leachables are almost exclusively cationic, therefore exchanged by the cation resin. Cation leachables still build up, albeit at a slow rate. Still, after somewhere around 5 or 6 years of storage the leachables build up to where the resin produces noticeably higher TOC than it did when it was new. This TOC build up can still limit the usefulness of old mixed bed for the highest purity requirements.

In conclusion, the storage of mixed resins is limited by carbon dioxide pick up by the anion resin component and by a slow increase in TOC leachables, primarily from the cation resin component. Poorly stored mixed bed will show significant deterioration after a few weeks or months. Carefully stored mixed bed packed in polyethylene lined drums lasts one to two years. Mixed bed that is carefully stored in gas barrier lined drums lasts five years or longer. For relatively modest purity requirements such as USP grade water and all but the highest-pressure boilers, an older mixed bed may still be good enough to use. However, for the really stringent requirements of electronics grade water, any mixed bed stored longer than a few months is suspect and should be analyzed periodically to verify it is still useable.