Part 1: Keys to Successful IX Resin Storage

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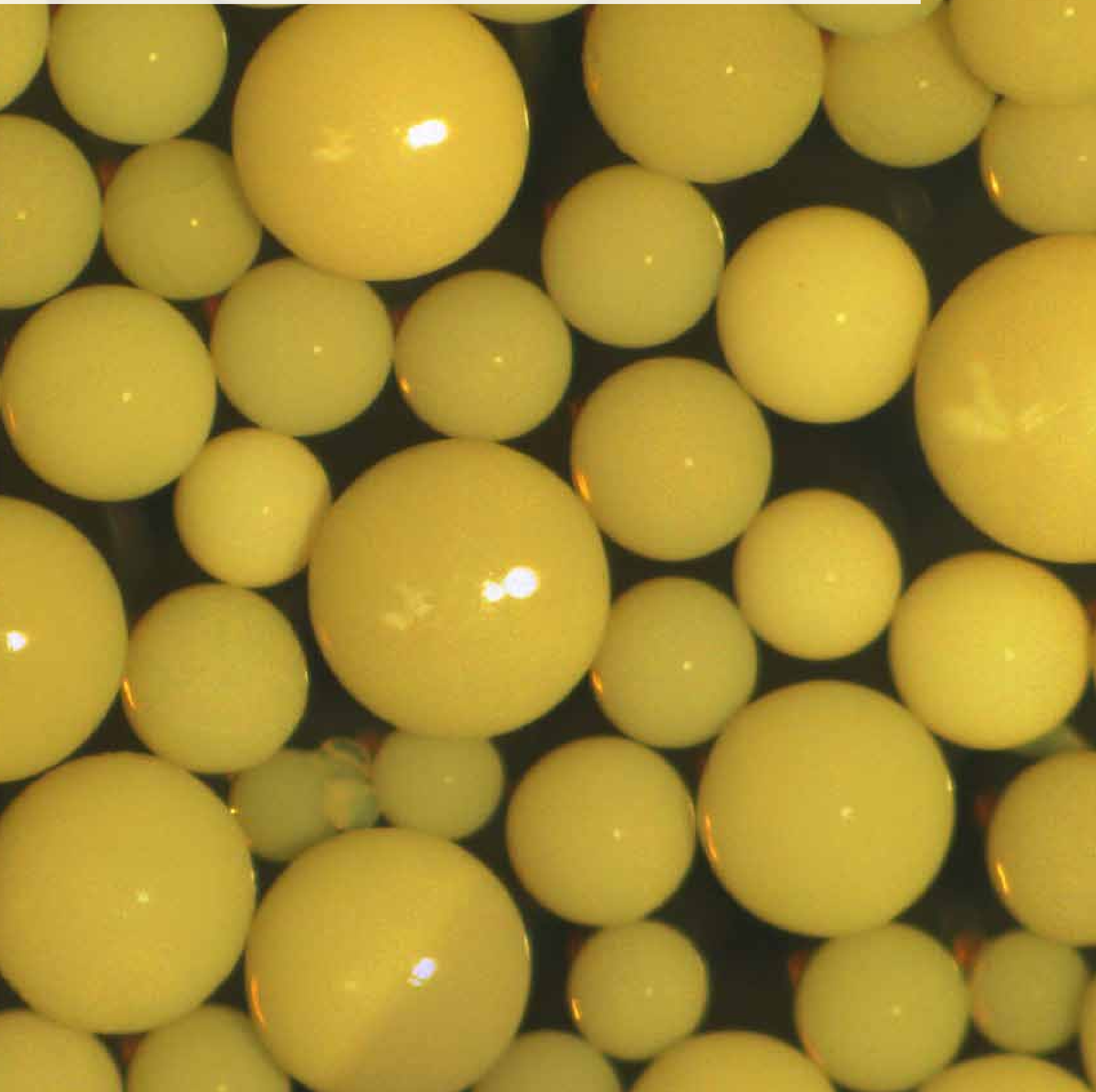

Generally, ion exchange (IX) resins may be safely stored for two to five years (or longer) without significant chemical or physical deterioration. Numerous exceptions exist, and salt-form resins (neutral pH) store better than hydrogen (H) or hydroxide (OH) forms. Indoor climate-controlled storage in the original shipping containers is ideal. Precautions should always be taken to store IX resins in their original undamaged shipping containers. These should be kept in sheltered, reasonably well-ventilated areas, protected from extremes of heat or cold and from rain or other forms of moisture. Following these precautions, there is little or no concern regarding the shelf life of the stored resins. So, with reasonable care, IX resins can be stored for five years or longer without any ill effects.

Circumstances Affecting Resin Conditions

Freezing and Thawing

During the shipment to and storage in areas where temperatures drop below 0 ˚C (32 ˚F), storage precautions should be taken to avoid subjecting IX resins to repeated freezing-thawing conditions. Although a few such cycles are generally harmless, repeated freezing and thawing of IX resins, regardless of the forms in which they are supplied, could physically damage the IX resin by cracking or breaking the resin beads. It takes about 10 freeze-thaw cycles before damage is noticeable, so a single episode of freezing is not a calamity. Frozen resin should be brought to a warm area and allowed to thaw before use. Do not plunge frozen resin into boiling hot water, as this can instantly crack and break beads.

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Hot Resin

Temperatures above 105 ˚F do not damage most resins chemically, although exceptions exist. Elevated temperatures, however, increase the rate at which organic leachables form in the resin, which can then complicate preconditioning requirements prior to use. Any resin that has been subjected to elevated temperatures during storage should be rinsed to waste before use. If the high temperature exposure was longer than a few days, it is a good idea to have the resin analyzed, just to make sure it has not been damaged, especially if the use is ultrapure water or if the downstream processes that use the treated water are of critical importance.

Dry Resin

Almost all resins are shipped in their moist water swollen forms. Although they may lose significant amounts of moisture and appear dehydrated, sufficient water usually remains inside the beads to prevent physical breakage when the resin is rehydrated. While air-dried resin usually will not fracture when rewetted, excessive contact with air causes chemical damage over time and a consequent increase in leachables. Physical damage due to rehydration may occur in cases of extreme moisture loss during storage. For these reasons, resins should remain moist during storage. Resins stored in unlined bulk sacks or fiber drums are far more susceptible to dehydration than resins stored in more robust packaging.

Precautions Before Using a Stored Resin

Before using any resin that has been stored for more than a few months, it is a good practice to soak the resin in water for a few hours and then rinse it thoroughly. Soaking allows the IX resins to swell back to their original volume slowly and to release any organic contaminants from the resin structure. Rinsing before use purges the organic contaminants. A four-hour soak is sufficient, although overnight is better if time permits. Rinse volume should be sufficient to rinse out any color throw plus some extra. Ten bed volumes (BVs) (75 gallons per cubic foot) are recommended for most applications, 20 BVs are suggested for resins used in potable or ultrapure water treatment applications.

Pro tip: Where onsite rinsing is not possible, either delay shipment until just before use or use a third-party supplier to rinse the resin for you.

Special Requirements for Hydroxide and Sulfite Anion Resin Forms

Hydroxide-form strongly basic anion resins undergo a slow decomposition during storage. This reaction is temperature dependent and occurs more rapidly in Type 2 anion resins than in Type 1 anion resins.

Sulfite-form strongly basic anion resins, unless stored in a way that prevents exposure to air, gradually convert from the sulfite form to the sulfate form (thus diminishing their ability to remove oxygen from water). The shelf life of these products is limited and is highly dependent on storage conditions. Consequently, no exact shelf life can be stated.

Sulfite-form anion resin and hydroxide-form Type 2 anion resins older than three months and hydroxide-form Type 1 anion resins older than 12 months, unless stored in gas barrier packaging, should be tested prior to use to verify they remain usable.

Resin Shelf Life

Shelf life relates to the resin type, ionic form, storage conditions, and customer expectations for use. For instance, potable water resins that develop an odor or taste during storage are often no longer suitable for use without extensive reprocessing, even though their chemical and physical characteristics are still "like new." For regenerated resins and resins used in ultrapure applications, packaging in gas barrier liners can greatly extend usable life. Table 1 provides a guideline for the acceptable length of resin storage.

Table 1: Guideline on acceptable resin storage length.

Storage method	Outdoor, covered with tarp	Indoor, not temperature controlled	Indoor and climate controlled	Climate controlled in gas barrier packaging
Na form SAC	1 to 2 years	2 to 5 years	5 to 10 years	> 10 years
Cl form SBA	1 to 2 years	2 to 5 years	5 to 10 years	> 10 years
H form SAC	1 to 2 years	2 to 5 years	5 to 10 years	> 10 years
OH form type I SBA	1 year	1 to 2 years	2 to 5 years	> 5 years
OH form type II SBA	NR*	0.25 years	0.5 years	1 to 2 years
H or Na form WAC	1 to 2 years	2 to 5 years	5 to 10 years	> 10 years
WBA any kind	1 to 2 years	2 to 5 years	5 to 10 years	> 10 years
Chelating resins	1 to 2 years	2 to 5 years	5 to 10 years	> 10 years
Mixed Bed	1 year	1 to 2 years	2 to 5 years	> 5 years
Ultrapure mixed bed	NR	1 year	1 to 2 years	2 to 5 years
Sulfite form SBA	NR	0.1 year	0.5 years	1 year
Cl form Acrylic SBA	NR	1 year	2 to 5 years	> 5 years
OH form Acrylic SBA	NR	0.5 years	Year	>1 year

Table Notes:
NR = Not Recommended
SAC = Strongly acidic cation resin
SBA = Strongly basic anion resin
WAC = Weakly acidic cation resin
WBA = Weakly basic anion resin

Regenerated resins deteriorate more rapidly in air than when protected from gas transfer. Hydroxide form anion resins absorb carbon dioxide (CO_2) from air and become exhausted. All resins develop leachables over time that may make them unusable for some applications or require reprocessing prior to use.

Changes as Resin Ages

Aside from possible dehydration and freeze damage, several other changes occur as resin ages. Mostly, these changes have to do with leachable formation and loss of functional groups. SAC resins gradually desulfonate, releasing sulfuric acid and aromatic sulfonic acids that separate from the polymer backbone. These acids remain trapped in the resin beads until the beads meet water, and then are released.

SBA resins release amines rather than acids. Anion degradation is somewhat faster than cation breakdown, particularly for anion resins in the hydroxide form. Since amines are somewhat volatile, older anion resins that have been kept in sealed containers (especially if stored in the hydroxide form) can release amines to the air well above Occupational Health and Safety Administration (OHSA) guidelines.

Mixed beds are "self-neutralizing." The cationic leachables are absorbed by the anion component, and the anionic leachables are absorbed by the cation component. Both components gradually exhaust the mixed resin, lowering the amount of regenerated capacity remaining.

All resins (except those stored in inert gas) gradually decompose, their plastic structure slowly weakening from exposure to oxygen. Degraded resins release bits and pieces of lower molecular weight (mwt) polymer as well as oxidative byproducts. *(Note: Molecular weight is the sum of the atomic weights of all the atoms in a molecule.)*

Leachables build up over time, requiring longer and more extensive rinses and possibly regeneration to purge them before use. Many cationic leachables foul anion resin and anionic leachables foul cation resin. Resins used in series that are not fully rinsed are therefore susceptible to fouling related to storage.

Over very long periods of time, drum liners, and even drums and bulk sacks themselves, begin to deteriorate. Packaging older than 10 years is at risk of shedding into the resin. For this reason, 10 years is generally considered the outer limit for resin storage, except under ideal storage conditions.

Storage of Used Resin

Outside the Vessel

If the resins are to be removed from the IX vessels for long-term storage, it is best if they are first fully exhausted or converted to their neutral salt form, drained of excess water, and placed in watertight containers, such as plastic drums with liners and locking ring seals, like those used for shipping new resin.

Steel drums are not recommended because of the risk that the resin will corrode the steel and then be contaminated by the rust. Fiber drums are not recommended because even a tiny hole will allow water to wet and weaken the fiber. For strong cation resin and strong anion resins, storage in the sodium and chloride forms is best, but almost any pH-neutral salt form is acceptable. Although resins can be stored in the hydrogen and hydroxide forms, shelf life is limited and handling a bit more difficult.

When storing used resins outside the vessel, follow the same general guidelines for storage of new resins.

Inside the Vessel

Unless the IX system is going to be shut down for more than a few weeks, the best practice is simply to leave the vessels filled with water, with all valves to and from the unit turned off. If the system will be shut down for more than a few weeks, some form of storage preparation is recommended. Depending on the nature of the system, the following suggestions are offered for successful resin storage:

Softeners and salt-regenerated anion units. Rinse monthly with a minimum of one vessel volume clean feedwater. For units in series (such as a softener followed by a chloride cycle dealkalizer), rinse the lead unit to waste first, then use the effluent to rinse the second unit. Regenerate each unit before returning to service.

Separate-bed demineralizers (and other H- and OH-form units). Cation and anion resins can be left in the regenerated (H and OH) forms and rinsed at two- to four-week intervals in the following manner:

1. Rinse one vessel volume of raw water through the first vessel (usually the cation) to waste.

2. Using the effluent from the first vessel, rinse a vessel volume through the second vessel (usually the anion) to waste.

3. Continue with any other vessels in series, first rinsing the preceding vessels to waste and then thoroughly checking out of each downstream vessel in turn.

4. Regenerate each unit before returning to service.

Warning: Cation Leachables Foul Anion Resin

As time passes with no water flowing, leachable organic material will form in the cation resin. These leachables irreversibly foul anion resins. Rinsing the cation resin to waste first removes these organics and prevents fouling of the anion resin.

Mixed Beds

The cation and anion resins should be separated by backwashing before storage so that the cation and anion layers can be rinsed individually. A simultaneous rinse of both resin types (up through the cation resin and down through the anion resin, with both rinses exiting through the interface collector) at approximately one-month intervals will help ensure the resin remains unfouled during storage. Before a return to service, the resins should be regenerated, remixed, and rinsed.

Polishing Demineralizers

When polishing mixed beds or other polishing demineralizers are used in high-purity water (also known as ultrapure water) applications, the decision must be made whether it is worth the extra work to re-purify the resins for reuse. This must be compared with the additional degradation that will otherwise happen if the resins are not converted to stable salt forms prior to shut down and storage.

> **"Cold temperatures do not damage resin chemically; the risk is physical cracking and breakage of the resin beads."**

For ultrapure water applications it is probably best to leave the resins in their highly regenerated forms and simply rinse them periodically to keep leachables to a minimum. Polishing mixed beds have been stored for more than a year this way and still rinsed up well when returned to service. Each case should be taken on a specific basis.

It is important to keep all valves to and from the demineralizer vessels in the "off" position so that resins remain submerged in water, thus minimizing contact with oxygen and microbe-containing air.

Very Long Storage

For very long-term storage in the vessel, it is best to store the resins in their most stable ionic forms. This retards the buildup of leachable organic matter, minimizes oxidation degradation of the sulfonic acid or amine groups, and prolongs the functional life of the resin.

For SAC and SBA resins, the most stable form is the salt form, typically the sodium form for SAC resins and the chloride form for SBA resins. The weak acid and weak base resins are most stable in their regenerated forms, hydrogen form for WAC resins and free base form for WBA resins.

It is beyond the scope of this article to provide detailed instructions for exhausting or regenerating resin. However, as a general guideline, avoid sudden changes in pH or in concentration. When exhausting with salt, keep the concentration below 1%. If in doubt, consult knowledgeable sources before proceeding.

Freeze Protection During Storage

Cold temperatures do not damage resin chemically; the risk is physical cracking and breakage of the resin beads. Many climates are moderate enough to not freeze the water in a vessel. However, if freezing is possible, the water in the vessel should be drained as a precaution. Otherwise, the expansion as water freezes could damage the internals or even the vessel itself.

If freezing is likely, a simple remedy is to drain the water and refill with salt brine. A 10% sodium chloride solution offers protection down to approximately 20 °F (-6 °C). Saturated calcium chloride offers protection down to approximately -40 °F (-40 °C). Sodium chloride is less risky to use; use of calcium chloride requires any anion resin to be carefully neutralized so that any hydroxide form capacity is removed from the resin.

Following storage in salt solutions, the brine should be slowly rinsed out with water so that the osmotic swelling that occurs as the resin rehydrates is spread out over time. A minimum of one hour is recommended for the first vessel volume of water, and then any additional rinsing can be at any convenient flowrate.

After the salt is rinsed out, the resin should be allowed to soak in water for a few hours prior to being regenerated. The soak time allows salt that has diffused into the beads to come back out. Finally, be sure to rinse to less than 5 parts per million (ppm) hardness before regenerating anion units with sodium hydroxide, otherwise hardness fouling is likely.

Although organic solvents such as alcohols and glycols can be used to prevent freezing, their use is rather problematic. For one, disposal of the spent solution is a problem. For another, it takes extensive rinsing to remove all the solvent. Lastly, most glycols contain additives that can foul resin. All in all, salt brine is better.

Preventing Biogrowth During Storage

Several strategies, including sterilization techniques, can be used to prevent biogrowth during storage. Brine may be used to retard biogrowths. In this case, the resin beds are deliberately left in a brine solution, like that used for freeze protection. Instead of rinsing the brine out after exhausting the resins, additional brine can be introduced such that the brine concentration is approximately 5% and left in the brine until the resins are ready to be used again.

Prior to use, the brine must be thoroughly rinsed out of the units (each separately). Then the resin must be super regenerated to restore it to its fully regenerated form, charged and ready to use.

Other strategies for controlling biogrowths include storing the resin in an inert nitrogen atmosphere and using various chemical biocides. Oxidizing biocides are a bad bet; they damage the resin and are used up over time.

Many nonoxidizing biocides damage IX resin or are not compatible with downstream processes. Various alcohols can be used without risk to the resin but are time consuming to rinse out and may be problematic to dispose of. All in all, brine is likely as good an alternative as any.

In any event, storing resin in a way that retards biogrowths does not guarantee sterility. Sterilization procedures may still be needed before return to service.

Precautions Before Using Stored Resin

Always rinse resins before returning them to service. Regeneration is advisable, even if the resin was stored in the regenerated form. For IX units in series (such as softeners followed by dealkalizers, or hydrogen-form cation units followed by hydroxide-form anion units), rinse the first unit thoroughly before using the effluent to rinse the second unit. Pre-rinsing removes leachables that could otherwise foul the downstream exchangers.

Where resin use is critical to downstream processes and has been stored for a long time, it is advisable to pull samples a month or two before return to service. These resins should be analyzed to ensure that the resin remains suitable for use.

Closing Thoughts on Resin Storage

Some older storage instructions suggest storage in glycol, alcohol, or in various sterilizing solutions. In the author's opinion, these practices do not make sense. At best, it takes so much water to purge and dispose of the chemicals from the resin after storage that the cost exceeds that of new resin. At worst, the chemicals foul the resin and are potentially washed into downstream processes where they create additional problems. Table 2 provides a list of guidelines to aid the successful storage of new and used IX resin storage.

Table 2: Guidelines for successful IX resin storage.

• Store in original undamaged shipping containers
• Store in a well-ventilated storage area
• Protect from extremes of heat or cold (above freezing, below 105 °F)
• Protect from rain, sun, and other weather extremes

Figures 1 and 2 show examples of IX resins that could be stored.

Figure 1: Macroporous resin.

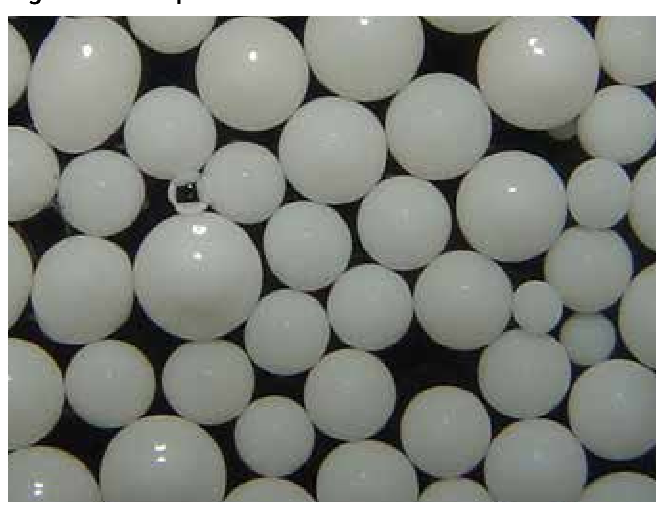
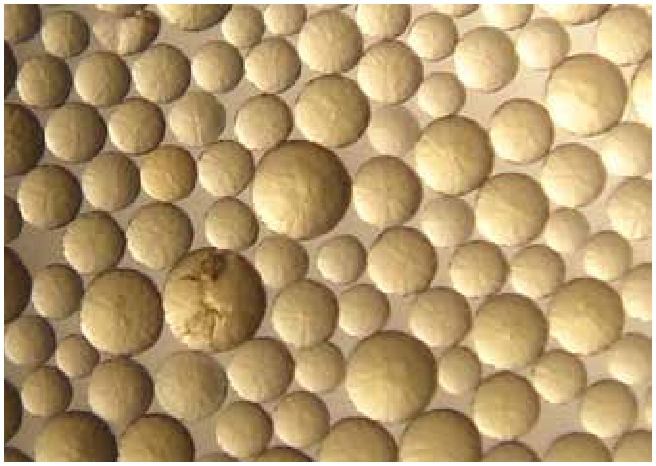


Figure 2: Sulfonated resin.



Closure

This discussion about the storage of ion exchange resins is the first part of this article series that describes the physical aspects of how resins are used. Other parts of the series include an introduction to using ion exchange resins; moving resins from place to place; and loading, unloading, disposal, and step-by-step procedure outlines.

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