O X I D A T I O N :

Oxidizers, Age and Softening Resins

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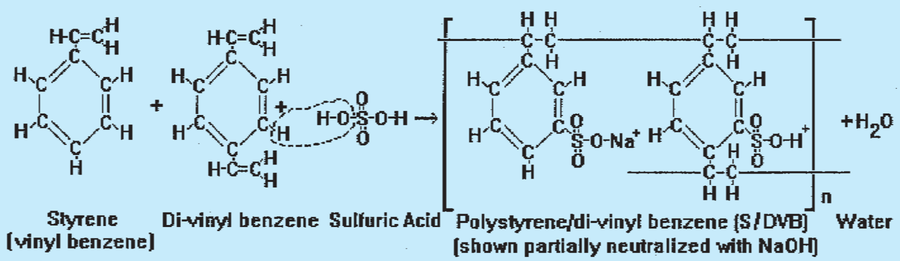
Summary: *Softener resins are reactive plastics. Oxidizers such as chlorine cause them to unzip and lose efficiency with age, as discussed below.*

It may be somewhat difficult to perceive an ion exchange softening resin as a "reactive plastic." Most of us think of plastic as an inert substance that's unaffected by corrosion (oxidation) or fatigue (embrittlement). However, ion exchange resins do oxidize and they do break down with time and use. This article takes a look at what happens physically and chemically as resins age.

Just as it was 50 years ago, ion exchange resin is the reactive heart of today's softener. The resins are plastic—consisting of polystyrene (S or vinyl benzene) held together with di-vinyl benzene (DVB) as the crosslinker. Resins get their spherical shape from their particular manufacturing process. Tiny droplets of monomer (the non-crosslinked liquid mono-styrene and DVB) suspended in water form spheres just like oil in water. Catalyzed and heated, these droplets polymerize into solids. These tiny solid beads, called copolymer beads, are crystal clear. To convert these copolymers to functional resins, the beads are reacted with a strong sulfuric acid solution that combines with the copolymer by attaching to the benzene ring of the styrene. Hence, the name sulfonated styrene / di-vinyl benzene—S / DVB for short. We now have a cation exchanger.

In the reaction process, these plastics acquire their familiar color (amber to brown to black). The color is incidental and has no effect or relationship to the quality, operating capacity or durability of the resulting resin. The sulfonated product swells greatly in water but doesn't dissolve (because of the crosslinking). This high water content allows ions such as calcium, magnesium and sodium to move inside the resin bead and "hook up" with millions of reactive sulfonated sites. Softening resins are highly porous on a molecular scale with wide-open structures and water-filled pores.

Figure 1. The inside look of cation resin



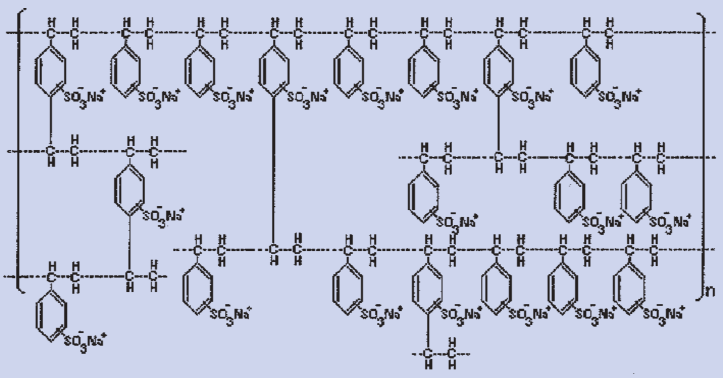
The role of crosslinking

Crosslinking plays an important role in the operation of a softening resin. The crosslinker level for softening resins may range from 6-to-10 percent DVB, with typical levels of 8 percent. As crosslinking goes up, the polymers are more restricted and don't swell as much. The resins are physically tougher and more compact. At higher crosslinking levels, there's less water in the bead and, therefore, more capacity per unit volume. Higher crosslinked resins have a high functional density and, subsequently, display higher selectivity for hardness compared to sodium. They also have a higher resistance to thermal deformation and can be used at higher temperatures. Many applications will exceed the 212°F (100°C) boiling point of water.

Crosslinking is a good thing but, like many things in life, too much is bad. The higher crosslinked resins have less moisture or water holding. Therefore, the pathways in and out of the beads are a little more congested. The kinetics are slower and regeneration more difficult, particularly in colder water (in a residential softener, they may be too slow to handle typical household flow rates). These resins will exhibit lower operating capacity as a result. The higher selectivity for hardness during service may be lost due to more difficult regeneration, requiring higher salt dosages and offering lower brine efficiency. All of the pluses of higher crosslinking may be given up as negatives to high flow rate softeners.

On the other hand, lower crosslinking levels produce resins with higher moisture and a more open structure. The lower crosslinked resins exhibit adequate selectivity for hardness, regenerate well and are quite efficient. Although physically weaker, they get by. Being lower in DVB, they're lower in cost. In many applications, they work well. On the downside, low crosslinked resins exhibit lower capacities and cannot physically handle excessive flow rates—10-to-15 gallons per minute per cubic foot (gpm / ft^3)—very well. They undergo greater deformation and higher pressure drops in hot or even warm water. This can lead to very high bead breakage and resin loss. In addition, they have marginal resistance to chlorine and other oxidants, even when new.

Figure 2. Highly crosslinked cation resin

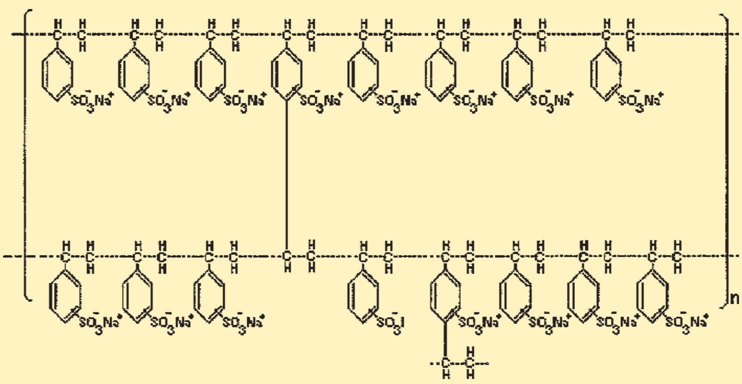


The 8-percent crosslinked resin has proven over the years to be close to optimum for residential applications. It represents the best combination of durability and kinetics and generally presents the best value for the majority of softening applications. Higher or lower crosslinked products should only be considered for applications that are out of the norm such as extremes of temperature or oxidant level or where selective removal of ionic species where they've demonstrated better performance.

Oxidizer sources

In recent years, more attention has been devoted to the disinfection methods used by municipalities. Chlorine remains the workhorse, but its reaction with natural organics and their by-products can produce chlorinated compounds called trihalomethanes (THMs). These are considered toxic. Stabilizing the chlorine with the addition of ammonia (NH_3) produces chloramines that are less reactive but have to generally be used at two to three times normal chlorine levels.[1]

Figure 3. Low crosslinked cation resin



Continuous exposure to high chlorine levels—above 1 part per million (ppm)—will speed the oxidation process resulting in more attack on and degradation of the resin. The general rule of thumb is the number 10 divided by the chlorine level (in ppm) predicts the resin life in years. Example: 1.5 ppm of chlorine (10 / 1.5) = 6.7 years. With the advent of higher chlorine levels, the "lifetime" warranty on resins is questionable. The presence of iron[2] or copper in feed water increases oxidation effects of chlorine. Before installing a softener, the dealer should look for telltale signs of iron or copper and try to determine whether it's from the feed water or the plumbing after the point of entry. Inspect bathroom plumbing (including the toilet tank) and look for brown, orange or greenish staining. If it's present, have a sample of the water checked from a water source outside the home. It's the feed source content that the softener will see. Consider a chlorine reduction filter such as granular activated carbon (GAC) or KDF if you have more than 0.5 ppm of iron or copper combined with more than 1 ppm of chlorine.

Fine mesh GAC can be layered on top of the softener resin on new installs, but there may not be enough freeboard in the softener tanks on retrofits. If you decide to add GAC, make sure you add enough to last several years—at least 0.5 cubic feet (ft^3) of 20×50 mesh. KDF can be retrofitted by placing it in a whole house cartridge ahead of the softener or inside the softener tanks with special cartridges designed for that purpose. Don't add KDF directly to the softener. It will drop to the bottom of the tank and won't protect the resin.

Figure 4. Predicting remaining life from moisture

Table 1. Effects of oxidation on softening resins

Lab Age (yrs.)	% Moisture	Total Capacity Dry meq/gm	Total Capacity Wet meq/ml	Volumetric Capacity Loss (%)	Density gms/ml	Swelling (%) Oxidation	Swelling (%) Ca—Na
0	48.7	4.55	1.94	—	0.837	—	1.8
1	49.0	4.55	1.94	—	0.832	0.80	2.3
3	50.5	4.50	1.85	4.64	0.824	5.6	6.3
9	57.1	4.45	1.54	21.1	0.806	16.0	8.6
11	61.1	4.48	1.38	29.4	0.793	32.0	10.5
13	66.9	4.56	1.13	41.8	0.749	33.2	12.7

The aging process

As resins age (oxidize), they begin to show an increased moisture content (swelling) due to the oxidative attack on the crosslinker and they become weaker.[3] The physical and osmotic stress of regeneration begins to break up the resin producing fines. These fines are backwashed out of the bed with each regeneration and a loss of capacity results. Remaining resin may occupy the same bed volume because of swelling. Therefore, the attrition may not be readily apparent. With the decrease in capacity, salt efficiency drops and operating costs increase.

In round numbers, new 8 percent DVB resin starts out at around 49 percent moisture. It has a capacity of 1.9-to-2.0 milliequivalents per milliliter (meq / ml), which translates to some 41-to-43 kilograins per cubic foot (kgr / ft^3). If we use 8 pounds of salt per cubic foot (lbs / ft^3) to regenerate this resin, we can expect a capacity of about 24-to-25 kgr / ft^3. Ten years down the road and after seeing a few million gallons of chlorinated water, the moisture content can rise to 60 percent or more. Moisture holding is so closely tied to crosslink level and capacity that some manufacturers test the "residual" life of resin simply by doing a moisture check. Figure 4 shows the relationship between moisture holding, apparent crosslink level and remaining life expectancy.[4]

In our 10-year-old example, the capacity has now dropped to 1.4 meq / ml (29 kgr / ft^3), a 30 percent loss (see *Table 1*).[5] Regeneration is more frequent now and, thus, the salt usage has increased. If this system regenerated once per day when new, the added salt consumption would be 876 pounds per year (assuming 8 lbs / ft^3). At 10 cents per pound from the local market, the consumer is spending an additional $87.60 / yr for soft water! Even if regeneration was every other day the cost has gone up by $43.80 / yr. The general consensus among resin manufacturers is that once a resin has gone beyond the 60 percent moisture level, the rapid degradation and added high salt expense are enough to justify replacement.

The article's beginning mentions higher crosslinked resin has higher selectivity. Older resin has lost some of its crosslinking potential due to oxidation. Does that also mean it has lower selectivity? The answer is yes! In our 10-year-old example, the older resin actually exhibits 38 percent higher leakage than new resin (see *Table 2*). Regeneration levels for this were at 5 lbs NaCl / ft^3.

Older resin has to work harder

The annual operational cost of resin (higher salt usage) goes up with time while the resin is seemingly doing less work (higher leakage). The stress placed on the resin also increases. New resin swells about 1.8 percent in converting from the calcium (exhausted)

Table 2. Effects of oxidation on softening resin performance

Lab Age (yrs)	Operating Cap (kgr/cu. ft.) End	Operating Cap (kgr/cu. ft.) Break	Average Leakage ppm as CaCO3	Strength (gms/bead)	Strength Loss (%)	Volumetric (psi/ft. bed depth) 10 gpm	Volumetric (psi/ft. bed depth) 20 gpm
0	19.4	15.2	13.5	283	—	1.0	2.3
1	19.0	14.6	15.8	284	—	1.0	2.3
3	18.6	14.7	15.5	188	33.8	1.0	2.4
9	16.8	13.9	18.6	146	48.6	1.1	2.5
11	16.4	13.6	18.4	121	57.4	1.6	4.5
13	15.6	12.2	17.3	68	76.1	1.7	4.8

to the sodium form (regenerated). Our aged resin swells about 10 percent. This causes more structural fatigue and more fracturing. Density has dropped from 0.837 grams per milliliter (gm / ml) to 0.793 gm / ml, so the same backwash flow carries away more resin and larger fines. The new resin could withstand almost 300 grams of force before being crushed. Our veteran breaks down at 130 grams. At 10-to-20 gpm / ft^2 flows typical of residential systems, the older resin exhibits twice the pressure drop of new resin (see *Table 2*).[5]

Conclusions

If our 10-year-old resin were an employee at your company, you would complain that as he / she had gotten older, they became less productive, less proficient, less tolerant, more demanding, more resistant to change and demanded a higher salary. If this were your employee, what would you do?

Although softening resin never dies, there's a point every 10 to 15 years on a typical residential application with less than 1 ppm of chlorine that it should be replaced. For commercial installations with frequent regenerations, 8-to-10-year lives produce 80 percent of original performance with a slight increase in costs. Industrial systems are usually designed with more conservative flow rates and lower leakage expectations. Use industrial grade resins (higher crosslinked) for industrial applications. The cost is a little higher up front, but an 8-to-10 year useful life is achievable while maintaining good leakage and strength characteristics. The best advice is to match your resin needs to the application.

References

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