LENNTECH
info@lenntech.com Tel. +31-152-610-900
www.lenntech.com Fax. +31-152-616-289

Dow
Liquid Separations

DOWEX™ Ion Exchange Resins

# The Advantages of Uniform Particle Sized Ion Exchange Resins

March 2006

## Description

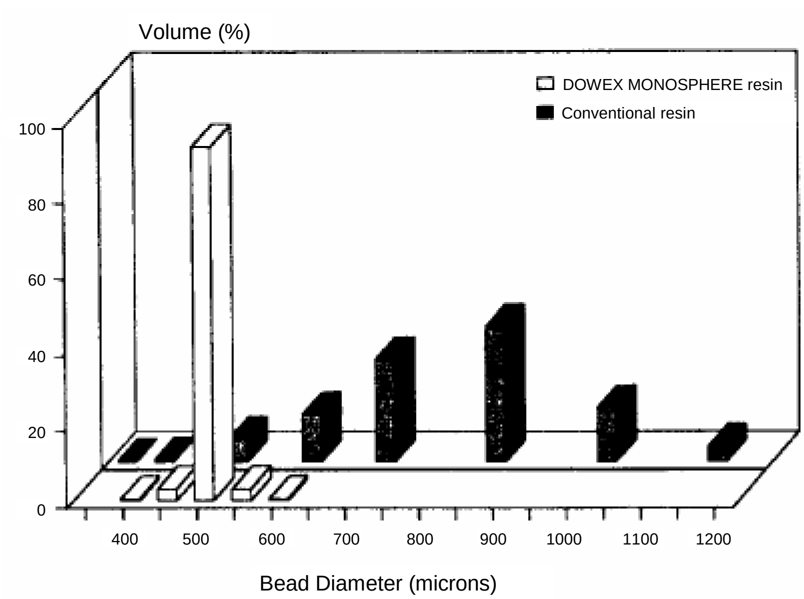
The technology for the manufacture of ion exchange resins has changed little since the development of the first synthetic styrene-divinylbenzene resins in the 40's. The production of resins in a stirred reactor results in the formation of resin beads with a polydispersed particle-sized distribution. Although new resin product development has been limited by this manufacturing process, ion exchange process application technology continued to develop with the introduction of e.g. mixed beds, layered beds and packed bed systems. In an attempt to overcome the disadvantages of a polydispersed bead distribution and to provide products to meet the increasingly demanding requirements of these application technologies, these resins had to be graded and screened.

With the introduction of uniform particle-sized resins by DOW in the 80's, the opportunity has now opened up to tailor resins and optimize their performance to meet the requirements of each specific application. This paper describes the properties of uniform particle-sized resins and demonstrates their improved performance over conventional resins in a number of application areas.

In contrast to the stirred reactor process, DOWEX™ MARATHON™ and DOWEX MONOSPHERE™ resins are manufactured directly as uniform beads. They are not screened from conventional resins. They have a high degree of bead size uniformity with 90 to 95 percent of the beads within ±50 µm of the mean diameter, and are typically made with a mean diameter in the range 300 to 1000 µm. This difference in particle size distribution is illustrated in Figure 1 for a conventional polydispersed resin and a 500 µm uniform particle-sized resin.

Screening of conventional resins is another possible method for producing uniform particle-sized resins. This procedure has a number of disadvantages for the resin manufacturer, however. In order to minimize costs, the resulting coarse and fine fractions would have to be blended, thereby compromising the quality of other resin batches. Any uniform resin produced by screening will, of course, retain the intrinsic characteristic of the original base product. Screening will not improve the mechanical stability of the resin and is in fact likely to cause increased resin damage. The improved mechanical properties are imparted to DOWEX MARATHON and DOWEX MONOSPHERE resins as a result of the manufacturing process.

**Figure 1. Particle size distribution of conventional and DOWEX MONOSPHERE resins**



## Resin Properties

The performance of an ion exchange resin is dependent upon a number of factors including the nature of the solution to be treated, the resin matrix type and the chemistry of the functional groups. The importance of resin bead size is widely described in the technical literature[1], [2], [3], [4] and is a direct consequence of mass transfer effects as described below.

### Ion Exchange Kinetics

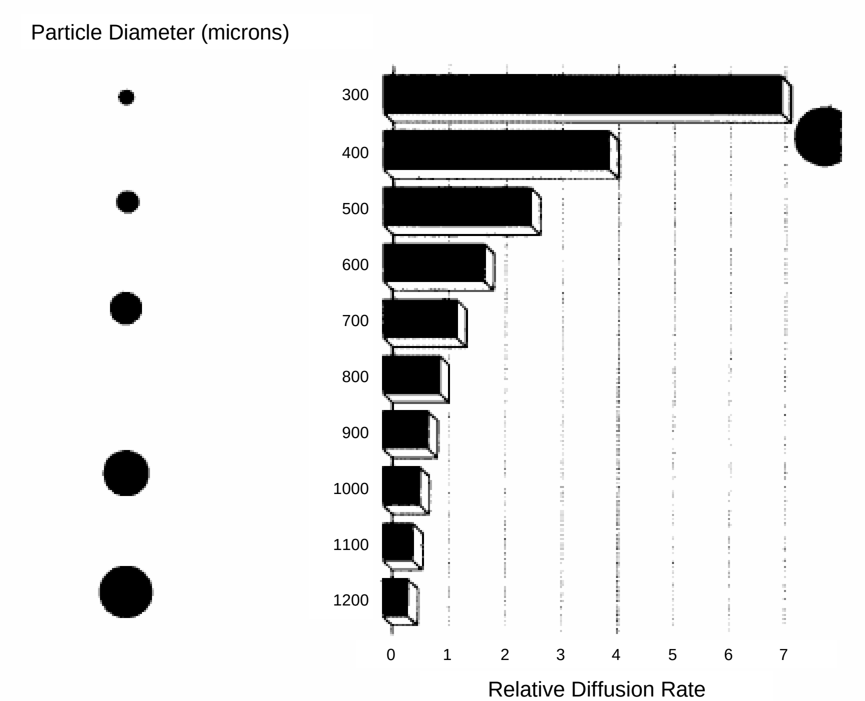
One of the major factors controlling the ion exchange reaction is the diffusion time required for the equilibrium of ions: between liquid phase and solid phase. The transfer of ions is diffusion controlled and described by the Fick equation[1]. There are three basic steps to consider:

a. Ion transfer from the bulk of the solution to the static boundary layer (film) surrounding the resin bead. This process is independent of the size of the resin beads.
b. Ion transfer through the film to the bead surface. The rate of this film diffusion process is a function of $1/r$ (where $r$ is the bead radius). During loading, the ion presentation rate to the resin bead is faster than the ion diffusion rate through the surface film. With smaller resin beads, the surface area is larger and the film diffusion rate is increased.
c. Ion transfer within the bead. The rate of this particle diffusion process is a function of $1/r^2$. In the regeneration phase, the increased ion concentration in the solution increases the diffusion rate through the film, and particle diffusion then becomes the limiting factor. Smaller resin beads have a shorter path within the solid phase and the particle diffusion rate is increased.

The consequence of reducing the bead size, therefore, is to improve the resin kinetics in both the loading (b) and regeneration (c) phases. The advantages of the small beads in a Gaussian distribution are not realized due to the presence of kinetically slower larger beads.

Figure 2 illustrates the relative particle diffusion rates as a function of bead diameter. As the diameter is reduced from the normal Gaussian mean value of between 700 and 800 µm, down to 300 - 600 µm, the diffusion rates increase substantially.

**Figure 2. Relative particle diffusion rates at different bead diameters**



## Mechanical and Chemical Stability

Standard tests and resin friability (stress), attrition (shear) and osmotic shock (shrink/swell) show that DOWEX™ MARATHON™ and DOWEX MONOSPHERE™ resins have higher mechanical stability than conventional resins. This can be attributed in part to the resin matrix structure (degree of cross-linking) and to the manufacturing process which imposes less mechanical damage to the resin beads. A summary is given in Table 1.

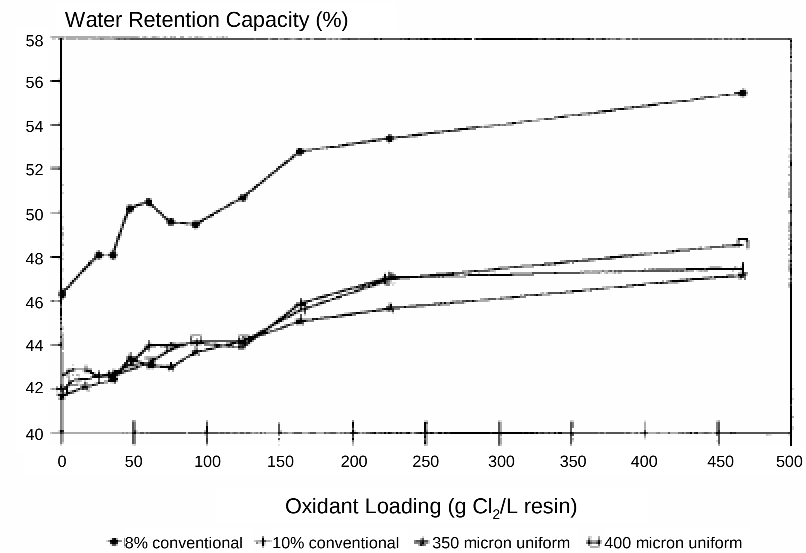
The improved mechanical and chemical properties result in a longer resin life and significantly fewer fines generation during operation.

Figure 3 shows the results of an oxidation stability test of two cation resins of 350 and 400 µm bead size (DOWEX MONOSPHERE C-350 and C-400) against 8 percent and 10 percent equivalent cross-linked conventional resins. Oxidative degradation of the uniform particle sized resins (measured by the increase in water retention capacity) is significantly less than for the 8 percent resin and is comparable to the 10 percent conventional resin.

**Table 1. Comparison of mechanical stability of conventional and uniform particle sized resins**

| | Conventional gel resins | DOWEX MONOSPHERE gel resins | Conventional macroporous resins |
|---|---|---|---|
| Friability (crush) (g/bead) | 400 - 700 | 600 - 800 | 400 - 800 |
| Bead sphericity after attrition | 75 - 95 | 98 | 60 - 85 |
| Bead sphericity after osmotic cycling with acid and NaOH | 50 - 95 (2N) | 95 - 99 (2N) | 95 (8N) |

**Figure 3. Oxidative resistance of uniform and conventional cation exchange resins**

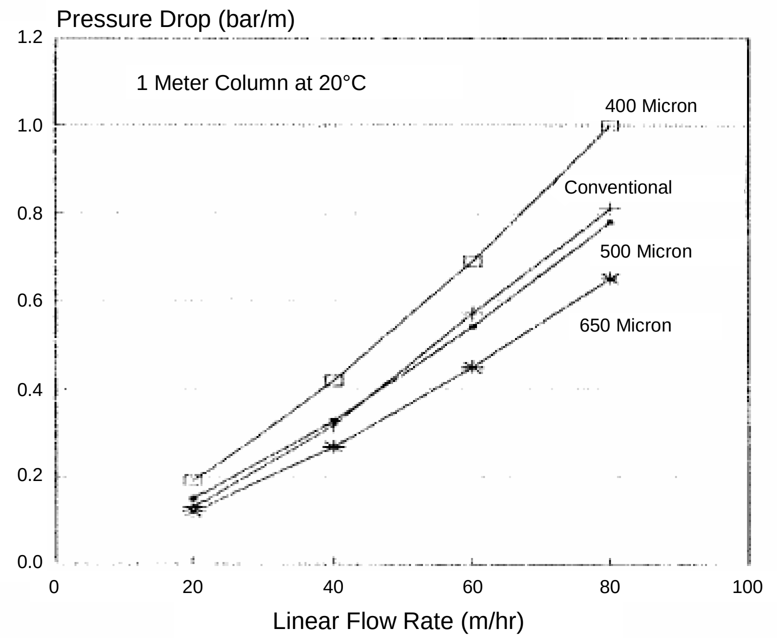



 ™® Trademark of The Dow Chemical Company ("Dow") or an affiliated company of Dow 

### Hydraulic Properties

Head loss ($\Delta P$) in a column of resin beads is described by the Leva equation[5]. Important factors relating to the resin itself are the bead diameter and the bed void fraction. The presence of smaller beads in a polydispersed resin results in filling of the interstitial spaces between the larger beads, thereby reducing the void fraction and increasing the head loss. This effect cancels the advantage of the larger mean diameter of the polydispersed resins, so that the small bed uniform particle sized resins have similar head loss characteristics to conventional resins. This is shown in Figure 4.

**Figure 4. Head loss data for uniform and conventional resins as a function of linear flow rate**




## Resin Performance

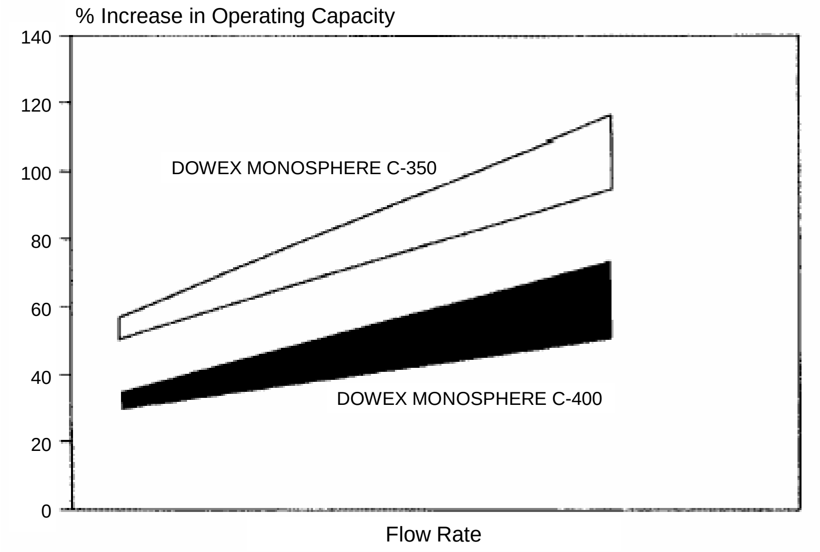
The advantage of uniform particle sized resins over conventional resins have been demonstrated both in the laboratory and in working plants in a number of applications using a wide range of operating conditions. Three major application areas are described in the following sections as examples to illustrate the benefits of these resins.

### Softening

Traditionally, softener units operate with a large excess of regenerant (typically over 250 percent of stoichiometry) and at low service flow rates (below 40 BV/h). The fast kinetics of small bead uniform particle sized resins challenge this technology by offering the possibility to run smaller units at high flow rates and with greatly improved chemical efficiency. This results in a substantial reduction of regenerant waste to the environment (3-5 fold at 70-200 g/L). Hardness leakage is also minimized by the improved kinetics of the small bead resins.

In comparative studies between 350 and 400 µm resins against conventional resins, increases in operating capacity of 30 to 100 percent can be achieved over conventional resins depending an the particular operating conditions used. This advantage is illustrated in Figure 5 by the continuously improving performance over conventional resins as the flow rate increases. This insensitivity to flow rate allows uniform particle sized resins to operate effectively over a wide range of conditions.

**Figure 5. Increase in operating capacity of uniform resins over conventional resins in softening**

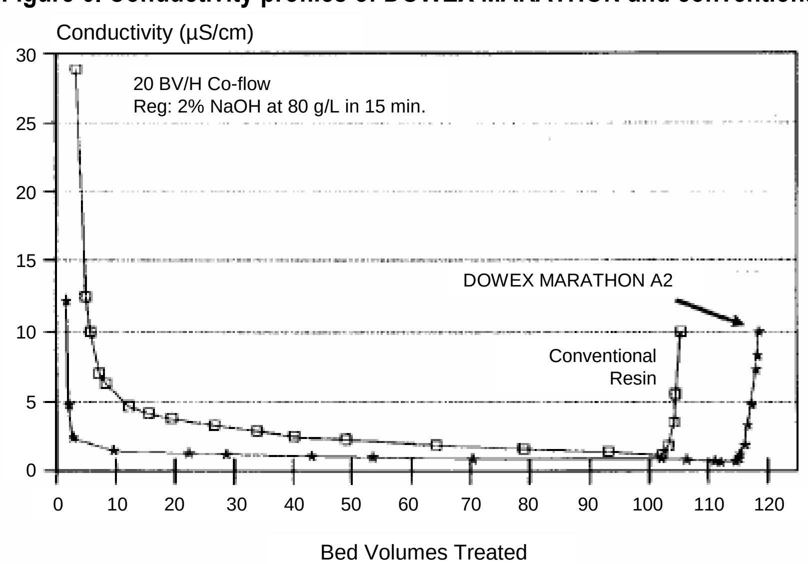



## Water Demineralization

Comparative studies of uniform particle sized resins against conventional resins in water demineralization show the same advantages as demonstrated in water softening in terms of higher chemical efficiency, operating capacity and rinse characteristics, together with better effluent quality. These effects are shown in Figure 6 for co-flow conditions using the 520 µm type II anion resin DOWEX™ MARATHON™ A2 compared to a conventional resin at 20 BV/h.

Similar advantages can be demonstrated in counter-flow systems such as the packed bed up-flow regeneration process. Due to the increased regenerability of DOWEX UPCORE™ Mono resins over conventional grades, regenerant savings of 20-25% on the cation and 15% on the anion can be made compared to a system with conventional resins. This is achieved on the basis of the same plant capacity.

**Figure 6. Conductivity profiles of DOWEX MARATHON and conventional anion resins in demineralization**

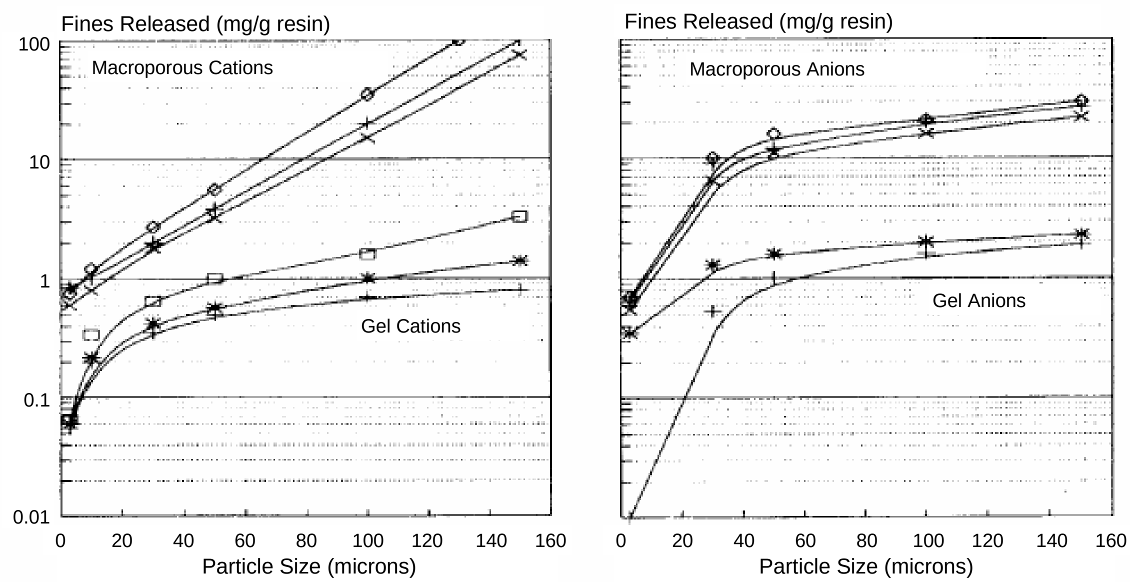


## Ultrapure Water for the Electronics Industry

The manufacture of solid state electronic components requires water of near-theoretical purity (18+ MΩ cm). In addition to ionic species, particulate matter and total organic carbon (TOC) levels are critical in defining the water quality. In order to produce such water, ion exchange resins are used in working mixed beds in the primary demineralization line to remove most TDS and in polishing cartridges in the (secondary) recirculation loop to provide the necessary final water quality prior to point of use.

These two applications place quite different demands upon the ion exchange resins. The working mixed beds must exhibit high operating capacities, good separability and regenerability, mechanical strength and resistance to fouling. Osmotically induced resin stress caused by cross contamination by regenerants has led to the use of conventional macroporous resins in the past for working mixed bed applications. These resins are notorious, however, in undergoing attrition damage, and releasing resin fines into the effluent stream. This is clearly illustrated in Figure 7 where attrition in both gel and macroporous resins are compared. The gel matrix is superior for both cation and anion resin types.

**Figure 7. Particulates release from gel and macroporous resins**




By using gel resins with uniform particle size, the additional advantages of higher operating capacities and better regenerability are combined with optimum separation and minimum cross contamination and osmotic damage.

The requirements for the polishing cartridges are quite different from the working mixed beds. Without the need to regenerate, it is important that the resins remain well-mixed during operation in order to maintain the equilibrium conditions between cation and anion. Any separation would compromise water quality. A low ionic loading means that operating capacity is a secondary consideration in this case. The ability to pick up and hold ions, low TOC and particle release, and short rinse of conductivity and TOC are the most critical parameters for the final water quality.

Uniform resin beads can be tailored to ensure that the resins remain mixed during operation. A 350 μm cation with a 550 μm anion (DOWEX™ MONOSPHERE™ MR-450 UPW resin) gives substantially better kinetic performance against a conventional mixed bed (Figure 8). Even at flow rates of over 400 BV/h, the effluent water quality remains excellent compared to the conventional mixed bed.

The ability of the uniform particle sized resins to remove organics is illustrated in Figure 9, where a series of TOC rinse down curves are shown for the DOWEX MONOSPHERE MR-450 UPW mixed bed resin. The test was carried out according to the AFNOR method[6] involving a 20 bed volume pre-rinse followed by a 24 hour soaking of the resin. The subsequent rinse was continued and finally the feed was loaded with 500 ppb TOC.

**Figure 8. Kinetic evaluation of conventional and DOWEX™ MONOSPHERE™ MR-450 UPW mixed bed grade resins: flow rate vs. effluent conductivity**

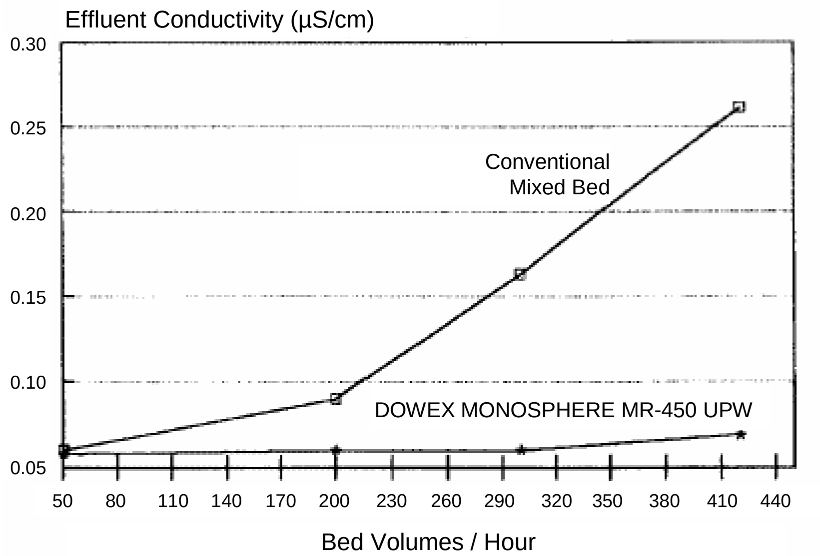
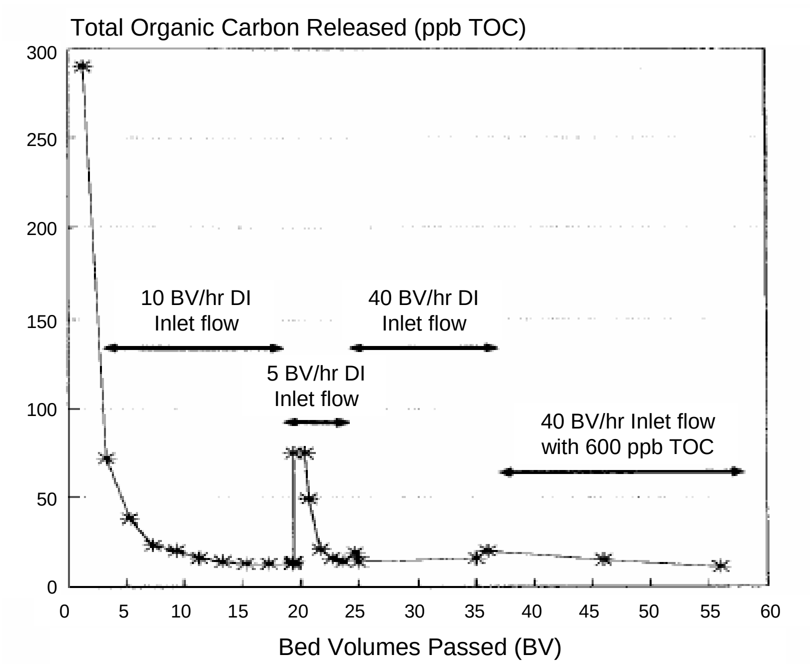


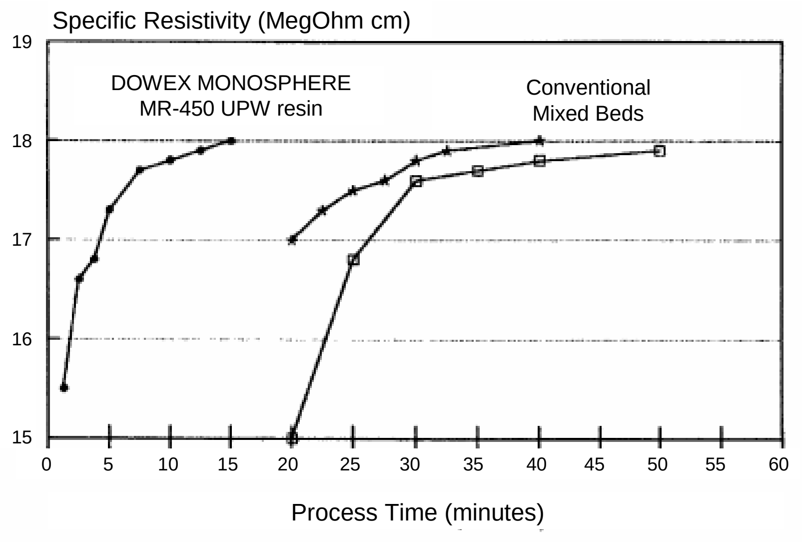

**Figure 9. TOC release from DOWEX MONOSPHERE MR-450 UPW resin using AFNOR PrT 90601 test and with 500 ppb TOC inlet feed**




The release of TOC from the resin under these extreme conditions was in the 10 ppb range, indicating excellent resin performance.

Ionic rinse down as shown in Figure 10 proves the conductivity profile of DOWEX™ MONOSPHERE™ MR-450 UPW resin to be shorter than conventional resin mixed beds. This is again a demonstration of the superior kinetics and results in saving both time and process water.

**Figure 10. Mixed bed rinse conductivity profiles of DOWEX™ MONOSPHERE™ MR-450 UPW resin and conventional mixed bed resins to 18 MΩ cm**




## Conclusions

The characteristics and properties of uniform particle sized resins have been described. The comparative test data given in this paper shows how these resins outperform conventional resins in all critical areas that are important in ion exchange resin applications:

- Chemical efficiency
- Operating capacity
- Organic reversibility
- Rinse down (TOC and conductivity)
- Effluent quality
- Mechanical/chemical stability
- Separability (in mixed beds)

As requirements for high quality water become more stringent and the need to provide highly efficient plants with minimal waste effluent intensifies, increasing demands will be made upon ion exchange resins in the future. Uniform particle sized resins offer the possibility to meet these challenges.

## References

(1) Ion exchange Technology F.C. Nachod; S. Schubert 1956 p.68.
(2) Water Purification by ion exchange TV Arden 1968 p. 41.
(3) Separation par echangeur d'ions Tremillon 1965 p. 64.
(4) R. R. Harries; CEGB The role of pH in ion exchange kinetics; SCI Cambridge 1988 presentation.
(5) Leva, Chem. Eng. 56 (5) 1 15-1 17 (1949).
(6) AFNOR PrT 90601 test.

**Dow Liquid Separations Offices.**
**For more information call Dow Liquid Separations:**

LENNTECH

info@lenntech.com Tel. +31-152-610-900
www.lenntech.com Fax. +31-152-616-289

Notice: Oxidizing agents such as nitric acid attack organic ion exchange resins under certain conditions. This could lead to anything from slight resin degradation to a violent exothermic reaction (explosion). Before using strong oxidizing agents, consult sources knowledgeable in handling such materials.



  Form No. 177-01842-0306