Oct. 19, 1965 D. S. GOWERS ET AL 3,213,016

ION EXCHANGE PROCESS

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Fig. 1

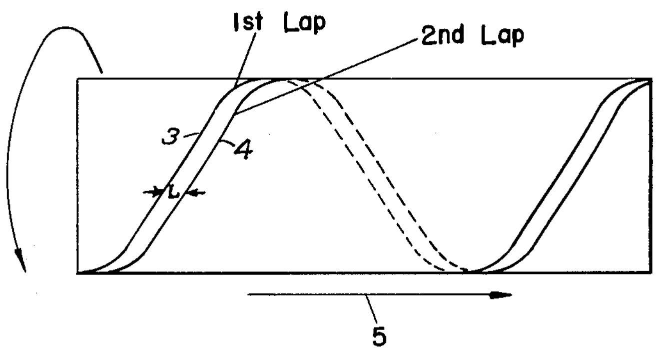

Fig. 3

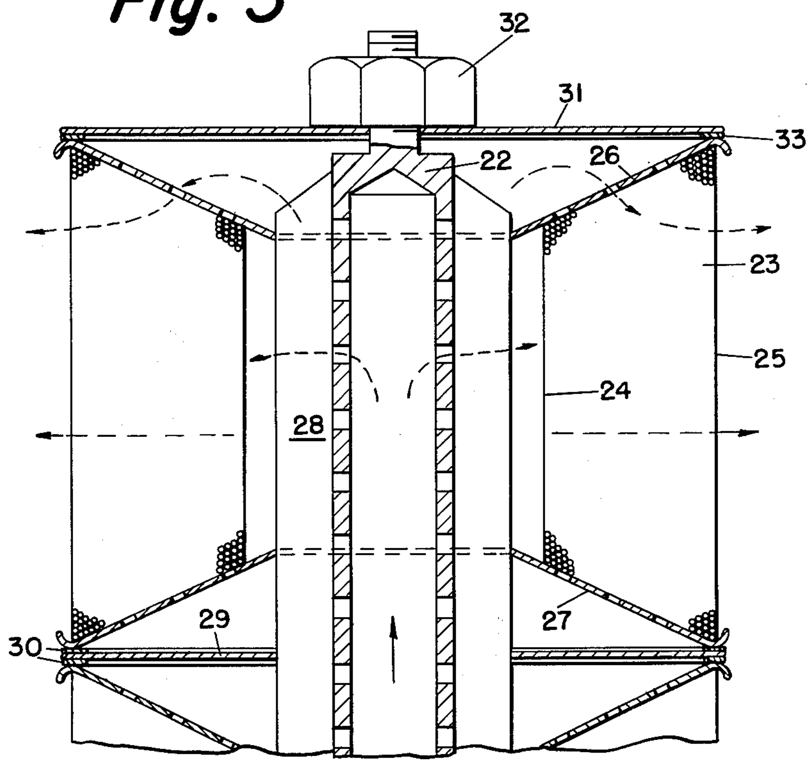

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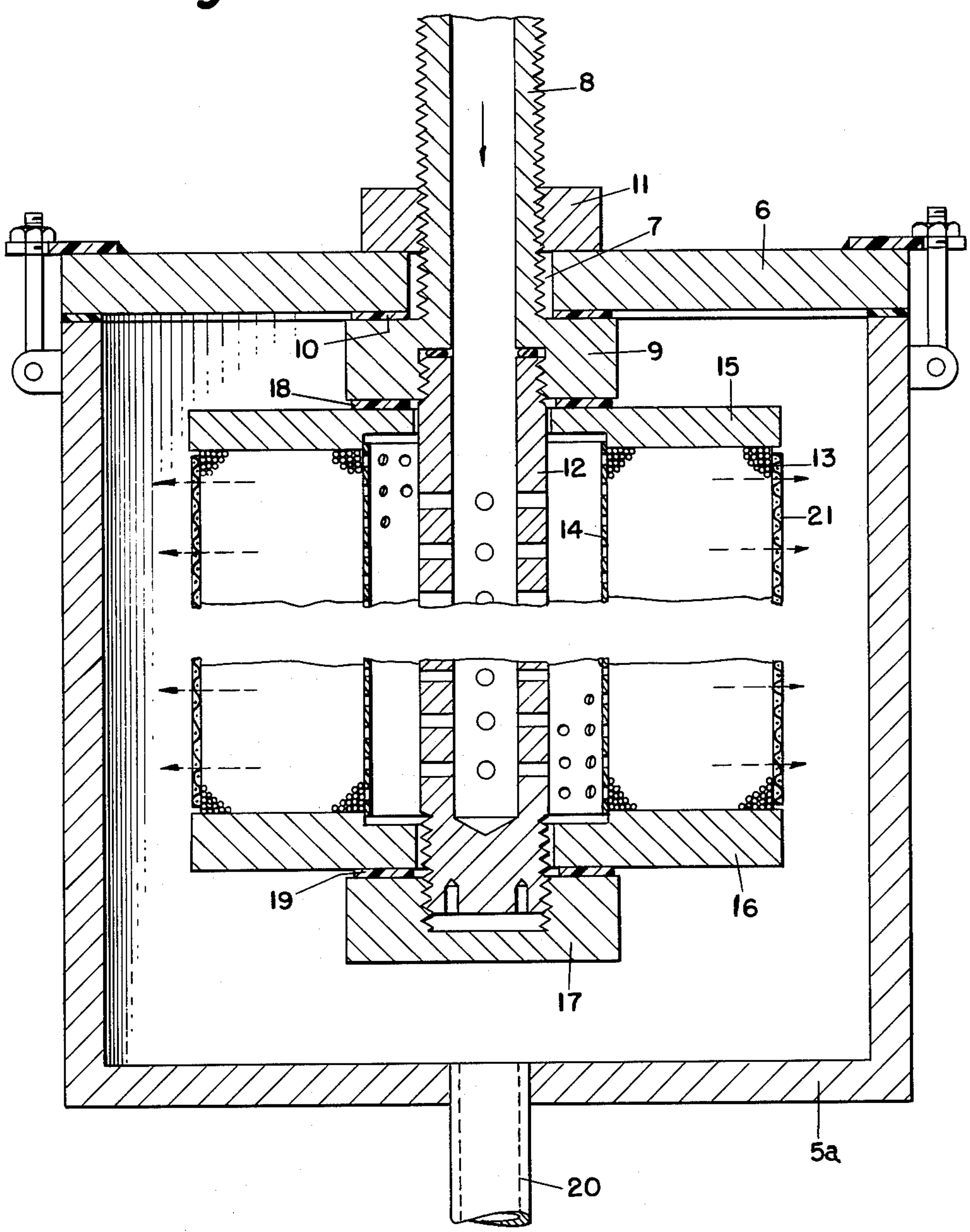
Fig. 2



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3,213,016
ION EXCHANGE PROCESS
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This invention is concerned with ion exchange processes. It is particularly concerned with an improved method for the removal of cations and/or anions from liquid systems, for example, in the purification of water or in the recovery of metals or other valuable substances from waste or by-product liquids.

Conventional ion exchange processes are normally carried out using a bed of ion exchange resins in the form of beads supported as a bed of 18 inches or more depth within a suitable housing to contain the liquid to be treated that is forced through the bed. Such systems generally require quite a large volume of resin beads and also in order to facilitate backwashing to remove any materials filtered through the system the housings containing the resin bed must be of considerable size including a head room space above the bed to allow the backwashing action.

In accordance with the present invention, it has been discovered that practical and efficient contact and exchange can be effected by passing the liquid containing the ions to be exchanged or removed through an annular winding or bobbin of a yarn formed of ion exchange fibers or filaments. Surprisingly, in spite of the fact that the thickness of the annulus through which the liquid flows is relatively small, highly efficient ion exchange and/or absorption is effected, and the operations can be controlled in such manner that a single passage of the liquid through such a winding provides adequate treatment of the liquid.

For the purpose of the invention, any of the multifilament yarns obtained by the processes described in U.S. Patent No. 2,933,460 may be employed. These filaments may be formed of any suitable ion exchange resin having cation exchange groups, such as carboxylic acid groups, sulfonic acid groups, phosphonic acid groups, or thiol groups. Similarly, the ion exchange fibers may be those containing any suitable anion exchange groups, such as amine, or quaternary ammonium groups. The ion exchange capacity of the filaments may be from 0.5 to about 3.5 milli-equivalents per gram or even as high as 5 or 6 meq. per gram. Preferred materials have at least 2.5 meq. per gram capacity. The size of the filaments may vary from 1 denier to 20 denier or higher. Preferred ranges are from about 2.5 to 10 denier. The size of the multifilament bundle or yarn may be from 25 to 3000 denier. The multifilament bundle may be completely without twist or it may have as much as 3 twists per inch length of the yarn. Lesser twist is desirable, particularly in the larger sized yarns, and, in general, it is preferred that the yarn contain no more than 1 twist per inch when the size of the yarn is greater than 75 denier and no greater than 1 twist in 4 inches length when the size of the yarn is greater than 200 denier.

The winding may be one which is formed on a perforated core of cylindrical or conical shape, or it may be a coreless winding such as is obtained by collection of the yarn in a centrifugal pot, such as is used in the rayon industry. The latter type of coreless winding is frequently referred to as a "cake." Preferably, the yarn is wound in a wet water-swollen condition so that as it is originally laid down in the bobbin it is in the approximate stage of swelling in which it is to be used. Desirably, also, the wound yarn should be stored in the aqueous system to retain it in the swollen condition until it is ready for use. The annular winding may be either of cylindrical or

conical shape. It is preferably provided with endwalls so that the thickness of the annuli at both ends of the winding are approximately of the same size regardless of whether the package is of cylindrical or conical shape. By so determining the thickness of the winding, the liquid passing through all parts of the winding is brought into contact with approximately the same surface area of ion exchange resin filament surface.

The lay, L, of the winding is chosen to provide a high degree of tortuosity to the path of flow of all the liquid that passes through the annular winding. The lay may be varied considerably and depends upon the particular size (diameter) of yarn or filamentary bundle used in making the winding. Generally, the separation between the yarn of one winding and the adjacent yarn of the next winding may be from about $\frac{1}{64}$ to $\frac{1}{8}$ of an inch to provide an optimum high degree of tortuosity of flow through the winding. For smaller diameter yarns, the lay may be from $\frac{1}{32}$ to $\frac{1}{16}$ of an inch, whereas for larger diameter yarns the lay may range up to $\frac{3}{16}$ of an inch. By lay is meant the distance parallel to the axis of the winding, between corresponding laps laid down by successive traverses of the guide. Either a headwind or an afterwind may be employed and the number of laps of yarn laid down in one traverse may vary widely from 2 to as high as 6 or 10 winds per traverse of the guide. The particular traverse used may be selected in conjunction with other factors such as the size of the yarn, the length of the wound package being formed, and the lay to aid in producing the desired high degree of tortuosity of flow through the winding. A 3 or 4 wind has been found quite practical for bobbins having a 6-inch width. The lay, the wind, and the size of the yarn are so correlated as to provide a high degree of tortuosity and to avoid open channels through the winding that would allow excessive channeling of the liquid to be treated. In general, also, the winding or wound package may have a void space of at least 25% and up to about 50%.

When the yarn is collected in the form of a cake, it may be desirable to insert an expansible perforated core or cuff within the interior wall of the cake to facilitate mounting of the cake on the liquid-distributing equipment which may be or may comprise a perforated pipe or sleeve. The liquid distributing system may comprise a manifold supplying a plurality of branch pipes having perforated walls upon each of which a plurality of cakes or bobbins may be mounted with their axes essentially concentric with the axis of the pipe. Each distributor pipe is provided with suitable flanges adapted to bear against the endwalls of the cakes or bobbins and retain them in position on the pipes. One of the endplates may preferably be resiliently urged against the cake wall in order to confine the cake tightly between the endplates.

Instead of mounting annular cakes in this fashion, an annular winding may be formed upon a perforated core which may be, but need not be, the liquid distributor-pipe itself. Alternatively, a cylindrical bobbin winding may be formed on a removable collapsible core which then may be removed and, if desired, replaced with a perforated core for mounting in the liquid-treating system. In general, the annular windings have endwalls which preferably lie in planes which are perpendicular to the axis of the winding. However, the winding may be formed on a core with sloped-end flanges so that the endwalls of the bobbin or winding lie in conical surfaces having their apices within the axis of the winding and between the endwalls of the winding. This gives rise to a package having tapered endwalls with the internal width of the package being narrower than the outer width.

For some purposes, the winding may be formed with a preliminary internal winding of glass yarn or of some other non-swellable inert yarn, for example, a yarn formed of polytetrafluoroethylene or polychlorotrifluoroethylene. This internal winding of an inert yarn which is not swelled by the liquid being treated serves as a distributor for the liquid and aids, in certain instances when the ion exchange filaments are extremely swellable, in keeping the conformation of the inside of the winding. Similarly, an external jacket winding of a similar inert polymeric or siliceous yarn may be wound on the outside of the winding, again for the purpose of aiding in retaining the configuration of the winding as a whole and assisting in the distribution of the liquid in the event it should be forced from the outside of the bobbin to the inside.

The liquid to be treated is forced through the annular winding from the interior wall to the exterior wall, or vice versa. Preferably, the liquid is forced from the inside to the outside. With this type of flow, there is a tendency to open up the winding and favor the flow with less build-up of pressure. Also, this system has the advantage of having reduced speed of flow past the windings at the end of the treatment because of the larger cross-sectional area through which the total liquid flows. After the liquid has been treated, a rinse liquid may be forced through the winding in the same or the opposite direction, and this may then be followed by a regenerating liquid, again in the same or opposite direction as desired. In those instances where a single pass through such a winding is inadequate to remove the entire amount of removable ions which are desired to be removed, the liquid may be passed through a battery or a series of such annular windings. The same is true of the rinse and regenerating liquids.

The system of the present invention has the advantage of utilizing ion exchange materials having a much greater surface for a given weight of material. Typical diameters of ion exchange beads in conventional systems are from 400 to 600 microns in wet condition, whereas typical filaments of the present invention may have diameters of 5 microns to 50 microns in wet condition. In the preferred system, wherein the liquid to be treated flows from the inside to the outside of the winding, the flow rate of the liquid drops as it moves outwardly. This has the advantage that the liquid is in contact with the yarns for a longer time at the stage near the end of the ion exchange operation where such longer contact is most desired and necessary to remove the ions which are, at that time, at a lower concentration in the liquid. Another advantage of the system of the present invention is the fact that the mounted bobbin may be centrifuged as a part of the liquid treatment to aid in the flow of the liquid from the interior through the annular winding during the ion exchange operation, during the rinsing, during the regeneration, or during all of these stages. The use of centrifuging action aids in uniform dispersal and distribution of the liquid through the windings.

These "bobbin type" installations may be used for a variety of ion exchange processes which include the dealkylization of water using a carboxylic type fiber, the softening of water using a sulfonic type fiber in the sodium form, and can be used in "two-bed" systems for the deionization of water by employing a bobbin employing a sulfonic type cation exchanger in the hydrogen form, the second bobbin containing a weak or strong base anion exchanger in the hydroxyl form. They may be used for the treatment of a variety of fluids, such as sugar solutions, streptomycin broths, glycerine solutions, etc.

In the drawing which is illustrative of the invention:

FIGURE 1 is a diagrammatic view of a cylindrical winding,

FIGURE 2 is a cross-sectional view of one embodiment of a liquid-treating arrangement, the section being through the axis of the winding, and

FIGURE 3 is a similar cross-section through a modified liquid-treating system.

FIGURE 1 shows the lay of a winding, the dimension L between the yarn 3 laid down by the previous traverse of the guide, and the adjacent lap 4 laid down on the last traverse of the guide. As stated hereinabove, this lay may amount to about 1/32 to 3/16 inch depending on the diameter of the yarn being wound. The lay, L, is selected to provide a separation between the edges of the yarns 3 and 4 equal to 1/64 to 1/8 inch or thereabout.

In FIGURE 2 there is shown a housing **5** provided with a lid **6**. The lid **6** has a port **7** receiving a hollow fitting **8** for the introduction of the liquid to be treated. The fitting **8** is provided with a flange **9** which bears against a sealing gasket **10**. The nut **11** is threaded over the exterior of the fitting **8** and serves to urge the flange **9** and the gasket **10** into a tight fit against the lid **6**. The flange **9** has a threaded recess adapted to receive a perforated pipe **12** having its interior communicating with the hollow interior of the fitting **8**. The pipe **12** is adapted to receive around its periphery a wound package of the ion exchange filaments consisting of the ion exchange filament winding **13** supported around a perforated cylindrical stainless steel core **14**. End plates **15** and **16** have annular surfaces bearing against the end surfaces of the winding **13** and these rigid annular plates **15** and **16** have central openings which allow them to be passed over the pipe **12**. A nut **17** is screwed upon the threaded end of the pipe **12** and serves to hold the winding in place. Gaskets **18** and **19** are provided to seal the inside of the wound package from the liquid in the housing **5**. The housing **5** has a discharge outlet **20** through which the treated liquid may be removed.

In the embodiment of FIGURE 2, there is also shown a perforated jacket **21** which may be formed of a glass yarn winding or of an expansible stainless steel mesh screen.

In FIGURE 3, a perforated distributor pipe **22** is shown carrying a plurality of packages of annular windings thereon. The annular winding **23** in this case consists of a cake, the interior wall **24** thereof being unsupported, and being of lesser width than the external wall **25**. The end walls are tapered or sloped, and rest upon perforated annular flanges **26** and **27**. If desired, these flanges may be perforated but they need not be. The pipe **22** is provided with three ribs **28**, spaced 120° apart around the periphery of the pipe and extending axially thereof, so that the inner edges of the flanges **26** and **27** are guided and supported thereon. Each pair of cakes are spaced apart by annular plates **29** and gaskets **30** are disposed between such spacer plates **29** and the flanges **26** and **27** of the windings. An end plate **31** carries an annular sealing gasket **33** at its outer rim and is held against the set of cakes by means of a nut **32**. This assembly is supported in a housing as in FIGURE 2, and the liquid to be treated is forced to the interior of the pipe **22**, and after flowing through the annular windings, is discharged from the housing to a point of collection such as a suitable receptacle or collecting vessel.

In the following examples which are illustrative of the invention, the parts and percentages are by weight unless otherwise indicated.

PREPARATION A

A strong acid-sulfonic, ion exchange fiber was prepared by soaking an 80/20 polystyrene-polybutadiene blend fiber in sulfuric acid in the manner described in Serial No. 846,777 (filed October 16, 1959, F. T. Fang, to Rohm & Haas Company) to give a cation exchange capacity of 2.5 meq./gm., based on the weight of the dry hydrogen form.

PREPARATION B

An anion exchange fiber was prepared by the procedure of Example 7 as described in U.S. 2,933,460 (filed May 29, 1956, by G. A. Richter et al.) to give an anion exchange capacity of about 2.2 meq./gm. A fiber comprising a copolymer of equal parts of acrylonitrile and methyl acrylate was converted to an anion exchange fiber using dimethylaminopropylamine.

PREPARATION C

A weak acid cation exchange fiber was prepared by the procedure of Example 1(*a*) as described in U.S. 2,933,460 (see Example B) to give a cation exchange capacity of about 3.2 meq./gm. based on the weight of the dry hydrogen form. The fiber comprising a terpolymer of acrylonitrile, butoxyethyl acrylate and methoxymethyl vinyl sulfide was cross-linked by treatment with phosphoric acid and iodine followed by heating under tension at 150° C. for one hour. The cross-linked fiber was hydrolyzed with aqueous, alcoholic sodium hydroxide.

PREPARATION D

The cross-linked fiber substrate of Example 1(*a*) of U.S. 2,933,460, prior to hydrolysis, was treated with dimethylaminopropylamine in dodecane as described in Example 7 of U.S. 2,933,460. The resulting fiber had an anion exchange capacity of about 2.0 meq./g. The amine functionality was completely of the weak-base type resulting from the exclusive presence of tertiary amine groups and no quaternary functionality. The fiber was heated under reflux for 6 hours in 95% ethanol containing two molar equivalents (based on 2 meq./g.), of dimethyl sulfate. The mixture was cooled and the fiber recovered and washed. The fiber had a salt-splitting capacity of 1.2 meq./g., and thus contained quaternary ammonium groups in the methosulfate form.

Example I

Take a stainless steel cylinder 6.25″ long, and 1.73″ diameter, perforated by 3/16″ diameter holes running in rows parallel to the cylinder's axis. The holes are 1/4″ apart, center to center, and the rows are 1/4″ apart, line of hole-centers to line of hole-centers. Wind on this core a tight 1/2″ thick layer of 3600 denier fiberglass yarn with a lay of 1/4″ and a precision, honeycomb wind. The length of the glass layer is 6″. On top of the glass layer wind a medium hard layer of wet sulfonic ion exchange fiber in the sodium form, prepared as in Example A. The sulfonic yarn is untwisted, and has approximately 500 fibers in it, the diameter of each fiber being approximately 25 to 30 microns. Wind the sulfonic fiber layer the same length as the underlying glass layer, but with a lay of 3/16″, and with a non-precise wind, until the outside diameter of the package is 5.7″. The "bed depth" of the ion exchange layer is, therefore, about 1.4 inch. Wrap the outside of the package with one turn of fine stainless steel wire mesh, and tighten the mesh into place by lacing the joint together with fine (28 S.W.G.) stainless steel wire. Clamp the package between two end plates as shown in FIGURE 2.

Pump water containing 14.5 grains/gallon hardness as $CaCO_3$ through the package at flow rates of from 4 to 6 gallons per cubic foot of resin-bed per minute. The pressure drop across the package is 20–25 p.s.i.g. When the effluent concentration reaches 1% of the influent concentration, 74% of the total capacity of the ion exchange fibers has been used up. This occurs after 43 gallons of water has been processed to a hardness not exceeding 0.145 grain/gallon as $CaCO_3$. To accomplish this result in a column of ion exchange beads would require a bed depth of 18″ or more. Thus, the processing by means of the wound package is characterized by considerable advantage in compactness and efficiency in that the effective bed depth of the package is only about 1.4 inches. This is the result of a highly tortuous path through the bed (in this case, the radial thickness of the wound package) and of the high exchange rate of the thin filaments.

Example II

Take the exhausted package from Example I, and pump 10% sodium chloride solution through it at 0.8 gallon/cu. ft. resin bed/min., until the volume of the effluent is 1.04 times the volume of the resin bed, i.e., 0.069 cu. ft. Pump deionized water through the package at the same

flow rate, until 2–3 bed volumes have been passed (i.e., 0.132 to 0.198 cu. ft.).

Pump the same hard water at the same flow rate as in Example I through the package. When the effluent concentration reaches 1% of the influent concentration, 61% of the total capacity of the ion exchange fibers will have been used, processing 38 gallons of water to a hardness not exceeding 0.145 grain/gallon as $CaCO_3$.

Example III

Take the exhausted package from Example II, and regenerate it with 0.52 bed volume (i.e, 0.034 cu. ft.) of 10% sodium chloride brine. Rinse with deionized water as in Example II.

The package will process 28 gallons of the same hard water, at the same flow rate as in Examples I and II, to a hardness not exceeding 0.145 grain/gallon as $CaCO_3$. This represents 46% of the total exchange capacity of the package.

Example IV

Take the exhausted package from Example III and regenerate it with 0.13 bed volume (i.e. 0.0086 cu. ft.) of 10% brine. Rinse with deionized water as in the previous examples.

The regenerated package will process 9.5 gallons of the same hard water as in the previous examples to a hardness not exceeding 0.145 grain/gallon as $CaCO_3$. This represents 14.9% of the total capacity of the package.

Example V

Take the exhausted package from Example IV, and convert it to the hydrogen form by forcing through it 3 bed volumes (0.2 cu. ft.) of 0.5 N sulfuric acid, at a flow rate of 0.8 gal./cu. ft. of resin/min. Rinse with 2–3 bed volumes of deionized water as in the previous examples.

Pump 0.1 N NaCl solution through the package at a flow rate of from 0.5 to 1 gallon/cu. ft. of resin/min. 8.5 l. of 0.1 N hydrochloric acid will be obtained before the NaCl content of the effluent reaches 0.001 N.

Example VI

Wind a package exactly as described in Example I, but use dry instead of wet yarn.

Pump the same hard water as in Example I through the package at a flow rate of 0.5 to 1 gallon/cu. ft. of resin/min. This will require a pressure of 30 to 50 p.s.i.g. The package will process 40 gallons of water to a hardness not exceeding 0.145 grains/gallon as $CaCO_3$.

Dry winding is not preferred over wet winding, because of the very much greater pressures required to force the liquid through.

Example VII

Wind a package as described in Example I, using wet yarn prepared as in Example D.

Convert the package to the hydroxide form by pumping through it three bed volumes (0.2 cu. ft.) of 0.5 N sodium hydroxide solution at 0.8 gal./cu. ft. of resin/minute. Rinse with 2 to 3 bed volumes of deionized water.

Pump 0.1 N ammonium chloride solution through the package at flow rates of from 0.5 to 1 gal./cu. ft. of resin/minute. 4.3 l. of 0.1 N ammonium hydroxide solution will be obtained before the ammonium chloride content of the effluent reaches 0.001 N. Approximately 75% of the total capacity is utilized at this point.

I claim:

1. A method for effecting ion exchange comprising forcing a liquid to be treated generally radially through an annular winding of a multi-filament bundle of ion exchange filaments, the laps of the winding being in a dispositional relationship resulting from the winding of the bundle while in a fully water-swollen condition.

2. A method as defined in claim **1** in which the radial thickness of the annular winding is substantially uniform throughout the axial extent of the winding.

3. A method as defined in claim 1 in which the lay and the diameter of bundle are correlated to provide a spacing of about 1/64 inch to about 1/8 inch between the lap of the bundle laid down in one traverse and the adjacent lap of the bundle laid down in the preceding traverse in the same direction.

4. A method as defined in claim 1 in which the diameter of the filaments in the bundle is between about 5 microns and 50 microns in water-swollen condition.

5. A method as defined in claim 1 in which the ion exchange capacity of the filaments is at least about 0.5 milliequivalent per gram.

6. A method as defined in claim 1 in which the ion exchange capacity of the filaments is at least about 2.5 milliequivalents per gram.

7. A method as defined in claim 1 in which the bundle has from zero to 3 turns of twist per inch length.

8. A method as defined in claim 1 in which the liquid to be treated is forced from the inside of the winding outwardly therethrough.

9. A method as defined in claim 1 in which the thickness of the winding is about 2 to 4 inches.

10. A method as defined in claim 1 in which the winding is an annular winding having concentric inside and outside substantially cylindrical surfaces and annular end surfaces lying in planes substantially perpendicular to the axis of the winding.

11. A method as defined in claim 1 in which the winding is supported with its inside wall in contiguity with an inside winding of glass yarn.

12. A method as defined in claim 1 in which the winding is supported on a hollow, perforated core.

13. A method for effecting ion exchange comprising forcing a liquid to be treated in a radial direction in succession through at least two annular windings each formed of a multi-filament bundle of ion exchange filaments, the laps of the winding being in a dispositional relationship resulting from the winding of the bundle while in a fully water-swollen condition.

14. A method according to claim 13 in which one of the windings is of a cation exchange filament and another is of an anion exchange filament.

15. A method comprising winding a multi-filament bundle of ion exchange filaments while in fully water-swollen condition to form an annular winding of liquid permeable character which is substantially free of open channels and through which the path of liquid flow is of highly tortuous nature, and subsequently, without allowing the filaments in the winding to shrink appreciably as a result of evaporation of moisture, forcing an ion-containing liquid to be treated through the annular winding and thereby removing ions therefrom.

16. A method according to claim 1 in which the winding has a void space of from about 25% to about 50%.

17. A method as defined in claim 2 in which the winding has a void space of from about 25% to about 50%.

18. A method as defined in claim 3 in which the winding has a void space of from about 25% to about 50%.

19. A method for effecting ion exchange comprising forcing a liquid to be treated generally radially through an annular winding of a multi-filament bundle of ion exchange filaments, the laps of the winding being in a dispositional relationship resulting from the winding of the bundle while in a fully water-swollen condition, the lay and the diameter of bundle in the winding being correlated to provide a spacing of about 1/64 inch to about 1/8 inch between the lap of the bundle laid down in one traverse and the adjacent lap of the bundle laid down in the preceding traverse in the same direction, the winding having a void space of from about 25% to about 50%, the radial thickness of the annular winding being substantially uniform throughout the axial extent of the winding.

References Cited by the Examiner

UNITED STATES PATENTS

Re. 22,651	6/45	Hastings	210—494
2,758,968	8/56	Williams et al.	210—24
2,798,850	7/57	Voigtman et al.	210—502
2,974,101	3/61	Richter	210—24
2,987,191	6/61	Wennberg	210—497
3,047,156	7/62	Wasson	210—497
3,062,379	11/62	Bryan	210—507
3,062,738	11/62	Read et al.	210—24

OTHER REFERENCES

Guthrie: Ion Exchange Cottons, Industrial and Engineering Chemistry, vol. 42, No. 9, September 1952, pp. 2187–2189.

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