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COMPLETE SPECIFICATION

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TREATMENT OF AQUEOUS LIQUIDS

We, ROHM AND HAAS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of Independence Mall West, Philadelphia, Pennsylvania 19105, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to the treatment of liquids, particularly aqueous liquids, to remove therefrom colloidal particulate matter such as colloidal silica or hydrous metal oxides. ✓

5 The removal of silica from boiler feed waters has become an important problem in recent years with the trend for higher pressure boilers and ion exchange methods have been known for the removal of soluble ~~sol~~ non-colloidal silica. The materials which have made removal by such methods possible are
10 the strongly basic anion exchange resins of the quaternary ammonium type, either of the conventional gel structure or of a macroreticular structure. Macroreticular resins are those having a true pore structure and are described for example, by Kunin et al in an article entitled "Characterization of Amberlyst
15 15" I. & E.C. Product Research and Development, Vol. 1, June 1962, p.40. (Amberlyst is a Registered Trade Mark)

 Since the operation of a high pressure boiler is affected adversely by the accumulation of any form of silica, the previously known methods for removing only non-colloidal silica have not been
20 enough to solve the problem satisfactorily. In fact, the inability of ion exchange resin systems to remove colloidal silica has been a severe drawback to the use of ion exchange methods in the deionization of waters for various applications. In addition to boilers, for example, the electronics industry and the various
25 industries dependent upon applications of nuclear energy have long had need for the removal of particulate matter from the waters which they are obliged to employ, and this need has not been satisfied by previously known silica removal or deionization techniques. Although shallow filter beds of finely powdered
30 ion exchange resins have been used to remove colloidal silica

and iron from deionized effluents, their use leaves much to be desired because of their limited effectiveness and their inability to be regenerated.

The present invention provides a

~~/~~ method of removing colloidal particulate matter from

5 a liquid which comprises intimately contacting the liquid with anion exchange resin particles having a macroreticular structure and having an average pore diameter which is within the range from about 10,000 to about 500,000 Angstrom units.

10 The average pore diameter of the resin particles is determined as described by Kun & Kunin in J. Polymer Science B2, 587 (1964), and for the purposes of this specification a resin having an average pore diameter of, say, 100,000 Angstrom units is one in which 50% of the total porosity is contributed by pores having a diameter of less than 100,000 Angstrom units
15 and the remainder of the total porosity is contributed by pores having a diameter of more than 100,000 Angstrom units.

The macroreticular resins employed in the present invention have a much larger average pore diameter than previously described macroreticular resins whose average pore diameters have ranged
20 from 30 to 800 Angstrom units. The resins employed in the process of the invention may be made by the general method described in U.K. Patent specification No. 932,126 appropriately modified to produce resins having the specified extra-large pores.

25 When one attempts to remove colloidal particulate matter by conventional methods, as by using a succession of filters and/or by the use of coagulants, only very small portions of these particles are removed. Customarily, carbon filters are employed for this purpose and this often is followed by use of a mixture of anion and cation exchange resins which will deionize or demineralize the water. The effluent from such a series of treatments will generally be devoid of all the ions

which one seeks to remove in order to make the water useful in boilers and other such applications, except for silica, metal oxides or other colloidal particulate matter. Now, by virtue of the present invention, such colloidal

5 particulate matter is readily removed from the water and the resin used can readily be regenerated so as to remove the particulate matter collected thereon and thereby enable the novel resins to be used over and over again in a commercially acceptable cyclical process.

10 A comparison of the efficiency of the present process with analogous processes using conventional gel and macroreticular type resins of the prior art, can be seen by reference to Figures 1 to 3 of the accompanying drawings which show graphs in which the vertical ordinates represent weight
15 per cent of colloidal silica removed and the horizontal ordinates represent time measured in days. The data presented was obtained using three different resins A, B & C (described in more detail below) and is plotted on the lines identified by the appropriate resin designation. In each case the resins
20 were contacted, with continuous agitation, with 200ml of water containing 1000 ppm of colloidal silica, the data presented in Figures 1-3 having been obtained using respectively (1) 4 grams of each wet resin at a contacting temperature of 27° C, (2) 14.0 grams of each wet resin at a contacting temperature of 27° F and (3) 4.0 grams of each wet resin at 50°C.

Resin A referred to above was a conventional gel type quaternary ammonium anion exchange resin in the hydroxide form, which is commercially known as Amberlite IRA-400, and which contains $-N-(CH_3)_3^+$ groups introduced by chloromethylating and aminating a styrene/divinyl benzene copolymer.

X
S L If desired, the liquid before treatment with the anion-exchange resin may be subjected to a filtration and/or coagulation treatment to effect partial removal of suspended solids therefrom.

Resin B was a generally similar quaternary ammonium anion exchange resin which is commercially known as (Amberlite is a Registered Trade Name) Amberlite IRA-904, such resin differing, however, from Resin

5 A in that it possessed a macroreticular structure and had an average pore diameter not exceeding 800 Angstrom units.

Resin C was similar in turn to Resin B except that it had an average pore diameter in the range from 10,000 to 500,000 Angstrom units

10 Resin C was prepared as follows. The raw materials used to form a copolymer intermediate were 900 ml. of water, 9.0 g. of dispersing agent and 0.09 g. of "Pharmagel" (a specially refined gelatine). The monomer phase was made with 301.3 g. of styrene, 16.7 g. of divinylbenzene (57.1%), 15 282.0g. of tert-amyl alcohol and 6.0 g. of azo-bis-isobutyronitrile. The dispersing agent (20% solids in water) was an ammonium salt of a styrene-maleic anhydride copolymer.

The polymerization was carried out in a 2-liter glass fiber-reinforced resin pot, equipped with a stainless steel stirrer, 20 a reflux condenser, an addition funnel and a thermoregulated heating mantle. The water, dispersing agent and Pharmagel were formed into a solution by warming to 40-45° C. and the solution was kept under agitation. The styrene, divinylbenzene, tert-amyl alcohol, and azo-bis-isobutyronitrile were mixed together, 25 and, when dissolved, the mixture was charged to the resin flask also. The batch was heated to 70° C. and held for 20 hours. The copolymer which resulted was washed several times with water to remove the dispersant and the tert-amyl alcohol was removed by steam distillation over a period of about 5 hours. The batch was then cooled to about 35-40° C., and again washed with water.

The polymer, which was in the form of beads, was drained on a suction filter and dried to constant weight in a steam oven at a temperature of approximately 70° C., the drying process taking about 20 hours. The dry beads were then screened
5 between 20-70 mesh screens(U.S. Standard Screen Series) to remove undesired fine and coarse particles.

The copolymer intermediate beads thus obtained were then chloromethylated and aminated in order to form the ion exchange resin. For these reactions there were used 212 g.
10 of intermediate copolymer beads, 484 g. (6.0 moles) of methyl, chloromethyl ether, 1200 ml. (1500 g.) ethylene dichloride, 160 g. (1.2 moles) of AlCl_3 , 800 ml. of a quench solution made up of 6.5% NaH_2PO_4 and 5.5% H_2SO_4 in water 20 g. of NaHCO_3 , and 500 ml. of 25% trimethylamine (2.0 moles).

15 The resin beads, methyl chloromethyl ether and ethylene dichloride were charged to a 5-liter flask equipped with a glass stirrer, a thermometer and a reflux condenser topped with a CaCl_2 drying tube. The batch was stirred for 1/2 hour to swell the beads. The AlCl_3 was added in a number of small portions at
20 20 minute intervals, keeping the temperature between 30-40° C., and stirring the batch for 4 hours. The chloromethyl ether and ethylene dichloride were distilled off until the flask temperature reached 80° C., and about half the quench solution was added in a fine stream through a dropping funnel with stirring and
25 external cooling to keep the batch temperature below 30° C. After stirring the batch for 20 minutes the entire liquid phase was drawn off with a stick filter. The balance of the quench solution was added and the batch stirred for 20 minutes, the liquid being drawn off as before. The resin was washed
30 several times with water, stirred for 15 minutes and the liquid again drained off with a stick filter.

A neutralizing solution containing about 20 g. of NaHCO_3 dissolved in 800 ml. of water was added, the batch being stirred for 1/2 hour and the neutralizer drained off. The resin was again washed with water.

5 At this point the amination was accomplished by adding the aqueous trimethylamine in a fine stream through a dropping funnel, keeping the batch at between 20 and 25° C., and stirring it for about 4 hours. Any remaining ethylene dichloride was stripped off by steam distillation and water added to keep the
10 slurry fluid.

The foregoing procedure provided a wet yield of approximately 1460 g., with a solids content of approximately 27% and a dry yield of about 5%. The moisture-holding capacity of the resin was about 70%, the anion exchange capacity about
15 and the 3.7 meq./g.,/porosity about 0.9 - 1.0 cc./g. The pores ranged in diameter from 30,000 to 200,000 Angstrom units, and the surface area was 8.9 sq.m./g.

A comparison of the physical structures of Resins A, B & C is set forth in Table 1 below. As reference to that table will
20 indicate, the gel Resin A, Amberlite IRA-400, has no pores and therefore no pore diameters which can be measured. The conventional macroreticular Resin B, Amberlite IRA-904, will be seen to have a range of pore diameters from below 300 to a maximum of 1,900. The third material, Resin C is also macroreticular in structure
25 but it has pore diameters ranging from 10,000 to at least 100,000 and an average pore diameter of 45,000. The remaining data in Table 1 indicate differences in the density and total porosity of each of the three resins,

Referring now to Figs 1-3, it will be seen that the ability of the three resins to remove colloidal silica varies tremendously. From Fig.1 it will be seen that the highly porous Resin C removed 30% of the colloidal silica in 4 days, whereas the gel type and prior art macroreticular type Resins A & B removed only about 5% colloidal silica. Similarly, under the conditions employed for the data plotted in Fig.2, Resin C removed 90% of the silica in a single day, whereas in the same period of time the other resins removed only about 5%. From Fig.3, Resin C will be seen to have removed almost 100% of the colloidal silica in less than 2 days, whereas the other two resins were able to remove less than 40% in a period of 2 to 3 days.

The nature of colloidal silica may vary from one geographical area to another. Accordingly, in order to test further the ability of the highly porous Resin C to remove colloidal silica, samples of surface water were obtained from various water supplies throughout the eastern portion of the United States and analyzed for colloidal silica and iron by means of the well-known Millipore ^{Millipore is a registered trade mark} filter technique. These waters containing significant amounts (0.01 ppm) of colloidal silica were then deionized with Amberlite MB-1 (a mixed bed of anion and cation exchange resins) and then treated with Resin C in the hydroxide form. The results of these studies are summarized in Table 2 below. The data in that table indicate quite clearly that colloidal silica was present in most of those surface waters, and in each case was combined with colloidal iron. Likewise, it is also apparent that Resin C was effective to remove the colloidal silica and iron present in each of those waters, even though the $\text{Fe}_2\text{O}_3/\text{SiO}_2$ ratio varied considerably.

It should be added that the influents to Resin C left appreciable deposits when passed through a membrane filter but, after passage through Resin C, the effluents left practically no residues on such a filter, indicating that Resin C is as effective as membrane filters for the removal of these colloids.

TABLE 1

Resin	Average Pore Diameter in Angstrom Units	Range of Pore Diameters	Density (g./cc.)		Total Porosity		Surface Area Sq.m./g. ⁵
			Apparent (g.a.) ¹	Skeletal (g.s.) ²	Densitometer cc./cc. ³	Penetrometer cc./g. ⁴	
A	None	None	1.13	1.13	None	None	<0.1
B	690	258 to 1900	0.55	1.114	0.502	0.906	42.2
C	46,000	10,000 to 100,000	0.583	1.147	0.603	1.035	8.9

1 - Apparent density as measured by mercury displacement.

2 - True skeletal density as measured by helium displacement.

3 - Volume of pores/volume of resin

4 - Volume of pores/g. of resin

5 - Square meters/g. of resin

TABLE 2

Water Source	Influent (ppm)		Effluent (ppm)		% Removal	
	SiO ₂	Fe	SiO ₂	Fe	SiO ₂	Fe
Wabash River Public Service Co. Terre Haute, Indiana	0.0001	7.1	0.00008	0.085	20.0	98.8
James River Owen Illinois Big Island, Virginia	0.000049	1.7	0.000045	0.050	12.2	97.1
Savannah River Continental Can Co. Augusta, Georgia	0.20	2.1	0.0 0012	0.045	99.9	97.9
Ohio River (42.1 miles above Camo, Ill.) Lock Dam 52 Brookport, Illinois	0.43	1.8	0.095	0.015	78.0	99.2
Mississippi River Arkansas Power & Light Co. Robt. E. Ritchie Station Helena, Arkansas	0.39	0.8	0.053	0.042	86.4	94.7

TABLE 2 Contd.

Water Source	Influent (ppm)		Effluent (ppm)		% Removal	
	SiO ₂	Fe	SiO ₂	Fe	SiO ₂	Fe
Tennessee River T.V. - Colbert Plant Tuscumbia, Alabama	0.031	2.7	0.000076	0.050	99.7	98.1
Tennessee River Pennsalt Chemical Co. Calvet City, Kentucky.	0.018	1.7	0.000076	0.0025	99.6	99.9
Peedee River International Paper Co. Georgetown	C.98	4.2	0.16	0.041	83.7	99.0

After a period of use to remove colloidal silica and metal oxide the highly porous resin used in the process of the invention becomes loaded with silica-metal oxide complexes or clay fragments which are normally quite resistant to removal by even hot caustic soda. Both the silicates and the colloidal metal oxides may, however, be solubilized with hot hydrochloric acid and the resin thus regenerated. Even more effective is the use of both hot caustic soda and the hot acid, the resin preferable being treated with acid first. To illustrate the effectiveness of such a regeneration procedure Resin C was permitted to become exhausted by virtue of having taken on a full load of colloidal silica from the water at the Consolidated Edison Co.'s New York City location and then regenerated with the results shown in Table 3 below. As will be noted, the hot acid regenerations removed 100% of the silicates and better than 90% of the colloidal iron oxides, while the caustic soda regeneration removed a small part of the iron oxide and between 60 and 80% of the silica.

TABLE 3

Resin Fraction	mg./g. dry resin - (% removed)					
	Before Regeneration		After Regeneration			
	Loaded Resin		Hot NaOH (aq.)		Hot HCl (aq.)	
A ¹	Residue ³	19.60	12.34	(37)	0.50	(97.5)
	SiO ₂	10.94	3.29	(66.7)	0.00	(100)
	Fe ₂ O ₃	6.02	5.65	(6)	0.54	(91)
B ²	Residue	5.18	4.51	(13)	0.07	(98.6)
	SiO ₂	1.17	0.16	(86.4)	0.00	(100)
	Fe ₂ O ₃	2.97	3.29		0.00	(100)

1. Resin fraction from top 10% of column
2. " " " next lower 10% of column
3. Total residue, i.e. silica, iron oxide or other materials.

The anion exchange resin used in the process of the invention can be used in the hydroxide or the salt form (Chloride, sulfate, nitrate, etc.)

5 The anion exchange resin may be employed as a bed or column through which the colloid-containing liquid is passed or the latter may simply be agitated with the resin.

The anion exchange resin can be used in conjunction with a cation exchange resin, so as to achieve deionization and colloid removal simultaneously or seriatim. Such deionisation may be achieved
10 by passing the colloid-containing liquid through a column of the hydrogen form of a sulfonic acid cation resin and then through a column of colloid-removing anion exchange resin in the hydroxide or free base form, or by first passing the system through the hydroxide form of the anion exchange resin and then through
15 the hydrogen form of any cation exchange resin. One may also simultaneously deionize and remove the colloids from the system by contacting the system, either in a column or batchwise, with a mixture of the basic form of the anion exchange resin and the hydrogen form of the cation exchange resin.

20 To demonstrate the ability of Resin C to function simultaneously as an anion exchange resin and as a colloid-removing resin, 80 ml. of this resin (which was regenerated with 100 mL of 1 N NaOH) was mixed with 20 ml. of Amberlite IR-120, a sulfonic acid cation exchange resin (which was regenerated with
25 30 mL. of 1 N HCl) and the mixture placed in a 1" diameter column. Two liters of a natural water supply containing 100 ppm of dissolved electrolyte and 0.05 ppm each of colloidal SiO_2 and Fe_2O_3 were passed through the mixture and the effluent analyzed for conductivity, colloidal SiO_2 and Fe_2O_3 . The analysis showed that 95% of the colloidal SiO_2 and Fe_2O_3 was removed and that the dissolved electrolyte was reduced to less than 1 ppm.

Because of its high macroreticular nature the resin used in the process of the invention can be employed to treat non-aqueous colloid-containing liquids for example a small column of the dry, hydroxide form of Resin C was found to remove a trace of colloidal iron oxide present in a sample of ethanol which had become contaminated.

Though resins with strong base functionality are preferred for the removal of colloidal silica and other such colloidal particulate matter, highly porous weak base anion exchange resins will also perform the desired operation. Such weak base anion exchange resins can be prepared as described for Resin C with the exception that the amination step is carried out with an amine such as ~~amine~~ *dimethylamine, diethylamine,* monomethylamine or ethanolamines. At this point it may be mentioned that resins of even greater porosity than Resin C may be prepared by increasing the polymerization temperature to 80-85° C. Apart from the removal of colloidal silica and metal oxides the process of the invention may be applied to the removal of other anionic colloidal species including humic acid and viruses.

What we claim is :

~~MEMORANDUM~~

1. A method of removing colloidal particulate matter from a liquid which comprises intimately contacting the liquid with anion exchange resin particles having a macroreticular structure and having an average pore diameter which is within the range from ~~about~~ 10,000 to ~~about~~ 500,000 Angstrom units.

2. A method according to Claim 1 in which the average pore diameter of the anion exchange resin is within the range from ~~about~~ 10,000 to ~~about~~ 100,000 Angstrom units.

3. A method according to Claim 1 or 2 in which the anion exchange resin is in the hydroxide form.

4. A method according to Claim 1 or 2 in which the ^{anion exchange} resin is in the salt form.

5. A method according to any one of the preceding claims in which the liquid being treated is an aqueous liquid containing colloidal silica or a hydrous metal oxide.

6. A method according to Claim 5 in which the liquid is deionized before, after or at the same time as it is treated with said anion exchange resin.

7. A method according to Claim 5 or 6 in which the liquid before treatment with said anion-exchange resin is subjected to a filtration and/or coagulation treatment to effect partial removal of suspended solids therefrom.

8. Liquid treated by a method according to any one of the preceding claims.

9. This invention, in all its novel facets, substantially as hereinbefore described.

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