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(19)



(54) COPOLYMERS

(71) 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 concerns novel hybrid copolymers.

As is well known, ion exchange resins or copolymers are generally divided into two classes:

1) those which are essentially non-porous and which are generally known as gel copolymers, and

2) those which are porous or macroreticular. Each class of copolymers when converted to or prepared in the form of ion exchange resins, that is by the introduction of or *in situ* formation of suitable functionality offers certain distinct advantages. For example, strong base resins prepared from macroreticular copolymers generally show an increase in physical stability and exchange kinetics relative to resins prepared from similar conventional gel copolymers which generally exhibit a higher column capacity.

In accordance with the invention there is provided a hybrid copolymer comprising a cross-linked macroreticular host copolymer, the pores of which contain a separately formed cross-linked filling copolymer.

The invention also provides—and this is the preferred product—a hybrid copolymer comprising a cross-linked macroreticular host copolymer, the pores of which contain non-macroreticular cross-linked gel copolymer.

There are numerous techniques that can be used to prepare the hybrid copolymers, which term, incidentally, has been coined to distinguish the novel copolymers of the present invention from the gel and macroreticular copolymers and resins of the prior art. One general approach for preparing the hybrid copolymers is to at least partially fill the pores of a macroreticular copolymer with monomer and polymerizing such monomer to give rise to non-macroreticular gel copolymer. Alternatively, the hybrid copolymers can be prepared by filling the pores of a macroreticular copolymer with monomer giving rise to microreticular copolymer having a different degree of cross-linkage than the host copolymer. The hybrid copolymers may, after formation thereof, have ion-exchange functional groups imparted thereto; alternatively the hybrid copolymers may be prepared using monomers having functional groups such as 2 - vinylpyridine - 4 - vinylpyridine, acrylic acid or methacrylic acid.

The host copolymer possesses a special porous structure which is referred to herein as macroreticular. Macroreticular copolymers possess a network of microscopic channels extending through the mass and while these microscopic channels are obviously very small, they are large in comparison with the pores in conventional homogenous cross-linked gels, pores of the latter type not being visable in electron photomicrographs and, as is well known, not being true pores at all (vide Kunin, " Ion Exchange Resins " page 45, et. seq. John Wiley & Sons. Inc. 1958). Typically, macroreticular polymers have a surface area of at least 1 sq. meter per gram, and more generally at least 5 sq. meters per gram and have pores larger than about 15 to 20 A° Units. It is

conventional to produce these macroreticular polymers in bead form, usually in an overall particle size of about 10 to 900 microns. Further information on the preparation and structure of macroreticular polymers, which are known materials, may be obtained by referring to British Patent Specifications 932,125, and 932,126 and U.S. Patent Nos. 3,275,548 and 3,357,158.

Usually, similar types of monomeric materials are used in preparing the host and the filling copolymer, while the preparation process is varied to impart difftrent characteristics, especially different porosity, to the two types of copolymer.

Preferably the backbone of both types of resin will be a cross-linked copolymer of (1) polyunsaturated monomer, containing a plurality of non-conjugated $CH_2=C<$ groups, which acts as a cross-linking agent and (2) a monoethylenically unsaturated monomer, either aromatic or aliphatic. If desired, the polymer can comprise essentially all of (1).

Suitable polyunsaturated cross-linking agents include divinylbenzene, divinylpyridine, divinyltoluenes, divinylnaphthalenes, diallyl phthalate, ethylene glycol diacrylate, ethylene glycol dimethacrylate, trimethylolpropane trimethacrylate, neopentyl glycol dimethacrylate, bis-phenol A dimethacrylate, pentaerythritol tetra- and trimethacrylates, divinylxylene, divinylethylbenzene divinylsulfone, divinylketone, divinylsulfide, allyl acrylate, diallyl maleate, diallyl fumarate, diallyl succinate, diallyl carbonate, diallyl malonate, diallyl oxalate, diallyl adipate, diallyl sebacate, divinyl sebacate, diallyl tartrate, diallyl silicate, triallyl aconitate, triallyl, citrate, triallyl phosphate, N,N′ - methylenediacrylamide, N,N′ - methylene dimethacrylamide, N,N′ - ethylenediacrylamide, trivinylbenzene, trivinylnaphthalene, polyvinylanthracenes and the polyallyl and polyvinyl ethers of glycol, glycerol, pentaerythritol, resorcinol and the monothio or dithio derivatives of glycols.

Preferred cross linking monomers for both the macroreticular host copolymer and the filling copolymer include polyvinyl aromatic hydrocarbons, such as divinylbenzene and trivinylbenzene, glycol dimethacrylates and polymethacrylates, such as ethylene glycol dimethacrylate, trimethylolpropane trimethacrylate, and polyvinyl ethers of polyhydric alcohols, such as divinoxyethane and trivinoxypropane. The amount of cross-linking agent or monomer can be varied widely. In the case of anion-exchange resins the total utilizable capacity of the final resin as an anion-exchange resin generally decreases with an increase in the amount of cross-linking agent, and an amount of 1/2% to 30%, and preferably 3 to 10%, on a weight basis is usually adequate. However, for other purposes and for cation exchange resins the cross-linking level can be significantly higher, i.e., up to 50% by weight or even higher based on the total weight of the monomers.

Suitable monoethylenecally unsaturated monomers for both the host copolymer and the filling copolymer include esters of acrylic acid, such as methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, butyl acrylate, tert-butyl acrylate, ethylhexyl acrylate, cyclohexyl acrylate, isobornyl acrylate, benzyl acrylate, phenyl acrylate, alkylphenyl acrylate, ethoxymethyl acrylate, ethoxyethyl acrylate, ethoxypropyl acrylate, propoxymethyl acrylate, propoxyethyl acrylate, propoxypropyl acrylate, ethoxyphenyl acrylate, ethoxybenzyl acrylate, ethoxycyclohexyl acrylate, the corresponding esters of methacrylic acid, styrene, *o*-, *m*- and *p*- methyl styrenes, and *o*-, *m*- and *p*- ethyl styrenes, vinyl toluene and vinyl naphthalene. A class of monomers of particular interest consists of vinyl aromatic monomers such as styrene and the esters of acrylic and methacrylic acid with a C_1—C_{10} aliphatic alcohol.

The polymerization reaction is generally carried out in the presence of a catalyst. Suitable catalysts, which provide free radicals to function as reaction initiators include benzoyl peroxide, *t*-butyl hydroperoxide, lauroyl peroxide, cumene hydroperoxide, tetralin peroxide, acetyl peroxide, caproyl peroxide, *t*-butyl perbenzoate, *t*-butyl diperphthalate, methyl ethyl ketone peroxide.

The amount of peroxide catalyst required is roughly proportional to the concentration of the mixture of monomers. The usual range is 0.01% to 5% by weight of catalyst with refer- to the weight of the monomer mixture. The optimum amount of catalyst is determined in large part by the nature of the particular monomers selected, including the nature of the impurities which may accompany the monomers.

Another suitable class of free-radical generating compounds which can be used as catalysts are the azo catalysts, including for example, azodiisobutyronitrile, azodiisobutyramide, azobis(α,α - dimethylvaleronitrile), azobis(α - methyl - butyronitrile), dimethyl, diethyl, or dibutyl azobis(methyl-valerate). These and other similar azo compounds, which serve as free radical initiaters, contain an —N=N— group attached to aliphatic carbon atoms, at least one of which is tertiary. An amount of 0.01% to 2% of the weight of monomer or monomers is usually sufficient.

In making the hybrid copolymers, a wide variety of polymerization conditions and processes well known in the art can be used. However, the preferred method is suspension polymerization in a liquid, such as water, which is not a solvent for the monomeric material. This method produces the polymer directly in the form of small spheroids or beads, the size of which can be regulated and

controlled. By adjustments in the composition of the suspending medium and in the rate of agitation during polymerization, the suspension polymerization process can be made to produce spheroids or beads of a wide range of effective particle sizes.

In preparing the base macroreticular copolymer or resin, and likewise in preparing the filling copolymer which may be a macroreticular resin of lesser or greater cross-linkage content, the polymerization reaction may be carried out in the presence of a precipitant which is a liquid (a) which acts as a solvent for the monomer mixture and is chemically inert under the polymerization conditions and (b) which is present in such amount and which exerts so little solvating action on the product cross-linked copolymer that phase separation of the product copolymer takes place as evidenced by the fact that the product copolymer is opaque when associated with a liquid having a different refractive index. Such a process, together with information regarding choice of precipitant liquids is discussed in detail in U.K. Patent Specification No. 932,126. It is also possible to use as solvent for the monomer mixture a liquid which swells the product copolymer provided that the cross-linker level is sufficiently high. Those of the hybrid ion-exchange resins of the present invention, in which the pores of the host copolymer are filled with a lightly cross-linked non-macroreticular gel copolymer, do in fact combine the high capacity of the conventional non-macroreticular gel resin with the stability of the macroreticular resin.

Typically, the hybrid copolymer is prepared by adding fresh monomer such as, for example, styrene, catalyst, and a suitable cross-linking agent such as divinylbenzene to a suspension of a macroreticular copolymer and water. The monomer is adsorbed or imbibed into the pores of the macroreticular copolymer, and the imbided monomer is polymerized within the macroreticular copolymer beads by heating the mixture and thereafter, ion exchange functional groups are introduced to the polymer complex thus formed. Not only do the resulting resins show a greater combination of capacity and stability than one obtains with a macroreticular resin and a non-macroreticular gel resin, but also there are significant improvements in leakage and pressure drop over the corresponding macroreticular and gel type resins. While there has undoubtedly been prior work copolymers, including ion exchange resins, prepared by multi-stage polymerization procedures the present hybrid copolymers differ from anything known or disclosed in the prior art in the following respects : the host copolymer can furnish, if desired, substantial ion exchange properties in its own right in contrast to the inert inorganic carriers or porous polymers (PVC,PE) of the prior art, thus leading to superior total capacity in the final product. Also, the host copolymer can be converted in whole or in part to an ion exchange resin by the introduction of suitable functional groups before the filling copolymer is introduced into the pores of the host copolymer. The monomer which is to be sorbed or imbibed into the host copolymer, herein designated as the second-stage monomer merely for ease of reference, is deposited within the pores of the substrate and no interaction with the substrate is sought although some interaction would not necessarily be harmful or undesirable. In any event, the final compositions are still heterogeneous. Thus, while the possibility of some swelling of the host copolymer cannot be exluded, no groups or treatments promoting grafting efficiency are generally provided or even deemed necessary. At higher levels of cross-linking in the host copolymer, imbibing is probably therefore due to capillary effects and the products are not interpenetrating networks as described in parts of the prior art. The hybrid resins may, therefore, be considered heterogeneous products characterized by two relatively independent phases which can cooperate in providing superior ion exchange capacity, particle stability, improved leakage characteristics, and other advantageous factors.

Other advantageous factors include, unexpectedly good hydraulic and good pressure drop characteristics, particularly, (1) for hybrid resins which contain a non-macroreticular gel phase which may be lightly cross-linked e.g. with as little as ½% cross-linker and still have excellent properties, for example, in sugar decolorisation, see Example 12 and Table IV infra, or (2) for hybrid resins which contain a lightly cross-linked macroreticular phase and which still have outstanding leakage characteristics, see, for example, Example 11, and Table 111, infra. This is rather surprising since lightly cross-linked resins are sometimes very soft and virtually unusable in many industrial applications.

The relative amounts of host copolymer and filling copolymer can be varied over a wide range. It is desirable, however, to use at least 5 parts by weight of filling copolymer per 100 parts by weight of macroreticular host polymer, with the maximum amount being dictated by that amount which can be accommodated by the pores of the host copolymer. This maximum will ordinarily be 300 parts by weight of filling copolymer per 100 parts by weight of host polymer, although higher amounts can also be used. Preferably, the amounts of filling copolymer to host copolymer will be in the range of 10 to 200 parts of the former per 100 parts of the latter, and more preferably, 25 to 100 parts of filling copolymer per 100 parts of host copolymer, all parts being on a weight basis.

The following examples (some of which are comparative) will further illustrate the inven-

tion but are not intended to limit it. In the examples, as well as in the other parts of the specification and claims, parts and percentages are by weight unless otherwise stated. All chemicals used are of good commercial quality. In the case of divinylbenzene (DVB) a good commercial grade is used which contains about 56% active material, i.e., pure DVB, the balance being essentially all ethyl vinyl benzene. The copolymers set forth below are in bead form and are prepared by suspension or pearl polymerization techniques. Porosity is reported as per cent porosity or as the volume of pores per dry volume of resin, usually as milliliter per milliliter (ml./ml.). Percent porosity can be obtained by multiplying this value by 100. All temperatures given in the examples are in ° C. unless otherwise stated.

Example 1 (Comparative)

a) Preparation of Starting Copolymer (Macroreticular)

To a three-liter, three-necked flask equipped with stirrer, a thermometer, and a reflux condenser is added 1.15 g. of sodium chloride, 1.5 g. of purified gelatin in 50 ml. of water, 10 g. of sodium polyacrylate (12.5% solids) in 100 ml. of water, and 500 ml. of water with stirring. The stirring speed is adjusted to ~ 145 rpm and after solution was achieved the stirrer was stopped and 400 g. of a 3% DVB* -styrene solution, 261.2g. of methylisobutylcarbinol (MIBC) and 5.0 g. of benzoyl peroxide are added. The mixture is stirred at 145 rpm until a suitable dispersion is achieved and is heated at 80° for 11 hours. The MIBC is removed by distillation while maintaining a constant fluid level by the gradual addition of water. The mixture is cooled to room temperature, and the copolymer is isolated and washed on a Buchner funnel. The resulting copolymer product is dried at 125° for 8 hours to give a 70% yield of beads having diameters in the range from 0.21 to 0.84 mm and is identified as Resin A in Table I below. The copolymer product has a porosity of 0.56 ml/ml. and a cross-linker level of 3% DVB. After chloromethylation and amination the copolymer is converted into a strongly basic anion exchange resin with a column capacity of 21 g/l as $CaCO_3$, and a porosity of 0.2 to 0.4.

b) Strong Base Gel Type Resin

A strong base gel type anion exchange resin, having a styrene—DVB matrix, is prepared in conventional manner. The gel resin has a column capacity of 27.5 g/l as $CaCO_3$, a porosity of 0.0 and DVB cross-linker level of 2%. The product is indentified as Resin B in Table I.

* DVB=divinylbenzene

Example 2

a) Preparation of Hybrid Copolymer

In a one-liter, three-necked flask equipped with an efficient stirrer, a condenser, and a thermometer, is placed 52 g. of a 3% divinylbenzene (DVB, 58.9% active)- styrene macroreticular copolymer (0.71 porosity particle diameters in the range from 0.25 to 0.59 mm) and 400 ml. of tap water. To this mixture is added 50 g of a 0.5% DVB-styrene solution in which is dissolved 0.5 g. of benzoyl peroxide. The resulting mixture is stirred rapidly at room temperature for one hour and at 80° for a total reaction time of 20 hours. The mixture is allowed to cool to room temperature and the resulting beads are isolated by filtration washed with 600 ml. of methanol, and dried to a constant weight in a steam oven (75°) The hybrid copolymer is used directly in the following chloromethylation procedure. The yield of hybrid copolymer is 99.4 g. (97.5%).

b) Chloromethylation of Hybrid Copolymer

In a one-liter, three-necked flask equipped with a mechanical stirrer, a condenser with drying tube attached, a thermometer, and a dropping funnel, is placed 52 g. of the above hybrid copolymer and 240 ml. of 1,2-dichloroethane (EDC). The mixture is stirred slowly for 30 min. allowing the beads to swell. To the swollen beads is added 95 g of chloromethyl methyl ether (CME) in one portion. The reaction mixture is cooled to 0° by means of an ice bath and 26.8 g of aluminum chloride dissolved in 26 g. of CME is added dropwise over a one hour time period while maintaining the temperature below 5°. The mixture which resulted is heated at 40° for 16 hours and is cooled to −10° with the use of an ice-methanol bath. The cooled slurry is poured into 600 ml. of anhydrous methanol while maintaining the temperature below 10. The mixture is stirred for 30 min., the liquid layer is removed with a filter stick, and the resulting beads are given two 30 min. washes with 600 ml. portions of absolute methanol to give the product as uncracked beads which are used directly in the following aminolysis.

c) Amination of the Chloromethylated Intermediate

In a one-liter three-necked flask equipped with a mechanical stirrer, a thermometer, and a gas difusion tube are placed the chloromethylated intermediate prepared as described above. Methanol (250 ml.) is added and the mixture is bought to pH 8 with 10% sodium carbonate. To the basic mixture is added 40 g. of trimethylamine (TMA) by means of a gas diffusion tube while maintaining the temperature below 15° with an ice bath. After the addition is complete the reaction is stirred at room temperature overnight. The un-

reacted TMA and the methanol are removed by distillation while maintaining a constant fluid level by the gradual addition of water. The reaction mixture is cooled and the product is backwashed to netrality and isolated by filtration. The product had an average DVB content of 2.02%; solids 42.3%; anion exchange capacity — 4.22 meq./g of dry resin; reversible swelling — 17.8%; column capacity — 23.4 g/l (as $CaCO_3$) at a flow rate of 0.8 bed volumes per min; whole bead content after two acid — base cycles with 1N HCl and 1N NaOH — 98%; cracked bead content — 7%.

Example 3

a) Preparation of Hybrid Copolymer

In a one-liter, three-necked flask equipped with an efficient stirrer, a condenser, and a thermometer, is placed 52 g. of a 3% divinylbenzene (DVB, 58.9% active) — styrene macroreticular copolymer (particle diameters in the range from 0.25 to 0.59 mm 0.71 porosity) and 400 ml. of tap water. To this mixture is added with rapid stirring 100 g of a 0.5% DVB-styrene solution in which is dissolved 1.0 g of benzoyl peroxide. The mixture is stirred rapidly for one hour during which time the added monomer mixture is absorbed by the initial preformed porous copolymer. The reaction mixture is then heated for 20 hours at 80°. The mixture is cooled, and the copolymer is isolated by filtration, washed with 600 ml. of methanol, and dried in a steam oven (75°) until a constant weight of copolymer is achieved to give 150 g. (98.7%) of product.

b) Chloromethylation of Hybrid Copolymer

In a one-liter, three-necked flask equipped with a mechanical stirrer, a condenser to which is attached a drying tube, a dropping funnel, and a thermometer is placed 52 g. of the hybrid copolymer described above. The beads are swollen in 300 ml. of 1,2-dichloroethane (EDC) for 30 min. and 95 g. of chloromethyl methylether (CME) is added. The mixture is cooled below 10° with an ice bath and 26.8 g. of aluminum chloride in 25 g. of CME is added dropwise over a one hour period. The mixture is warmed between 35—40° overnight and is cooled to 0° by means of an ice-methanol bath. The resulting beads are washed once with 600 ml. of EDC and three times with 600 ml. portions of methanol. The resulting chloromethylated product is used directly in the following aminolysis.

c) Amination of the Chloromethylated Intermediate

In a one-liter, three-necked flask equipped with an efficient stirrer, a thermometer, a condenser, and a gas diffusion tube is placed the chloromethylated intermediate described above. Methanol (300 ml.) is added and the mixture is bought to pH 8 with 10% aqueous sodium carbonate.

Trimethylamine (TMA 40 g.) is added below the surface of the liquid by means of the gas diffusion tube over a period of two hours. The reaction mixture is heated to 35—40° overnight and the unreacted TMA and methanol are removed by distillation while maintaining a constant liquid level in the flask by the gradual addition of tap water. The resulting product is backwashed to neutrality and is isolated by filtration. The product has an average DVB content of 1.35%; solids 41.1%; anion exchange capacity — 4.33 meq/g. of dry resin; reversible swelling 17.0%; column capacity — 24.4 g/l, (as $CaCO_3$) at a flow rate of 0.32 bed volumes per min; whole bead content after two acid-base cycles with 1N HCl and 1N NaOH—100%; cracked bead content — 5%.

Example 4

a) Preparation of Hybrid Copolymer

A 3% divinylbenzene (DVB)-styrene macroreticular copolymer (107.7 g.) having a porosity of 0.56 is suspended in 800 ml. of tap water in a two-liter, three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a thermometer. To the rapidly stirred mixture is added in one portion a 0.5% DVB—styrene solution (30 g.) containing benzoyl peroxide (1.37 g). The resulting mixture is stirred at room temperature for 55 minutes and is heated at 80° for a total reaction time of 22 hours. The reaction mixture is cooled and the product is isolated by filtration, rinsed with methanol, and dried in a stream oven (75°) to a constant weight to give 134.1 g. (97.8%) of white opaque beads. Effective size before, .322 mm; after, .346mm.

b) Chloromethylation of Hybrid Copolymer

In a two-liter, three-necked flask equipped with a mechanical stirrer, thermometer, and a condenser to which is attached a drying tube was placed 107 g. of the hybrid copolymer prepared as described above and 350 ml. of 1,2-dichloroethane (EDC). The mixture is stirred for 5 min., 241.5 g. of chloromethyl methyl ether was added, and the resulting mixture is cooled to 0° by means of an ice bath. Aluminum chloride is added over a two hour period while maintaining the reaction temperature at 0°. Upon completion of the addition the reaction mixture is heated at 35° and 24 hours. The mixture is cooled and the liquid phase is removed by means of a filter stick. The crude product is washed with 600 ml. of EDC for 30 min. followed by 3×600 ml. washes with methanol. This material is used directly without further purification in the aminolysis described below. Calculated % Cl: 22.96; Found 20.4.

c) Amination of the Chloromethylated Intermediate

To the chloromethylated intermediate described above is addtd 250 ml. of anhydrous methanol and enough 20% sodium carbonate (~10 ml.) to bring the mixture to pH 8. To the basic slurry is added 75 g. of anhydrous trimethylamine by means of a gas diffusion tube placed below the surface of the liquid while maintaining the reaction temperature between 5—10°. Upon completion of the addition the mixture was warmed to 35° for three hours. Excess TMA and methanol are removed by means of distillation using a Barrett trap while maintaining a constant volume by the addition of water. When the temperature of the reaction mixture reached 100°, the reaction mixture is allowed to cool to room temperature. The resulting product is backwashed to neutrality with tap water. The final product has an average DVB content of 2.45%; solids — 38.5%; anion exchange capacity — 4.25 meq./gm. of dry resin; density — 0.64 g./ml.; porosity — 0.044; reversible swelling — 20.8%; column capacity — 25 g/l (as $CaCO_3$) at a flow rate of 0.8 bed volumes per min; whole bead content after two acid-base cycles with 1N HCl and 1N NaOH — 100%; cracked bead content — 1%.

Example 5

a) Preparation of Hybrid Copolymer

In a two-liter, three-necked flask equipped with a mechanical stirrer, reflux condenser, and a thermometer is placed 800 ml. of water and 107.6 g. of preformed 3% divinylbenzene-styrene macroreticular bead copolymer (particle diameters in the range from 0.25 to 0.85 mm.) having a porosity of 0.56. To the resulting mixture is added 60 g. of a 0.5% divinylbenzene-styrene solution containing 1.67 g. of benzoyl peroxide while rapid stirring is maintained. After 55 min. the reaction mixture is heated to 80° for a total reaction time of 22 hours. The reaction mixture is cooled to room temperature and filtered. The product is washed with 400 ml. of methanol and is dried in a steam oven for 4 hours to give 166.1 g. (99.1%) of white opaque beads. Average bead diameter before polymerization, .322mm. after, .382 mm.

b) Chloromethylation of Hybrid Copolymer

In a two-liter, three-necked flask equipped with a mtchanical stirrer, thermometer, and a condenser to which is attached a drying tube is placed 107 g. of dry copolymer prepared as described above and 350 ml. of a 1,2-dichloroethane (EDC). The mixture is stirred slowly for 15 min. to allow the copolymer to swell. To the swollen copolymer is added 241.5 g. of chloromethyl methyl ether (CME) in one portion. The resulting mixture is cooled to 0° by means of an ice bath and 53.4 g. of aluminum chloride was added over a two hour period while maintaining the temperature at 0°. The reaction mixture is heated to 35° for 24 hours and the liquid layer is removed by means of a filter stick. The resulting beads were washed with 600 ml. portions of anhydrous methanol. Calculated % Cl: 21.3; Found 21.0.

c) Amination of the Chloromethylated Intermediate

The copolymer prepared in the manner described above is placed in a two-liter, three-necked flask equipped with a mechanical stirrer, condenser, and a gas inlet tube. The copolymer is slurried in 250 ml. of absolute methanol and brought to pH 8 with 20% aqueous sodium carbonate. The mixture is cooled to 5—10° by means of an ice bath and 75 g. of trimethylamine (TMA) is added below the surface of the liquid in the flask. After addition the reaction mixture is heated to 35° for a period of 24 hours. The methanol and excess TMA are removed by distillation while maintaining a constant liquid level in the flask by the gradual addition of tap water. When the temperature in the reaction pot reaches 100° distillation is discontinued and the mixture is cooled to room temperature and backwashed to neutrality with tap water. The product has an average DVB content of 2.11%; solids — 38.5%; anion exchange capacity 4.43 meq./gm of dry resin; density — 0.645 g./ml.; reversible swelling — 13.7%; column capacity — 26 g/l (as $CaCO_3$) at a flow rate of 0.8 bed volumes per minute; whole bead content after two acid-base cycles with 1N HCl and 1N NaOH —98% cracked bead content — 13%.

Example 6 (Comparative)

a) Copolymer (Macroreticular)

A 3% divinylbenzene (DVB) — styrene macroreticular copolymer having a porosity of 0.56 which was used in the preparation of Example 5 and Example 4 is used directly without hybridization in the chloromethylation step described below.

b) Chloromethylation of Copolymer

In a two-liter, three-necked flask equipped with a mechanical stirrer, a condenser to which is attached a drying tube, and a thermometer is placed 107.6 g of the copolymer described above and 650 ml. of 1,2 dichloroethane (EDC). The mixture is stirred for 5 min. and 241.5 g. of chloromethyl methyl ether was added and the resulting mixture is cooled to 5—10° over a 25 min. period by means of an ice bath. Aluminum chloride (53.4 g.) is added over a two hour period while maintaining the temperature between 5—10°. The reaction mixture is heated at 35° for 24 hours and the liquid phase is removed with a filter stick. Half hour washes with one 600 ml. portion of EDC and 3×600 ml. portions of absolute methanol were used to purify the

crude reaction product. Calculated % Cl; 23.1; Found 20.1.

c) Amination of the Chloromethylated Intermediate

In a two-liter, three-necked flask equipped with a mechanical stirrer, a condenser, a gas diffusion tube, and a thermometer is placed the chloromethylated resin descibed above. Methanol (300 ml) was added and the slurry was brought to pH 8 with 10% aqueous sodium carbonate The resulting mixture was cooled to 0.—10° and 75 g. of trimethylamine (TMA) is added below the liquid surface through the gas diffusion tube. Upon completion of the addition the reaction mixture is heated at 35° for three hours and is stirred at room temperature for 16 hours. The excess TMA and methanol are removed by distillation while maintaining a constant liquid level by the gradual addition of water. When the temperature reaches 100° distillation is discontinued, the reaction mixture is allowed to cool, and the product is backwashed to neutrality. The product has an average DVB content of 3.0%; solids — 38.5%; anion exchange capacity — 4.25 meq./gm of dry resin; density — .65 g./ml.; reversible swelling — 20%; column capacity — 22.2 g/l (as $CaCO_3$) at a flow rate of 0.8 bed volumes per minute; whole bead content after two acid-base cycles with 1N HCl and 1N NaOH — 100%; cracked bead content — 1.5%.

Example 7 (Comparative)

a) A strongly acidic, macroreticular cation exchange resin, having a styrene-DVB matrix, is prepared in a conventional manner. This resin has a column capacity of 27.6 g/l as $CaCO_3$ at a flow rate of 0.32 bed volumes per minute, a porosity of 0.3—0.36 and a DVB cross-linker level of 20%. This product is indentified as Resin C in Table II below.

b) A strongly acidic, gel type cation exchange resin, having a styrene-DVB matrix is prepared in conventional manner. This resin has a column capacity of 50.5 g/l as $CaCO_3$ at a flow rate of 0.32 bed volumes per minute, a porosity of zero (0) and a DVB cross-linker level of 12%. This resin is identified in Table II below as Resin D. Neither Resin C or Resin D has any imbibed monomer.

Example 8 (Comparative)

a) Preparation of macroreticular base or host copolymer

In a two-liter, three-necked flask equipped with a mechanical stirrer, condenser, thermometer and a positive nitrogen flow is placed 500 g. of water and 1.5g. of sodium. To this mixture is added 1.33 g. of gelatin dissolved in 30 ml. of water and 4.4 g. of sodium polyacrylate in 50 ml. of water. The mixture is stirred for 10 min. The stirring is stopped and a solution containing 350 g. of 20% divinylbenzene-styrene, 290 g. of methylisobutylcarbinol (MIBC) and 3.5 g. of benzoylperoxide is added in one portion. The mixture is heated and stirred for 16 hours at 80°. The MIBC is removed by distillation while maintaining a constant liquid level by the gradual addition of water. Upon completion of the distillation, the reaction mixture is cooled and the product is isolated by filtration, washed with methanol and dried at 75° to a constant weight to give 336 g. (96%) of cross-linked macroreticular product having a porosity of about 0.54 ml./ml.

b) Control Sulfonation

In a one-liter, three-necked flask equipped with a stirrer, a thermometer, and a Barrett trap to which is attached a condenser with a drying tube is added 52 g. of a 20% divinylbenzene (DVB)-styrene macroreticular copolymer *from Example 8 a) above,* 16 g. of 1,2-dichloroethane and 260 g. of 98% sulphuric acid in that order with stirring. The mixture is stirred at room temperature for 30 min., heated at 60° for one hour (at this point 180 g. of additional sulfuric acid is added to maintain fluidity), and at 110° for three hours. While heating, approximately 7 ml. of EDC is collected in the trap. The product is quenched over a period of one hour while maintaining the temperature between 90—110°. The acid washings are siphoned to the top of the bead layer and the resulting beads are washed with successive 400 ml. portions of water until the washings are less than 3% sulfuric acid (5 washes). The beads are neutralized with a 25% excess of 10% sodium hydroxide (21.75-g. of NaOH) while maintaining the temperature below 30°. The basic beads are backwashed to neutrality with tap water. It is observed that relative to hybrid resins (Example 9 and Example 10, below) the beads are more highly fragmented. Initial whole bead content — 5%; fragmented — 95%; 100% fragmented after one wet-dry cycle.

Example 9

a) Preparation of Hybrid Copolymer

In a one-liter, three-necked flask equipped with a mechanical stirrer, thermometer and condenser, is placed 52 g. of a 20% divinylbenzene (DVB)-styrene macroreticular copolymer *from Example 8 a) above* and 400 ml. of tap water. To this mixture is added with rapid stirring 30 g. of a 4% DVB-styrene solution in which is dissolved 0.3 g. of benzoyl peroxide. The mixture is stirred for one hour during which time the preformed copolymer absorbed the added monomer mixture. The mixture is heated at 80° for 16 hours and the product is isolated by filtration, washed with 600 ml. of methanol and dried in a steam oven

(75°) to a constant weight to give 81g. (98.9%) of opaque white beads.

b) Sulfonation of Hybrid Copolymer.

To 50 g. of hybrid copolymer, prepared as described above, in a one-liter, three-necked flask equipped with a stirrer, thermometer, and a Barrett trap to which is attached a condenser with a drying tube is added 16 g. of 1,2-dichloroethane and 260 g. of sulfuric acid in that order. The reaction mixture is stirred at room temperature for 30 min., at 60° for one hour and at 110° for three hours. During this time *ca.* 8 ml. of EDC distilled into the Barrett trap. The reaction mixture is cooled to 90° and 300 ml. of water is added over a period of 30 min. while maintaining the temperature below 110°. The aqueous phase is removed to the bead surface by means of a filter stick and 300 ml. of water is added in one portion. The product is washed with 3×400 ml. portions of water and is neutralized with 10% aqueous sodium hydroxide. The excess caustic is removed by backwashing the sample to neutrality. The product containing 98% whole uncracked beads. After one wet dry cycle the product contained 98% whole beads and 5% cracked beads; salt splitting cation capacity — 4.25 meq./gm. of dry resin; solids — 52.2%; reversible swelling 4.5%; column capacity 5% g/l (as $CaCO_3$) at a flow rate of 0.32 bed volumes per minute; porosity — 0.43; average % DVB — 14.1.

Example 10

a) Preparation of Hybrid Copolymer

In a one-liter, three-necked flask equipped with a mechanical stirrer, thermometer, and condenser is placed 52 g. of a 20% DVB-styrene macroreticular copolymer and 400 g. of tap water. To this mixture is added 60 g. of a 4% DVB-styrene solution in which was dissolved 0.6 g. of benzoyl peroxide. The resulting mixtrue is stirred rapidly for 30 min. and the temperature is brought to 80° and held there for 20 hours. The product is isolated by filtration, washed with methanol, and dried to a constant weight in a steam oven (75°) overnight to give 107.5 g. (96%) of material.

b) Sulfonation of Hybrid Copolymer

In a one-liter, three-necked flask equipped with a mechanical stirrer, a Barrett trap to which is attached a reflux condenser, and a thermometer is placed 50 g. of the hybrid copolymer prepared in the manner described above. To the copolymer is added 16 g. of 1,2-dichloroethane (EDC) and 260 g. of 99% sulfuric acid. The mixture is stirred for 30 min. at room temperature, for one hour at 60°, and for 3 hours at 110°. During this time 7.8 ml. of EDC is collected. The reaction mixture is cooled to 90° and 300 ml. of water is added over a period of 30 min. while maintaining the temperature below 110°. The liquid is siphoned to the bead level and 400 ml. of water is added in one portion. The mixture is stirred for 15 min. and the process is repeated three times. The resulting product is made basic with excess 10% sodium hydroxide while keeping the temperature below 50° and the excess base is removed by backwashing. The product contained 99% whole and uncracked beads; appearance after one wet — dry cycle — 99% whole beads, 28% cracked beads; salt splitting cation capacity — 4.15 meq./g. of dry resin; solids — 55.1%; reversible swelling — 20.7%; porosity — 0.13; average % DVB — 11.4; column capacity — 47.5 g/l at a flow rate of 0.32 bed volumes per minute.

TABLE 1

Properties of Strong Base Ion Exchange Resins

Resin Sample	Imbibed Monomer		Column*** Capacity	Porosity	Appearance**		Total % DVB
	gms.	% DVB	Grams/Liter as $CaCO_3$		Before	After	
Resin A (Example 1a)	—	—	21	0.2—0.4	100/0/0	98/0/2	3
Resin B (Example 1b)	—	—	27.5	0	100/0/0	2/98/0	2
Hybrid Resins							
Example 2	50	1/2	23.4	0.02	99.5/0/.5	99.5/0/.5	1.8
Example 3	100	1/2	24.4	0.00	100/0/0	99.8/0.2/0	1.4
Example 4	30	1/2	25.0	0.04	100/0/0	99/1/0	2.5
Example 5	60	1/2	26.0	0.01	97/1.5/1.5	85/13/2	2.1
Example 6	—		22.2	0.15	—	—	3.0

** Appearance — represents untouched whole beads, cracked beads, and fragmented beads in that order both before and after acid base cycling. In acid base cycling the resin is contacted with 1N HCl for 1/2 hour, rinsed with water, then contacted with 1N NaOH for 1/2 hour and rinsed with water for one complete cycle.

Beads having particle diameters in the range from 0.59 to 0.84 mm are used.

*** Column Capacity — reported at a regeneration level of 64 g. NaOH/liter of resin, Regeneration with 1N NaOH and a flow rate of 0.16 bed volumes per minute.

Exhaustion with 500 ppm HCl at a flow rate of 0.32 bed volumes per min.

TABLE II

Properties of Strong Acid Ion Exchange Resins

Resin Sample	Imbibed Monomer		Column*** Capacity	Porosity	Appearance**		Total % DVB
	gms	% DVB	Kgr. as $CaCO_3$ per ft^3 of resin		Before	After	
Resin C (Example 7a)	—	—	27.6	0.3 — 0.36	100/0/0	99/1/0	20
Resin D (Example 7b)	—	—	50.5	0	77/19/4	56/22/22	12
Hybrid Resins							
Example 8	—	—		0.5	5/0/95	0/0/100	20
Example 9	30	1/2	51.0	0.34	98/0/2	93/5/2	14.1
Example 10	60	1/2	47.5	0.13	99/0/1	71/28/1	11.4

** Appearance — represents untouched whole beads, cracked beads, and fragmented beads in that order both before and after wet — dry cycling. In wet — dry cycling the beads are dried in an oven at 125° C. and then re — wet rapidly.

*** Column Capacity — reported at a regeneration level of 160 g. NaCl/liter of resin. Regeneration with 10% NaCl at a flow rate of 0.16 bed volumes per minute. Exhaustion with 500 ppm of $CaCl_2$ at a flow rate of 0.22 bed volumes per minute.

In Table 1, above, the properties of representative strong base hybrid ion exchange resins are compared with a similar macroreticular strong base resin (Resin A) and with a similar strong base gel resin (Resin B). It can be seen that the physical stability of the hybrid resins, i.e., the resins of examples 2,3,4, and 5, as judged by the appearance before and after acid base cycling, is greatly improved relative to the gel resin, i.e., Resin B, and is at least as good in most instances, and in some instances better than the related macroreticular resin, i.e., Resin A. In addition, the column capacities of the hybrid ion exchange resins are significantly greater when compared with the macroreticular control, Resin A.

Table 11 illustrates a similar improvement in properties namely physical stability and column capacity for hybrid strong acid (cation) ion exchange resins when compared with a similar gel type resin, Resin D, and a similar macroreticular resin, Resin C. It is particularly striking that the column capacities of the hybrid resins, e.g., resins of Examples 9 and 10 are almost double that of the counterpart macroreticular resin (Resin C) and in the case of example 9 is even greater than a corresponding gel resin, e.g., Resin D.

Example 11

a) Preparation of Hybrid Copolymer

In a one-liter, three-necked flask equipped with an efficient stirrer, a reflux condenser, and a drying tube is placed 100 g. of a 3% divinylbenzene (DVB)-styrene cross-linked macroreticular copolymer having a porosity of 0.56 and 300 ml. of tap water. The mixture is heated to 80° and a solution consisting of 100 g. of 8% DVB (55.9% active)—styrene monomer and 1 g. of benzoyl peroxide is added in one portion. The resulting mixture is stirred rapidly at 80° for three hours and at 95° for two hours. The beads are filtered, washed with methanol, and dried at 75° overnight to give 198.2 g. (99%) of product.

b) Sulfonation of Hybrid Copolymer

A two-liter, three-necked flask is equipped with a mechanical stirrer, thermometer, Barrett trap, and a condenser is charged with 100 g. of the hybrid copolymer described above in Example 11 a) 30 g. of 1,2-dichloroethane (EDC), and 600 g. of 99% sulfuric acid. The mixture is stirred at room temperature for 30 min., 60° for one hour, and 110° for three hours. During this time 16.2 ml. of EDC distilled into the Barratt trap. Water (300 ml.) is added over a three hour time period and 3000 ml. over an additional three hour (with periodic removal of excess washings) period. At the end of the quenchsiphon, the liquid is removed to the bead level and the beads are neutralized with 3×500 ml. portions of 5% sodium hydroxide. The product is backwashed to neutrality and is isolated by filtration. The resin exhibits a sodium leakage of 6.34% measured at 10 ppm above the lowest sodium leakage point (11.52 ppm); rinse requirements —12.9 bed volumes; solids — 43.8% salt splitting cation capacity — 4.61 meq./g. of dry resin. The overall cross-linker level is 5.5%.

c) Preparation of Hybrid Copolymer

In a one-liter, three-necked flask equipped with an efficient stirrer, a reflux condenser, and a drying tube is placed 100 g. of a 3% divinylbenzene (DVB)-styrene macroreticular copolymer, porosity 0.56, and 270 ml. of tap water. The mixture is heated to 80° and a solution consisting of 80 g of 8% DVB (55.9% active)-styrene monomer and 0.8 g. of benzoyl peroxide is added in one portion. The resulting mixture is stirred rapidly at 80° for three hours and at 95° for two hours. The beads are filtered, washed with methanol, and dried at 75° overnight to give 178 g. of product.

d) Sulfonation of Hybrid Copolymer

A two-liter, three-necked flask equipped with a mechanical stirrer, thermometer, Barrett trap, and a condenser is charged with 100 g. of the hybrid copolymer (bead diameters in the range from 0.21—0.84 mm), 30 g. of ethylene dichloride (EDC), and 603 g. of 96% sulfuric acid. The mixture is stirred at room temperature for 30 min., 60° for one hour, and 110° for three hours. 13.6 ml. of EDC is collected in the Barrett trap while heating to 110°. The reaction is quenched at 100—10° using the following schedule: 2 ml./min. for 80 ml., 4 ml./min, for 200 ml., 8 ml./min. for 200 ml., and 10 ml./min for 720 ml. The liquid is removed to the top of the bead layer by means of a filter stick and the beads are washed with 6 × 600 ml. portions of water. To the resulting product is added 500 g. of 10% sodium hydroxide while keeping the temperature below 35°. The resin in the sodium form is stirred for 30 min. and is backwashed to neutrality. The resin exhibits a sodium leakage of 4.15% with an end point taken at 10 ppm above the lowest sodium leakage point (5.65 ppm); rinse requirements — 1.92 bed volumes; solids — 42.0%; salt splitting cation capacity — 4.60 meq./g. of dry resin.

e) Preparation of Hybrid Copolymer

In a one-liter, three-necked flask equipped with an efficient stirrer, a reflux condenser, and a drying tube is placed 100 g. of a 2% divinylbenzene (DVB)-styrene macroreticular copolymer (porosity — 0.56) and 240 ml. of tap water. The mixture is heated to 80° and a solution consisting of 60 g. of 8% DVB (55.9% active)-styrene monomer and 0.6 g. of benzoyl-peroxide is added on one portion.

The resulting mixture is stirred rapidly at 80° for three hours and at 95° for two hours. The product is isolated by filtration, washed with methanol, and dried at 75° to a constant weight to give 154.8 g. of beads.

f) Sulfonation of Hybrid Copolymer

The procedure followed was the same as that for 11 d). The resin exhibited a sodium leakage of 2.15% with an end point taken at 10 ppm above the lowest sodium leakage point (1.85 ppm); rinse requirements — 3.2 bed volumes; solids — 40.1%; salt splitting cation capacity — 4.61 meq./g of dry resin.

g) Another cation exchange resin, commercially available, having a small amount of porosity believed to be achieved by solvent leaching linear polymer from an intermediate gel material. The sodium leakage is 7.45%; solids 44.6%; salt splitting cation capacity— 4.67 meq./gm. of dry resin; lowest sodium leakage point — 14.78 ppm; rinse requirements — 12.9 bed volumes. This product is manufactured by Diamond-Shamrock Company and is available under the tradename Duloite C—25D (Duloite Data Leaflet No 25 A lists the rinse requirements for C—25D as 3.2—4.7 bed volumes).

h) A standard, commercially available, gel type strongly acidic exchange resin having a cross-linker level of 8% DVB shows a representative 12.84% sodium leakage when measured at 10 ppm above the lowest sodium leakage point.

The Table below, Table 111, compares % sodium leakage for the various resins described in Example 11.

TABLE 111

Sodium Leakage

With Cation Exchange Resins[1]

Resin Sample	Cross-Linker Level, %	% Sodium[2] Leakage	Rinse Requirements Bed Volumes
Example 11b	5.5	6.34	29.8
Example 11d	5.2	4.15	19.3
Example 11f	4.9	2.15	32.4
Example 11g	6	7.45	12.8
Example 11h	8	12.84	14.2

[1] The data represent the average of two runs and are expressed in terms of equivalent calcium carbonate.

[2] Measured at 10 ppm above the lowest sodium leakage point.

Sodium leakage is determined, after placing the resin in the hydrogen ion form, by exhausting with a 500 ppm NaCL solution to a flow rate of 0.32 bed volumes per min. of resin for the influent. The regenerant is H_2SO_4, 160 g. of regenerant/liter at a 0.16 bed volumes/min. flow rate. Low sodium leakage is very desirable in ion exchange resins, particularly resins useful in water-treating applications. As is shown in Table 111 above, the ion exchange resins of the present invention, e.g., 11b, 11d, and 11f, show a significant and distinct improvement in % sodium leakage value, as compared with a porous resin of the prior art, 11g, and a gel type resin of the prior art, i.e., 11h. Also, it should be noted that the rinse requirements are much less with resins of the present invention, 11b, 11d and 11f, than they are with the resins of the prior art, i.e., 11g and 11h.

Example 12

a) Preparation of the Hybrid Copolymer

In a two-liter, three-necked flask equipped with an effective stirrer, a condenser, and a thermometer is placed 107.6 g. of a 3% divinylbenzene (DVB) (55% active)-styrene macroreticular copolymer (bead diameters in the range from 0.25—0.59 mm porosity 0.56) and 800 ml. of tap water. To this mixture is added 110 grams of a 0.5% DVB-styrene solution in which is dissolved 2.17 g. of benzoyl

peroxide. The resulting mixture is stirred rapidly at room temperature for one hour and at 80° for a total reaction time of 22 hours. The mixture is allowed to cool to room temperature and the resulting beads are isolated by filtration, washed with 600 ml. of methanol and dried to a constant weight in a steam oven (75°). The hybrid copolymer is used directly in the following chloromethylation procedure. The yield of hybrid copolymer is 214.70 g. (98.5%).

b) Chloromethylation of Hybrid Copolymer.

In a two-liter, three-necked flask equipped with a mechanical stirrer, a condenser with a drying tube attached and a thermometer was placed 106.03 g. of the above hybrid copolymer and 350 ml. of 1,2-dichloroethane (EDC). The mixture is stirred slowly for 10 minutes allowing the beads to swell. To the swollen beads is added 241.5 g. of chloromethyl ether (CME) in one portion. The reaction mixture is cooled to 0° by means of an ice bath and 53.36 g. of aluminum chloride was added over a two hour time period, while maintaining the temperature below 5°. The mixture which resulted is heated at 40° for 16 hours. The resulting beads are washed once with 600 ml. of EDC and three times with 600 ml. portions of anhydrous methane. The resulting chloromethylated product was used directly in the following aminolysis.

c) Aminolysis of the Chloromethylated Intermediate

In a two-liter, three-necked flask equipped with a mechanical stirrer, a thermometer, and a gas diffusion tube is placed the chloromethylated intermediate prepared as described above. Methanol (250 ml.) is added and the mixture is brought to pH 8 with 10% sodium carbonate. To the basic mixture is added 75 g. of trimethylamine (TMA) by means of a gas diffusion tube while maintaining the reaction temperature below 15° with an ice bath. After the addition is completed the reaction is stirred at room temperature overnight. The unreacted TMA and the methanol are removed by distillation while maintaining a constant fluid level by the gradual addition of water. The reaction mixture is cooled and the product is backwashed to neutrality and isolated by filtration. The product has an average DVB-content of 1.6 g; solids — 52.43, anion exchange capacity 4.51 meq./g. of dry resin; reversible swelling — 14.5%; column capacity — 24.2 g/l (as $CaCO_3$) at a flow rate of 0.8 bed volumes per minute.

The following table, Table IV, shows the improvement in sugar decolorization that can be obtained with the novel hybrid ion exchange resins of the present invention.

TABLE IV

Sugar Decolorization with Hybrid Resins

Resin	Weight Capacity	% Sorp of Color Bodies	% Sorp of Color Bodies from Resin	Thruput	Stability (after cycling)
Sample ———	(milliequivalents quat. ammonium functionality per gm. of dry resin)				
Resin E[1]	4.25	84.4	79.9	235	98/2/0
Resin F[2]	4.18	81.9	76.6	269	84/15/1
Resin G[3]	3.7	86.5	56.1	168	0/99/1
Resin H[4]	4.20	85.9	70.8	190	95/4/1

[1] hybrid resin 30 g. of 0.5% DVB — 99.5% styrene/mole of 0.56 porosity macroreticular base having quat. ammonium functionality prepared according to teachings of Example 4, above.

[2] hybrid resin 60 g. of 0.5% DVB — 99.5% styrene/mole of 0.56 porosity macroreticular base having quat. ammonium functionality prepared according to teachings of Example 12, above.

Footnotes to Table IV (Continued)

[3] gel — type quat, ammonium resin commercially available, styrene — DVB (1%) cross-linked matrix.

[4] macroreticular quat. ammonium resin commercially available styrene — DVB (3%) cross-linked matrix.

The above data show the unexpected improvement in the ability of the hybrid resin to decolorize sugar solutions. In particular, the hybrid resins E and F lasted for 235 and 269 bed volumes, respectively, (to a given endpoint) while related gel and macroreticular resins lasted only for 168 and 190 bed volumes, respectively, to the same endpoint. The decolorization data is obtained as follows.

The color is monitored colorometrically at 420 mμ. The influent sugar is light cane (approx. 55% by wt. cane sugar) from activated carbon beds at Sucrest Sugar Co. U.S.A. The conditions of the column runs are as follows:

Treatment temperature	—	70°C
Treatment flow rate	—	0.2 bed volumes/min.
Bed size	—	30 mls
Bead diameters	—	0.42—0.84 mm
Endpoint	—	40% color leakage
Regeneration temperature	—	70°C
Regeneration flow rate	—	0.04 bed volume/min
Regeneration level	—	9.6 kg/liter of NaCl (10%)

Example 13

a) Preparation — Acrylic Hybrid Copolymer

In a one-liter, three-necked flask equipped with a mechanical stirrer, a condenser and a thermowatch-thermometer combination is placed 114.13 g. of a 20% divinylbenzene-(DVB)-styrene macroreticular copolymer (bead diameters in the range from 0.21—0.59 mm.) and 216.64 g. of tap water. To this is added with rapid stirring 30 g. of a 10% DVB-methylacrylate solution in which is dissolved 1.44 g. of benzoyl peroxide. The reaction mixture is stirred rapidly and heated at 80°C. for 3 hours and the temperature increased to 95°C for 2 hours. The mixture is cooled and the copolymer is isolated by filtration, washed with 600 ml. of methanol and dried in a steam oven (75°C) until a constant weight of hybrid copolymer is achieved to give 133.40 g. (92.55%) of product.

b) Acrylic Hybrid Copolymer Hydrolysis

In a two-liter, three-necked flask equipped with a mechanical stirrer, a condenser to which is attached a drying tube, an addition funnel, distillation head, and thermometer is added 111.40 g. of the hybrid copolymer described above and 305.65 g. of a 55.21% sulfuric acid solution. The solution is distilled for 15 hours with concurrent addition of make-up water. A non-ionic wetting agent is added as necessary to control forming. When the distillation is complete, the hydrolyzed copolymer is back-washed until the effluent is neutral. The copolymer is isolated by filtration, washed with 600 ml. of methanol, and dried in a steam oven (75°) until a constant weight of copolymer is achieved.

c) Sulfonation of the Styrene Acrylic Hybrid Copolymer

To 100 g. of the hydrolyzed copolymer (KT 1492) in a three-liter, three-necked flask equipped with a stirrer, thermometer and a Barratt trap to which is connected a condenser with a drying tube was added 600 ml. of 97% sulfuric acid. The mixture is stirred until thoroughly mixed and is heated at 120° for 6 hours. The mixture is cooled to 50°C. with the aid of an ice bath and water is added dropwise at such a rate as to maintain the temperature at 70°. When 500 ml. of water has been added one half of the liquid layer is drained by means of a filter stick. The washing procedure is repeated three times and the product is back-washed to neutrality.

Example 14

a) Preparation of a Vinyl Pyridine Hybrid Copolymer

In a one-liter, three-necked flask equipped with a mechanical stirrer, a condenser and a thermometer is placed 107.6 g. of a 3% DVB-styrene macroreticular copolymer (0.56 porosity bead diameters in the range from 0.21—0.59 mm.) and 206 g. of water. To this mixture is added, with rapid stirring, 30 g. of a 3% DVB-2-vinylpyridine solution in which is dissolved 1.37 g. of benzoyl peroxide. The reaction mixture is stirred rapidly at 80° for 3 hours and at 95° for 2 hours. The resulting mixture is cooled and the copolymer is isolated by filtration, washed with 600 ml. of methanol and dried to a constant weight at 75° to give 133.7 g. (97.1%) of product.

While the examples given herein above deal with addition type polymers, the present inven-

tion also embraces other types of polymers which may form one or more of the components of the hybrid copolymers. Thus, condensation polymers, or mixtures of condensation polymers and addition polymers, may be used as the host copolymer or as the filling copolymer.

WHAT WE CLAIM IS:—

1. A hybrid copolymer comprising a cross-linked macroreticular host copolymer, the pores of which contain a separately formed cross-linked filling copolymer.

2. A hybrid copolymer comprising a cross-linked macroreticular host copolymer, the pores of which contain non-macroreticular cross-linked gel copolymer.

3. A hybrid copolymer according to Claim 1 or 2, wherein the host copolymer and the filling copolymer are made by copolymerizing poly-unsaturated monomer and monoethylenically unsaturated monomer molecules.

4. A hybrid copolymer according to Claim 3 in which the polyunsaturated monomer comprises divinylbenzene and the monoethylenically unsaturated monomer comprises styrene.

5. A hybrid copolymer according to any one of the preceding claims, wherein both copolymers contain, or have imparted thereto after formation thereof, ion exchange functional groups.

6. A hybrid copolymer according to Claim 5 in which the filling copolymer is present in an amount of 5 to 300 parts by weight per 100 parts by weight of host copolymer.

7. A hybrid copolymer according to Claim 6 in which the filling copolymer is present in an amount of 10 to 200 parts by weight per 100 parts by weight of host copolymer.

8. A hybrid copolymer according to any one of the preceding claims, wherein the degree of cross-linking of the filling copolymer is less than that of the host copolymer.

9. A hybrid copolymer according to any one of Claims 1—7 in which the degree of cross-linking of the filling copolymer is greater than that of the host copolymer.

10. A hybrid copolymer according to any one of the preceding claims and which is in particulate form.

11. A method of making a hybrid copolymer according to Claim 1 which comprises at least partially filling the pores of a cross-linked macroreticular host copolymer with monomer and polymerizing the monomer to form polymer and introducing cross-links therein.

12. A method according to Claim 11 which comprises contacting particles of a macroreticular copolymer having a significant degree of porosity with a liquid mixture of monomer containing at least one polymerizable double bond and monomer containing at least two polymerizable double bonds, imbibing said monomeric liquid mixture into the particles of the macroreticular copolymer and polymerizing said imbibed monomer within the particles of the said macroreticular copolymer and thereafter introducing ion exchange functional groups to the hybrid polymer thus formed.

13. A method according to Claim 11 or 12 as applied to the preparation of a hybrid copolymer according to any one of Claims 6—9.

14. A hybrid copolymer when prepared by a method according to Claims 11 or 12.

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WHAT WE CLAIM IS:—

1. A hybrid copolymer comprising a cross-linked macroreticular host copolymer, the pores of which contain a separately formed cross-linked filling copolymer.

2. A hybrid copolymer comprising a cross-linked macroreticular host copolymer, the pores of which contain non-macroreticular cross-linked gel copolymer.

3. A hybrid copolymer according to Claim 1 or 2, wherein the host copolymer and the filling copolymer are made by copolymerizing poly-unsaturated monomer and monoethylenically unsaturated monomer molecules.

4. A hybrid copolymer according to Claim 3 in which the polyunsaturated monomer comprises divinylbenzene and the monoethylenically unsaturated monomer comprises styrene.

5. A hybrid copolymer according to any one of the preceding claims, wherein both copolymers contain, or have imparted thereto after formation thereof, ion exchange functional groups.

6. A hybrid copolymer according to Claim 5 in which the filling copolymer is present in an amount of 5 to 300 parts by weight per 100 parts by weight of host copolymer.

7. A hybrid copolymer according to Claim 6 in which the filling copolymer is present in an amount of 10 to 200 parts by weight per 100 parts by weight of host copolymer.

8. A hybrid copolymer according to any one of the preceding claims, wherein the degree of cross-linking of the filling copolymer is less than that of the host copolymer.

9. A hybrid copolymer according to any one of Claims 1—7 in which the degree of cross-linking of the filling copolymer is greater than that of the host copolymer.

10. A hybrid copolymer according to any one of the preceding claims and which is in particulate form.

11. A method of making a hybrid copolymer according to Claim 1 which comprises at least partially filling the pores of a cross-linked macroreticular host copolymer with monomer and polymerizing the monomer to form polymer and introducing cross-links therein.

12. A method according to Claim 11 which comprises contacting particles of a macroreticular copolymer having a significant degree of porosity with a liquid mixture of monomer containing at least one polymerizable double bond and monomer containing at least two polymerizable double bonds, imbibing said monomeric liquid mixture into the particles of the macroreticular copolymer and polymerizing said imbibed monomer within the particles of the said macroreticular copolymer and thereafter introducing ion exchange functional groups to the hybrid polymer thus formed.

13. A method according to Claim 11 or 12 as applied to the preparation of a hybrid copolymer according to any one of Claims 6—9.

14. A hybrid copolymer when prepared by a method according to Claims 11 or 12.

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