Ion Exchange Resins

1970

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Thirty-Five Dollars

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FOREWORD

The detailed, descriptive information in this book is based on U.S. Patents since 1960, relating to production of ion exchange resins.

This book serves a double purpose in that it supplies detailed technical information and can be used as a guide to the U.S. Patent literature in this field. By indicating only information that is significant, this book then becomes an advanced review of processes for producing ion exchange resins.

The U.S. Patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical, commercial timely process information assembled here than is available from any other source. The technical information obtained from the patent literature is extremely reliable and comprehensive; sufficient information must be included to avoid rejection for "insufficient disclusure".

The patent literature covers a substantial amount of information not available in the journal literature. The patent literature is a prime source of basic commercially utilizable information. This information is overlooked by those who rely primarily on the periodical journal literature. It is realized that there is a lag between a patent application on a new process development and the granting of a patent, but it is felt that this may roughly parallel or even anticipate the lag in putting that development into commercial practice.

These publications are bound in paper in order to close the time gap between "manuscript" and "completed book". Industrial technology is progressing so rapidly that hard cover books do not always reflect the latest developments in a particular field, due to the longer time required to produce a hard cover book.

The Table of Contents is organized in such a way as to serve as a subject index. Other indexes by company, inventor, and patent number help in providing easily obtainable information.

CONTENTS AND SUBJECT INDEX

INTRODUCTION

The diversity of the patent literature dealing with the production of ion exchange materials mirrors the diversity of the materials themselves and the processes which use ion exchange — from something as commonplace as water purification to the more exotic rare earth separation processes. And to gauge, from even a perfunctory search of the patent literature, which patent deals with which type of ion exchange agent becomes a formidable task without the aid of some guideposts.

This report thus not only provides detailed information on 134 patents (issued since 1960) which are concerned with the composition and manufacture of ion exchange materials, but also groups these patents according to their physical form, behavior characteristics, etc.

Ion exchange materials are commonly grouped into anion and cation exchange categories, and this report includes these two groups of resins (Chapters 1 and 2, respectively) but only for those patents concerned with resins labeled as such. Chapter 3 includes resins which, although perhaps broadly qualifying as anionic or cationic, are aimed at more narrow uses — demetalation, for instance — or whose efficacy stems from their abilities to sequester or chelate various chemical entities. Patents covering resins that may perform any combination of two or more functions described in the first three chapters make up Chapter 4.

Then, because of the furor during the 1960's concerning detergents and their biodegradability, Chapter 5 deals with an ion exchange material specific to removal of alkylbenzenesulfonates, chemicals which made up the main foam-producing agents of detergents. Also, ion exchange resins peculiar to manufacturing bisphenols are noted in that chapter, as is a vinylation reaction catalyst. Chapters 6, 7 and 8 cover those patents concerned essentially with facets independent of the ion exchange capabilities of the materials, and which emphasize characteristics such as: materials that may be usable in producing some ion exchange agents, such as the polyphenylenes (Chapter 6); processes used in making ion exchange agents, such as cross-linking (Chapter 7); properties of ion exchange agents, such as high temperature stability (Chapter 8).

Ion exchange membrane developments during the past decade are grouped into Chapter 9, and those patents which emphasize shapes are dealt with in the final chapter.

ANION EXCHANGE RESINS

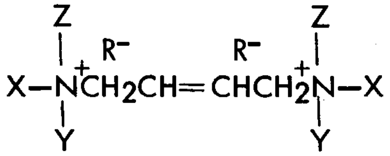
QUATERNARY-AMMONIUM BASED WITH HIGH REGENERATION RATES

Anion exchange resins perform one primary function— very simply put, they remove acids from a liquid medium. Two of the chief parameters determining how well an ion exchange material does its job is its degree of acid removal and the ease with which the resin can be regenerated. Quaternary-ammonium based resins that combine improved anion exchange characteristics with faster regeneration rates than earlier materials would thus be a significant improvement, since regeneration of such resins is generally very difficult.

A process developed by G.B. Butler and R.L. Goette (U.S. Patent 2,946,757; July 26, 1960) produces quaternary ammonium salts by treating diallyl amine with 1,4-dichlorobutene-2 or 1,4-dibromobutene-2 to produce 1,4-bis-(diallylamino)-butene-2, followed by treatment of this amine with alkyl, alkenyl, aralkyl, or aralkenyl halides. Although, from a capacity standpoint, it is advantageous to use as quaternizing groups those compounds of lowest molecular weight, other factors such as cost, reactivity, etc., are important.

Polymers and copolymers of these quaternary ammonium salts have the properties of anion exchange resins. Because of the presence of the butene-2 double bond which does not lose its identity in the polymerization, these polymers and copolymers are markedly more readily converted to the hydroxide form from the salt form than other known materials of this type.

This process gives cross-linked water insoluble polymers of symmetrically-substituted quaternary ammonium salts of the structure:



$$X-\underset{\underset{Y}{|}}{\overset{\overset{Z}{|}}{\overset{+}{N}}}\overset{R^-}{C}H_2CH=CH\overset{R^-}{C}H_2\underset{\underset{Y}{|}}{\overset{\overset{Z}{|}}{\overset{+}{N}}}-X$$

where X stands for allyl radicals, Y and Z stand for lower alkyl or allyl radicals, and R^- is a chloride or bromide ion. The polymers are suitable for use as ion exchange resins capable of rapid regeneration rates and are characterized by polymerization and cross-linking through the ethylenic double bonds of the allyl groups, the butene double bonds remaining intact. These polymers include homopolymers of such salts and copolymers of the salts with different ethyleneically unsaturated quaternary ammonium compounds. While use of 1,4-bis-(diallylamino)-butene-2 is preferred as an intermediate for preparation of the monomeric quaternary ammonium salts, it is not essential. 1,4-bis-(dimethylamino)-butene-2 and 1,4-bis-(diethylamino)-butene-2, as well as other members of this series of organic compounds can serve. Such derivatives when quaternized with alkenyl or aralkenyl halides possess properties which permit them to produce copolymers which possess the pronounced property of decreased basicity which permits their more ready regeneration.

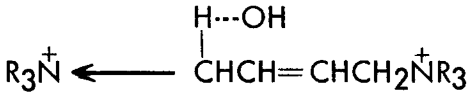
Although it has not been definitely established why polymers and copolymers of quaternary ammonium salts of 1,4-diamino-butene-2 possess decreased basic properties, thus permitting the very desirable more rapid regeneration rate, this does not affect the utility or novelty of the products.

Results of polymerization studies of 1,4-diamino-butene-2 derivatives containing two, four and six allyl groups in addition to the butene-2 double bond show that those compounds containing only two double bonds, e.g., bis-(allyldimethylammonium)-butene-2 dibromide, produce water-soluble polymers, while those containing four or six double bonds result in the formation of water-insoluble polymers. Since previous results have shown that water-insoluble polymers result from those compounds containing three or more double bonds, the failure of bis-(allyldimethylammonium)-butene-2 dibromide to produce a water-insoluble polymer is conclusive evidence that the butene-2 double bond did not enter into the polymerization.

This is substantiated by the pronounced effect of this double bond on the regeneration rates of the resulting polymers as discussed below. Even though those monomers containing only two allyl groups would not produce water-insoluble polymers suitable for further study alone, their copolymers with monomers containing three or more allyl groups were prepared.

It might be expected that this residual double bond would have an effect on the basic properties of the quaternary ammonium center due to its electrophilic nature. This effect appears to be analogous to that which results in a decrease in the ionization constant of an amine when, e.g., a propyl group is replaced by an allyl group. Dipropylamine has $K_b = 1.02 \times 10^{-3}$ at 25°, and diallylamine has $K_b = 3.12 \times 10^{-6}$ at 25°. This effect could conceivably be the result of one or both of two mechanisms: (1) the electrophilic group decreases electron density in the immediate vicinity of the nitrogen atom, thus increasing the electropositive nature of this atom, resulting in decreased mobility of the hydroxyl ion, or (2) the C—N bond between the allyl group and the nitrogen may possess a certain degree of ionic character, as the result of resonance, thus increasing the electropositive nature of the nitrogen center.

This latter effect would result in a more complete distribution of the positive charge over the entire ion, and likewise decrease the mobility of the hydroxyl ion. Since a quaternary ammonium hydroxide, according to present accepted ideas of structure, cannot exist in a nonionized state except by hydrogen bonding through some mechanism such as that suggested below, this observed decrease in basic properties in polymers containing the butene-2 double bond must be attributed to the presence of this double bond. This decrease must be explained either on the basis of decreased mobility of the hydroxyl ion by one of the above mechanisms, or by hydrogen bonding. Since the quaternary ammonium structure has no proton attached directly to the nitrogen atom as in the ammonium and alkyl ammonium ions, hydrogen bonding could result only between the oxygen of the hydroxyl ion and a hydrogen atom attached through carbon. Since it has been shown that compounds such as allylbenzene react to produce an ionic sodium derivative, it is likely that hydrogen bonding could be a factor in the manner



$$R_3\overset{+}{N} \longleftarrow \overset{H\cdots OH}{\overset{|}{C}}HCH{=}CHCH_2\overset{+}{N}R_3$$

Further evidence is available for the partial ionic character of the methylene hydrogen atoms in allyl groups in the extensive work on allylic arrangements.

Since it has previously been shown that the swelling coefficient is an important factor in the ion exchange rates of quaternary ammonium polymers, this factor was considered in these studies. For comparison, samples of polymers were selected which had approximately equal swelling coefficients, the polymer containing the butene-2 double bond having a slightly lower value. The polymer having the higher swelling coefficient, all other factors being equal, would be expected to have the higher exchange rate; however, in these studies, the reverse was true by two-fold.

Another factor which would be expected to affect the exchange rate is the mol fraction of strong electron-releasing groups, e.g., methyl. The polymers selected containing the butene-2 group having the larger mol fraction (0.343 as compared to 0.300) of methyl groups, which effect alone would be to decrease the rate of regeneration, giving this polymer a slight disadvantage in the comparison. Other bis-substituted allylaklylammonium butene-2-dihalides can be made by the process.

A process developed by H. Zenftman (U.S. Patent 2,946,758; July 26, 1960; assigned to Imperial Chemical Industries Limited, England) also produces quaternary-ammonium-based resins featuring easier regeneration. A resin produced by this process consists of a polymeric ester made up at least substantially of units which contain at least one quaternary ammonium group connected to not less than two acyloxy groups each derived from acrylic or methacrylic acid.

Examples of these anion exchange resins are the polymeric esters of N,N'-dimethyl N,N'-di(2-methacryloxyloxyethyl) piperazinium di(monomethyl sulfate), of N,N-dimethyl N,N-di(2-methacryloyloxyethyl) ammonium monomethyl sulfate, of N-methyl N,N,N-tri(2-methacryloyloxyethyl) ammonium monomethyl sulfate.

The process comprises polymerizing an ester-salt containing at least one quaternary ammonium group connected to not less than two acyloxy groups each derived from acrylic or methacrylic acid. The ester-salt, which is in fact a quaternary ammonium ester-salt, is produced by forming a tertiary-amino ester by ester interchange between at least 2 mols of an ester of acrylic or methacrylic acid, for example, a methyl or ethyl ester of acrylic or methacrylic acid, and 1 mol of a polyhydric tertiary-amino alcohol and treating the resulting tertiary-amino ester with a methylating agent, i.e., an alkyl ester of an inorganic acid as for instance a dialkyl sulfate or an alkyl halide. The polyhydric tertiary-amino alcohols are, for example, methylamine-N,N-diethanol, 1,4-piperazine dimethanol, 1,4-piperazine diethanol, ethylamine N,N-diethanol, methylamine N,N-dipropanol, triethanolamine, and ethylenediamine N,N,N',N'-tetraethanol.

These polyhydric tertiary-amino alcohols after their conversion into tertiary-amino esters of acrylic or methacrylic acid are converted into the corresponding quaternary ammonium ester-salts by reacting them with, for instance, an alkyl ester of an inorganic acid in the presence of a polymerization inhibitor as, for example, 1,4-dimethyl 6-tertiary-butylphenol. The alkyl ester of an inorganic acid may be, for instance, dimethyl or diethyl sulfate or ethyl, methyl or propyl chloride, bromide or iodide.

The alkyl ester of an inorganic acid is introduced into a solution of the tertiary-amino ester which solution should preferably contain the polymerization inhibitor and be at a reaction temperature until the reaction is complete. The phase containing the resulting ester-salt is separated from the diluent phase and is washed with an organic solvent for the inhibitor until the inhibitor is removed. The purified ester-salt is then polymerized, preferably in the presence of water, and if desired in suspension in a water-immiscible liquid boiling at a temperature above 70°C., in the presence of a catalyst of the kind used for polymerizing acrylic or methacrylic esters or acrylic and methacrylic acids. These catalysts may be, for instance, ammonium persulfate, potassium persulfate, azodiisobutyronitrile or benzoyl peroxide. The resulting product, depending on the conditions of polymerization, may be irregular granules or regular spherical beads and may be separated by filtration or washed free from diluent by displacement with water and subsequently dried.

Alternatively the ester-salt may be polymerized in bulk in the absence of a diluent and thereafter broken up or it may be polymerized in any desired shape as sheet or foil or if desired supported on a carrier of porous or felted or woven fiber of material resistant to dilute acids and alkalis. For this purpose glass or polyethylene terephthalate fabrics are suitable. An alternative process comprises polymerizing a tertiary-amino ester of acrylic or methacrylic acid and treating the resulting polymerization product with an alkyl ester of an inorganic acid to convert said polymerized product into a polymeric ester made up at least substantially of units which contain at least one quaternary ammonium group connected to not less than two acyloxy groups each derived from acrylic or methacrylic acid.

The tertiary-amino esters of acrylic or methacrylic acid are washed free from polymerization inhibitor with ether before their polymerization is effected. The tertiary-amino ester of acrylic or methacrylic acid may be polymerized as such or as a suspension in an aqueous medium. The polymerization is preferably carried out at raised temperature in the presence of a polymerization catalyst. If water has been included this is removed prior to the treatment with an alkyl ester of an inorganic acid as this treatment is to be carried out on the dry polymer and at raised temperature preferably in the presence of an organic diluent.
If it is desired to obtain the resins in their basic form they are treated with a solution of an alkali metal hydroxide and washed with water until the wash water is substantially neutral.

The resins in their basic form are insoluble in water and the normal solvents, stable to prolonged exposure to hot water, and of high gravimetric and volumetric anion exchange capacity. Swelling and other physical properties of the resin may be modified by carrying out the polymerization in the presence of a minor proportion of suitably reactive monomers other than the ester salts, such as methacrylic esters, but the extent to which this may usefully be done is limited. The resins of this process after use require less caustic soda to regenerate them into their basic form than commercially available anion exchange resins containing quaternary ammonium groups.

STRONG AND WEAK BASE WITH HIGH CAPACITIES

A process by H. Corte and O. Netz (U.S. Patent 3,006,866; October 31, 1961; assigned to Farbenfabriken Bayer AG, Germany) gives anion exchange resins by reacting cross-linked vinyl aromatic polymers with a haloalkylimide.

It is known from U.S. Patent 2,591,573; 2,591,574; 2,616,877; 2,629,710; 2,631,999; 2,632,000; 2,642,417; 2,725,361; 2,794,785; 2,597,439 and 2,597,440 that anion exchange resins may be obtained by introducing halogenalkyl groups into cross-linked polymers produced from aromatic vinyl compounds, and by reacting the resulting haloalkylated insoluble copolymers with an amine. If, in carrying out such a process, ammonia is introduced in the second stage of reaction, secondary reactions occur to a considerable degree with the formation of products having secondary or tertiary amino groups, so that it is not possible to produce derivatives of the said cross-linked polymers which contain exclusively primary aminoalkyl groups.

To overcome this difficulty, the halogenoalkylated cross-linked polymers have already been reacted with potassium phthalimide to form the corresponding phthalimido compounds, which are then saponified to the corresponding aminoalkyl derivatives. This process, however, requires three stages for the introduction of the aminoalkyl groups, namely, 1) the introduction of the halogenoalkyl groups, 2) the reaction with potassium phthalimide and 3) the saponification of the resulting products.

It has now been found that synthetic resins having anion exchange properties can be obtained in a substantially simpler manner if cross-linked benzene insoluble organic polymers containing aromatic nuclei the carbon atoms of which constitute the major proportion of the total number of the carbon atoms of the polymer are condensed in the presence of a swelling agent and of a Friedel-Crafts catalyst with a N-(halogenoalkyl)-imide and the resulting products are saponified. Also, the synthetic resins obtained by this process have a noticeably higher anion exchange capacity than the products obtained by the known process. The reason for this may be that the known processes, which include the halogenoalkylation, cause additional cross-linking effects due to the halogenoalkyl groups which are introduced reacting further with aromatic nuclei. As a result, some of the chloralkyl groups introduced are obviously lost for the purpose of the intended amination, since it is known that insoluble, i.e., cross-linked, products, are formed when polystyrenes which are not cross-linked are halogenoalkylated, as for example with chloromethyl ether and aluminum chloride.

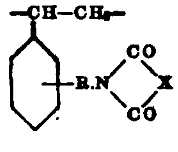
The introduction of aminoalkyl groups by means of chloromethyl phthalimide into aromatic hydrocarbons of low molecular weight, such as, for example, benzene or naphthalene, certainly constitutes a known reaction, but it was not to be expected that it would be possible to transfer this reaction to cross-linked insoluble polymers containing aromatic nuclei and that, in addition, it would be possible in this way to produce anion exchangers having a capacity substantially higher than that of the aforementioned known exchangers. Whereas the capacity of the anion exchangers obtained by the previously known process from the halogenoalkyl compounds by amination is in the region of 1.3 to max. 1.5 meq./cm.^{3}, anion exchangers with capacities from 1.7 to 2.5 meq./cm.^{3} are obtained by this process.

The cross-linked polymers containing aromatic nuclei as used for carrying out the process, are copolymers of a predominant proportion of at least one aromatic monovinyl compound, such as, for example, styrene, substituted styrene (such as vinyl toluene, ethylstyrene) or vinyl naphthalene, and a subordinate proportion of a polyethylenically unsaturated cross-linking agent preferably divinyl benzene, furthermore, a substituted divinyl benzene (trivinylbenzene, divinyltoluene) divinylxylene, divinylethylbenzene, divinylether, ethyleneglycol dimethacrylate, ethyleneglycol diacrylate, diallymaleate, a polyester of polyhydric alcohol and an olefinically unsaturated carboxylic acid, such as for example, ethylene glycol and maleic acid. These copolymers can have both a gel structure and a sponge structure. The amount of cross-linking agent may vary within wide limits.

In case of copolymers having a gel structure amounts of about 0.5 to 15% by weight of cross-linking agent as calculated on the amount of total monomers and in the case of copolymers having a sponge structure amounts of about 0.5 to 30% by weight are preferably used. As halogenoalkylimides there are N-halogenoalkyl derivatives of the cyclic imides of organic dicarboxylic acids, such as phthalic acid, diglycolic acid, succinic acid as for instance the N-chloromethyl succinimide, N-bromomethylphthalimide, N-chloromethyl phthalimide, N-chloromethyl diglycolic acid imide. $SnCl_4$, $ZnBr_2$, $ZnCl_2$, $AlCl_3$ and concentrated sulfuric acid are examples of compounds which can be used as Friedel-Crafts or haloalkylation catalysts.

Examples of suitable swelling agents are liquid halogenated hydrocarbons, such as ethylene chloride and methylenechloride, carbontetrachloride, sym. tetrachloroethane, trichloroethylene, 1,1,2-trichloroethane, tetrachloroethylene, ethylenedibromide, dichloropropanes, pentachloroethane, trichloropropanes, tetrachloropropanes, pentachloropropanes, 1,2,3,3-tetrachloropropylene, tribromoethylene. Mixtures of these solvents may also be used.

The reaction of the said copolymers with the cyclic N-(halogenoalkyl)-imides can be effected, for example, by reacting said components in the presence of a swelling agent and a Friedel-Crafts catalyst at an elevated temperature, and preferably at the boiling point of the swelling agent (about 30° to 150°C.) until the splitting off of hydrogen halide is completed. The halogenoalkylimides are advantageously employed in quantities of about 1 to 5 mols of halogenoalkylimido per 2 mols of the aromatic nuclei present in the copolymer. The catalysts may be applied in quantities ranging from 5 to 50% as calculated on the weight of polymers. The swelling agents serve to swell the polymers and to dissolve the halogenoalkylimides. The cross-linked water and benzene-insoluble polymers thus produced contain structural units of the formula



in which R stands for a lower bivalent aliphatic group such as methylene, ethylene, propylene, butylene, preferably methylene, and X stands for a bivalent organic radical, such as a benzene nucleus to which the CO groups are bonded, in ortho-position, a bivalent lower aliphatic group such as ethylene, propylene, a $-CH_2-O-CH_2-$ or a $-CH_2-S-CH_2-$ group. In order to saponify the imidoalkyl derivatives formed, as intermediates, it is possible to use the known processes, such as, for example, alkaline or acid hydrolysis, or conversion with hydrazine and subsequent acid hydrolysis in the presence or absence of solvents or swelling agents.

The reaction products can thereafter be alkylated, it being possible for this purpose to use alkylation agents which are known per se, for example, alkyl halides (methyl-, ethyl-, propyl-, butyl-chloride, bromide or iodide), dialkyl sulfates (dimethylsulfate, diethylsulfate), alkylene oxides (ethylene oxide, propyleneoxide), halohydrins (ethylene chlorohydrin, propylenechlorohydrin, glycerolchlorohydrin), polyhalogen compounds (ethylenechloride, ethylenebromide, 1,4-dibromobutane, glyceroldichlorohydrin) or epihalohydrins (epichlorohydrin, epibromohydrin). It is possible in this way to obtain strongly as well as weakly basic anion exchangers which also have a distinctly higher capacity than the known anion exchangers which are formed by amination of halogenoalkyl derivatives of cross-linked polystyrenes.

BEHAVIOR IN USE

A series of four patents covering anion exchange resins, three of them weak base and one strong base, were issued to Nalco Chemicals scientists. Each patent deals with resins of different composition and features certain characteristics of the resins in use— for instance, nonswelling, high temperature stability, etc.

Swelling and Crumbling

One process developed by C.A. Feldt and G.T. Kekish (U.S. Patent 3,047,516; July 31, 1962; assigned to Nalco Chemical Company) results in a weakly basic resin which has a high operating capacity and porosity, coupled with excellent resistance to swelling and crumbling, exhibiting little or no swelling from regenerated to exhausted form.

Anion exchange resins, to be satisfactory commercially, must also be substantially insoluble in water, and must be resistant to physical deterioration such as swelling or shattering while at the same time having a high porosity and correspondingly high operating capacity. Resins which are highly porous and have a high capacity also tend to be soft and susceptible to substantial swelling, when changing from the regenerated to the exhausted form. Weakly basic anion exchange resins swell from the regenerated to the exhausted form while strongly basic anion exchange resins swell from the exhausted to the regenerated form. The percent of swelling depends on a variety of properties such as cross-linking, capacity, and method of preparation. Softness is coupled with a tendency to crumbling. High swelling leads to various engineering problems with respect to the design of the equipment used to provide contact of liquid fluids with exchange resin in commercial systems. A relatively hard highly cross-linked resin, which is resistant to swelling and crumbling, correspondingly tends to lack porosity and consequently has a relatively low operating capacity.

Anion Exchange Resins

Weakly basic anion exchange resins prepared by this process do not swell from regenerated to exhausted state due to the apparent formation of strongly basic quaternary nitrogen groups in the reaction product. In general, excellent anion resins may be made by blending and reacting polymers of nitrogen heterocyclic vinyl compounds with condensation copolymers of ammonia and epihalohydrin. The polymerized nitrogen heterocycle may be selected from polymerized basic 5 or 6 membered ring structures containing 1 to 4 nitrogen atoms.

Anion exchange resins made by blending and/or reacting polymerized vinylimidazole with copolymers of ammonia and epihalohydrin, have satisfactory oxygen stability coupled with low shrinkage and resistance to physical degradation. In a specific example, highly satisfactory resinous terpolymers may be prepared by blending and reacting poly N-vinylimidazole in a weight ratio of 1:99 to 30:70 parts by weight of polyvinylimidazole to copolymer, with ammonia-epichlorohydrin copolymer prepared using reactants in a molar ratio of from 1 to 4 mols of ammonia to each mol of epichlorohydrin. A preferred weight ratio of polyvinylimidazole to ammonia-epichlorohydrin copolymer is 9:91, and a molar ratio of ammonia to epichlorohydrin in the copolymer itself of 1.7:1.

Superior weak base terpolymeric resin beads can be produced by adding the ammonia-epichlorohydrin-polyvinyl imidazole blend to a hydrocarbon system with vigorous agitation in the presence of a dispersing agent, at temperatures of 20° to 120°C., and in the further presence of added epihalohydrin — suspension polymerization.

In addition to being satisfactorily stable in the presence of oxidizing agents, the anion exchange resins have other desirable characteristics. The following table sets forth the water holding capacity, total capacity, operating capacity, and other properties of these resins. A comparison of the beads was made with a resin prepared by a simple copolymerization of epichlorohydrin and ammonia without blending with polyvinylimidazole. Such a resin is considered to have very satisfactory capacity, and to be highly desirable from that standpoint, but to have somewhat less than desirable expansion or swelling characteristics. The simple copolymer is designated in the table as "Epi-NH$_3$." The terpolymeric resin composed of a copolymer of epichlorohydrin and ammonia interreactively blended with polyvinylimidazole is designated as "Epi-NH$_3$-PVI."

	WHC[1]	Total meq./g.	Capacity meq./ml.	Column Test Operating Capacity kgr./cu. ft.	SSC[2]		Percent Expansion[3]
					meq./g.	meq./ml.	
Epi-NH$_3$	68.2	11.6	2.06	24.8	0.5	0.1	39.9
Epi-NH$_3$-PVI, Example II, Beads	57.3	10.3	2.85	39.5	1.2	.33	3.0
Epi-NH$_3$-PVI, Example III, Beads	56.5	10.0	2.63	48.5	1.03	.27	13.0
Epi-NH$_3$-PVI, Example III, Type Beads	58.1	9.56	2.52	38.0	1.02	.26	11.2
Epi-NH$_3$-PVI, Example IV, Beads	58.4	10.03	2.53	40.6	1.38	.35	10.7
Epi-NH$_3$-PVI, Example IV, Type Beads	56.6	9.68	2.51	37.7	1.38	.37	10.9

[1] Water holding capacity.
[2] Salt splitting capacity.
[3] Percent expansion of resin in use as it changes from free amine form to hydrochloride salt form.

Each of the above enumerated tests is conducted after one elution of the resin tested. Beads referred to by "type" in the table, are those obtained by reruns of the preparation outlined in the designated example. As apparent from the above collected data, the resins have a high water holding capacity as well as operating capacity as high as almost two times that of a resin not derived from reaction of a polymerized nitrogen heterocycle. The excellent capacity characteristics of the new resins are coupled with relatively low expansion properties.

Stability to Oxidizing Agents

A process by G.T. Kekish (U.S. Patent 3,137,659; June 16, 1964; assigned to Nalco Chemical Company) gives weakly basic resins that remain stable in the presence of oxidizing agents and can be regenerated easily.

In general, it has been found that anion exchange resins made from ammonia and epichlorohydrin have much improved oxygen stability. More particularly, resins having a molar ratio of from 1.5 to 4 mols of ammonia to each mol of epichlorohydrin provide highly satisfactory anion exchange materials. Superior weak base resin beads can be produced by adding a polymeric water system to a hydrocarbon system in the presence of a dispersing agent and in the presence of additional epichlorohydrin. Epichlorohydrin-ammonia anion exchange resins can be quaternized or partially quaternized in an improved manner by using epichlorohydrin as the sole quaternizing agent.

The following table sets forth the results of 1 to 3 week oxidation tests of the subject anion exchange resins as compared with several other well known weak base anion resins. Oxidation stability is determined by passing 180°F. water through 25 ml. of resin in a column having a 3/4" diameter (the resin is three inches high in the column) at a rate of 140 to 150 ml. per minute flow rate. The column capacity is determined on the resin before and after the oxidation test, and the loss in capacity is indicative of the extent of the oxidation.

1 and 3 Week Oxidation Stability Test

Commercial Resin	Initial oper. col. cap., kgr./cu.ft.	After 1 week of oxid. test. kgr./cu.ft.	Percent loss or gain	After 3 weeks of oxid. test. kgr./cu.ft.	Percent loss or gain
1	24.3	14.1	−42.0	0	Lost 100%
2	28.4	24.9	−12.3	18.8	Lost 33.8%.
3	20.6	23.5	+14.1	22.1	Gained 7.3%.
4	17.2	20.7	+20.3	22.3	[1] Gained 29.7%.
5	23.7	22.3	−5.9	15.7	Lost 25.4%.
EPI-NH_3, gran. quat.	22.4	30.6	+36.5	29.5	Gained 31.8%.

[1] Resin becomes sticky after 3 weeks of test.

As is evident from the above data, a resin prepared by the subject process gained 36.5% of capacity after one week and had an increased capacity of 31.8% after 3 weeks. The only resin that approached the stability of this product was resin No. 4 which became sticky after 3 weeks of testing.

High Operating Capacities

Another process for making weakly basic resins by C.A. Feldt and G.T. Kekish (U.S. Patent 3,092,617; June 4, 1963; assigned to Nalco Chemical Company) condenses a water