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Preparation of Thermally Regenerable Ion-Exchange Resins by Polymerizing a Heterogeneous Mixture of Monomers

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Preparation of Thermally Regenerable Ion-Exchange Resins by Polymerizing a Heterogeneous Mixture of Monomers

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ABSTRACT

Crosslinked resin beads containing regions of acidic and basic groups are the preferred structures for the efficient operation of a thermally regenerable ion-exchange process. In the present study they were prepared by polymerizing a heterogeneous mixture of acrylic esters and allylamines. Polymerization of unstable emulsions of acrylic esters and allylamines by heating the stirred emulsions gave very hard, strong resins which after hydrolysis had good acid, amine and thermally regenerable capacities. The thermally regenerable capacity depended very much on the nature of the acrylic ester and the allylamine. The order of increasing thermally regenerable capacity for the resins prepared is methyl acrylate (MA)/triallylamine (TAA), MA/diallylamine (DAA), MA/methyldiallylamine (MDAA) $<$ ethyl acrylate (EA)/TAA, EA/DAA $<$ EA/MDAA, butyl acrylate/MDAA. The dispersion of the unstable emulsions in a third phase resulted in immediate breakdown of the emulsion. The dispersion of partly prepolymerized emulsions in a third phase of paraffin oil containing talc, followed by completion of the polymerization and hydrolysis, gave hard resin beads with acid, amine and thermally regenerable capacities comparable to those prepared as a two-phase emulsion. Their shape, size, strength, and degree of agglomeration depended on the stirring rate, the shape and material of construction of the stirrer, the potential acid/base ratio of the monomers, the nature of the solid dispersant, and the acrylic ester and the allylamine. Satisfactory resin beads could be obtained from only the MA/TAA and MA/DAA combinations which are those that give resins with the poorest thermally regenerable capacities. Partial prepolymerization of the two-phase emulsion is easy on the laboratory scale, but would be impracticable on the commercial scale. Although polymeric dispersants gave stable two-phase emulsions, the amine monomer migrated into an aqueous third phase more rapidly than it polymerized.

INTRODUCTION

Thermally regenerable ion-exchange resins must be composed of discrete acidic and basic domains, grouped together in a porous particle of the conventional size of 300-1200 μm [1]. In the simplest conceivable method of preparing such resins, triallylamine hydrochloride (TAA) and acrylic acid were polymerized in aqueous solution to give a resin which, however, had no thermally regenerable capacity [1]. The lack of capacity has been attributed to internal salt formation between the carboxylate and protonated amino groups [1]. Several approaches have been taken to diminish this interaction during the polymerization, and these include a counterion route [1], the use of a precipitating solvent [1], and an approach in which either or both monomers are employed as solutions of electrically neutral precursors [2]. The latter approach was the most successful, with resins being obtained which had thermally regenerable capacities of 1.1 meq/g. Nevertheless, this value is still considerably less than the theoretical value of about 2 meq/g for these systems, which suggests that a considerable amount of internal salt formation is still occurring. This paper reports the results of attempts to reduce further the interaction between the charged sites by using heterogeneous emulsions rather than homogeneous solutions of acrylic esters and allylamine monomers.

It was first necessary to find surface active agents which would stabilize 1-5 μm droplets of one monomer within the other. Thus, the first part of this paper discusses the preparation of stable emulsions. The second part of the paper gives the results of a study of the polymerization of such two-phase emulsions and presents the properties of the resins formed. Finally, the results of studies of the polymerization of droplets of the two-phase emulsion in a third phase to obtain resin beads are given.

RESULTS AND DISCUSSION

Preparation and Stability of Emulsions of Acrylic Esters and Allylamines

Conventional Surfactants. The effect of surfactants on the stability of emulsions of acrylic esters and allylamines is summarized in Tables 1-6. The nature of the emulsion, either water-in-oil (w/o) or oil-in-water (o/w) was sometimes difficult to determine. All w/o emulsions as determined by microscopic examination were stabilized by the addition of chlorobenzene and, conversely, all o/w emulsions were destabilized.

TABLE 1. Effect of Surfactant on the Stability of Emulsions of Methyl Acrylate (MA) and Triallylamine Hydrochloride (TAA)[a]

		Stability[b]	
Surfactant	HLB No.	T_1 (min)	T_2 (min)
None	-	<0.5	1
S85/T85[c]	1.8	<0.5	1
S85/T85	2.8	<0.5	1
S85/T85	3.8	1.2	4
S85/T85	4.8	0.7	3
S85/T85	5.8	0.5	1.5
Brij 92	4.9	<0.5	1
S20/T20	10	0.5	1
Teric 151	11.6	0.5	1
Tergitol No. 2	14	0.5	1

[a] As a 70% aqueous solution; concentration of surfactant was 3% on the organic phase; ratio of aqueous to organic phase was 1.6.

[b] T_1 = time when phase separation commenced; T_2 = time when phase separation was complete. All emulsions were the oil-in-water type.

[c] S = Span, T = Tween.

TABLE 2. Effect of the Ratio of Aqueous to Organic Phase on the Stability of Emulsions of MA and TAA[a]

Ratio to aqueous to organic phase	Stability[b] T_1 (min)	T_2 (min)	Nature of emulsion
5	Homogeneous and stable		
2.5	1	2	o/w
1.7	0.5	1	o/w
1.25	0.5	0.5	o/w
0.77[c]	3	5	uncertain
0.11[c]	5	8	w/o

[a] Surfactant was S85/T85 of HLB 3.8; concentration of surfactant was 3% on the organic phase.

[b] T_1 = time when phase separation commenced; T_2 = time when phase separation was complete.

[c] Some chlorobenzene was added to increase the volume of the organic phase.

TABLE 3. Effect of Surfactant on the Stability of Emulsions of MA and Diallylamine Hydrochloride (DAA)[a]

Surfactant	HLB	Stability T_1 (min)	T_2 (min)
Vantoc CL	-	0.5	5
S85/T85	3.8	1	5
Teric 18M5	9.5	0.5	5
S20/T20	10	1	30
S20/T20	12	1	25
Tergitol No. 2	14	0.5	5
S20/T20	16	0.5	5

[a] As a 67% aqueous solution; concentration of surfactant was 15% on the organic phase; ratio of aqueous to organic phase was 2. All emulsions were the oil-in-water type.

TABLE 4. Effect of Surfactant on the Stability of Emulsions of Ethyl Acrylate (EA) and DAA[a]

		Stability	
Surfactant	HLB	T_1 (min)	T_2 (min)
Vantoc CL	-	2	7
S85/T85	3.8	0.5	5
S85/T85	3.8	0.5	1[b]
Teric 18M5	9.5	0.5	2
S20/T20	10	2.5	5
S20/T20	12	3.5	25
Tergitol No. 2	14	0.5	2
S20/T20	16	0.5	2

[a] Concentration of surfactant was 12% on the organic phase; ratio of aqueous to organic phase was 1.63. All emulsions were the oil-in-water type.

[b] Ratio of aqueous to organic phase was reduced to 0.8 with chlorobenzene.

The tables show that few surfactants give stable emulsions, irrespective of whether they are w/o or o/w emulsions. The stability was only slightly dependent on the method of preparation of the emulsion; emulsions were no more stable when prepared by stirring in an Omnimix than when prepared by shaking. The size of the dispersed drops was usually within the required range, but clustering, followed by coalescence, usually occurred rapidly.

Tables 1-6 show that most surfactants give o/w emulsions. This is the less desired type of emulsion, since a w/o emulsion, when polymerized as 1 mm drops, would give a resin bead with a polyacrylic matrix, whereas o/w emulsions, when polymerized, would give a resin bead with a polyamine matrix. A polyacrylic matrix would be expected to be harder than a polyamine one. Although the w/o emulsions appear to be just the inverse of the o/w emulsions as regards drop size, the literature suggests that their properties are quite different. The drop size of w/o emulsions is usually an order of magnitude or more smaller [3], and this has given rise to such terms as microemulsions [4] and reversed micellar systems [5]. It has been stated that in such systems, the formation of micelles is uncertain [5].

TABLE 5. Effect of Surfactant on the Stability of Emulsions of EA and Methyldiallylamine Hydrochloride[a]

Surfactant	HLB	Stability T_1 (min)	 T_2 (min)
Vantoc CL	-	0.5	1
S85/T85	3.8	0.5	1
Teric 18M5	9.5	0.5	1
S20/T20	10	0.5	1
S20/T20	12	0.5	1
Tergitol No. 2	14	0.5	1
S20/T20	16	0.5	1

[a] As a 53% aqueous solution; concentration of surfactant was 12% on the organic phase, ratio of aqueous to organic phase was 2.24. All emulsions were the oil-in-water type.

TABLE 6. Effect of Ionic Surfactants on the Stability of Emulsions of MA and TAA

Surfactant		Ratio of aqueous to organic phase	Stability		Nature of emulsion
Type[a]	Concn (%)[b]		T_1 (min)	T_2 (min)	
IPADBS	3	2.5	2	3	o/w
CTAB	5	1.5	milky, stable		w/o
Vantoc CL	10	2.0	stable		o/w
Vantoc CL	10	1.25[c]	5	10	o/w
Vantoc CL	10	1.0[c]	2	5	o/w

[a] IPADBS = isopropylammonium dodecylbenzene sulfonate; CTAB = cetyltrimethylammonium bromide.

[b] Concentration of surfactant on the organic phase.

[c] Chlorobenzene added.

It is obvious that the formation of either an o/w or w/o emulsion depends on the ratio of the volumes of the aqueous to organic phase. In order to achieve the optimum acid to base ratio in the final resin, ratios of the volumes of the aqueous to organic phase need to be greater than 1, usually about 2.5, which is unfavorable to the formation of a w/o emulsion. The volume of the organic phase could be increased by using an organic solvent such as chlorobenzene but this must be kept to a minimum in order to get rapid polymerization and a physically strong product.

The only surfactant which gave a w/o emulsion at practical ratios of the volumes of the aqueous phase to the organic phase was cetyltrimethylammonium bromide (CTAB). CTAB is usually considered to be a solubilizer rather than a surfactant [6]. Tables 1, 3, 4, and 5 show that surfactants with HLB numbers in the usual range for w/o emulsions (i. e., 3-6) do not give w/o emulsions in this system. This may be a result of the fact that the water and oil phases here are really quite different from what is normally understood by these terms. A saturated aqueous solution of the amine hydrochloride and acrylic esters are quite different from water and an oil, respectively.

The nature and the stability of the emulsions changed dramatically if any one of a number of variables was changed. Thus, the nature and stability depends on the surfactant, phase ratios, organic solvent, nature of the ester, nature of the amine, the temperature, and other things such as the presence of initiators. The effect of the nature of the ester, amine and organic solvent is apparent from Fig. 1.

Although an attempt to distinguish o/w from w/o emulsions by conductivity titrations was unsuccessful, the results gave useful information on the relative solubilities of the amines in acrylic esters (Fig. 2). The relative solubilities influence the extent of internal salt formation and hence the thermally regenerable capacity of resins prepared from these systems.

Solid Dispersants. Solid dispersants such as talc and colloidal silica are often used to stabilize emulsions which are difficult to stabilize with the usual surfactants. Hydrophilic colloidal silica (Aerosil 200) (Table 7), dramatically increased the stability of some emulsions providing high amounts (up to 10%) of Aerosil were used. However, such emulsions immediately disintegrated when added to either water or paraffin oil, irrespective of the amount or nature of the Aerosil. It thus appears that the silica stabilizes the emulsions formed from two phases, but when the emulsion is added to a third phase, the silica has a strong tendency to incorporate the third phase into yet another stable emulsion.

Polymeric Dispersants. The exotic "comb" and "star" dispersants [7] were not considered because specialized techniques are required to prepare them, but the effect of random copolymers on stabilization of emulsions was studied. An oil-soluble polymer

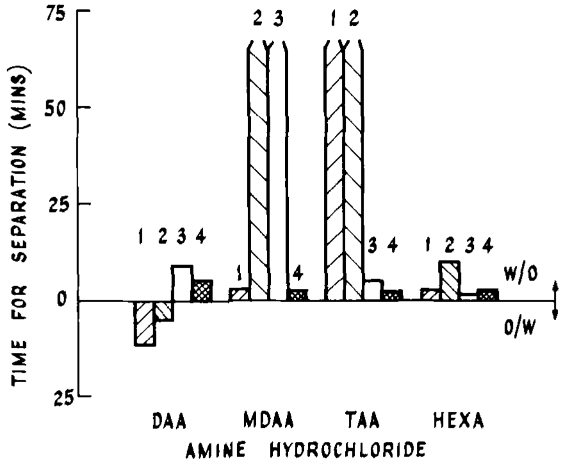

FIG. 1. Stability at 20° C of emulsions of acrylic esters and allylamine hydrochlorides stabilized with CTAB (10% w/v on the total organic phase): (▨) methyl acrylate (aqueous phase: organic phase = 2.0); (▧) methyl acrylate + chlorobenzene (aqueous: organic = 0.8); (□) ethyl acrylate + chlorobenzene (aqueous:organic = 0.8); (▩) ethyl acrylate (aqueous:organic = 2.0).

with about 10% hydroxy groups is required [8] in order to form a w/o emulsion. Copolymers of ethyl acrylate (EA) and 10% hydroxyethyl methacrylate (HEMA) were made. An emulsion of MDAA, EA, chlorobenzene (CB), and divinylbenzene (DVB) (ratio of aqueous to organic phase was 1.06) with an EA:HEMA (10%) copolymer (11.5% on the organic phase, 5.6% on total volume) was stable for at least 24 hr. The least compatible component was DVB; any reduction in the amount of the polymeric dispersant resulted in separation of the DVB. A less stable emulsion was formed when CB was replaced by toluene, possibly due in part to the lower density of toluene compared with both the CB and the aqueous phase.

A polymeric dispersant of butyl acrylate (BA) and HEMA (5%) was not effective in stabilizing an emulsion made from MDAA, BA and DVB. A BA:HEMA (10%) dispersant resulted in an improvement, but was not as good as EA:HEMA (10%) for the EA/MDAA system.

A polymeric dispersant suitable for preparing o/w emulsions was obtained from dimethylaminoethyl methacrylate (DMAEMA) and EA (10%) and then converted to the hydrochloride salt. An emulsion of EA, DVB and MDAA was not very stable with 8% on the aqueous phase of the DMAEMA:EA dispersant, but stable for several hours with 18%.

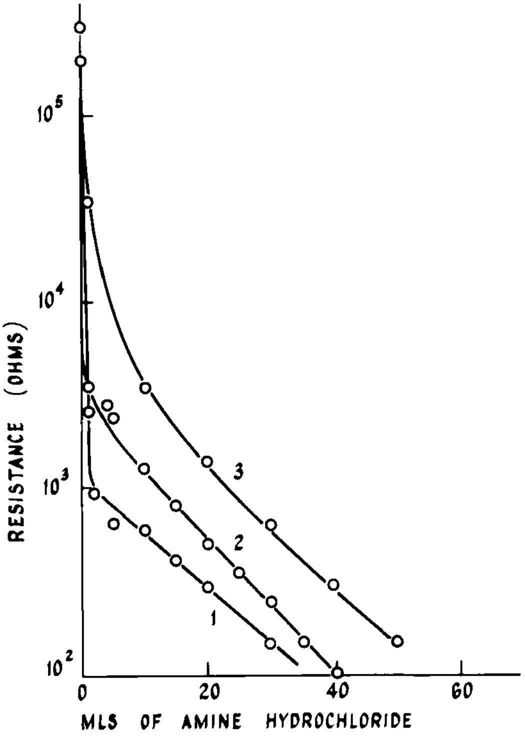

FIG. 2. Effect of the addition of allylamine hydrochlorides on the resistance of (methyl acrylate + surfactant): (1) 30 ml MA (plus CTAB) + TAA; (2) 30 ml MA (plus Span/Tween, HLB 3.8) + TAA; (3) 30 ml MA (plus Span/Tween, HLB 3.8) + DAA.

Polymerization of Two-Phase Systems

The preparation of thermally regenerable ion-exchange resins by polymerizing a two-phase heterogeneous system of monomers is summarized in Table 8, and the properties of the resins are listed in Table 9. Since all the emulsions, except those prepared with colloidal silica or polymeric dispersants, were unstable the heterogeneous mixtures were stirred at 300-600 rpm until gelation (usually 30-60 min). The surfactant was usually a Span 85/Tween 85 mixture (o/w) or CTAB (w/o, with one exception). No difference in the thermally regenerable capacity or physical hardness of the resins was noticed whether the emulsion was a w/o or o/w one.

TABLE 7. Stabilization of Emulsions with Colloidal Silica (Aerosil)

Aerosil type[a]	Amount (% on total volume)	Other surfactant		Organic phase	Aqueous phase	Ratio of aqueous to organic phase	Stability[a]	
		Type	Amount (% on organic phase)				T_1 (min)	T_2 (min)
200	8	S/T	10	EA	DAA	1.63	-	> 1500
200	1	18M5	10	EA	MDAA	2.24	1	2
200	1.5	18M5	10	EA	MDAA	2.24	-	> 200
200	6	CTAB	2	EA + CB	MDAA	1.0	50	100
R972	4	CTAB	2	EA + CB	MDAA	1.0	100	300

[a] All emulsions were the oil-in-water type.

TABLE 8. Preparation of Thermally Regenerable Ion-Exchange Resins by Polymerizing a Two-Phase Heterogeneous System[a]

			Acid precursor phase						Amine phase[f]			
	Surfactant		Acid precursor		Crosslinker		Solvent and/or diluent		Amine		Crosslinker	
Expt.	Type[b]	Amt (g)	Type[c]	Vol (ml)	Type[d]	Vol (ml)	Type[e]	Vol (ml)	Type[g]	Vol (ml)	Type[h]	Vol (ml)
P10	S/T	0.15	MA	6	DVB	0.3	-		TAA	9	-	
T1	S/T	0.05	MA	2	DVB	0.1	-		TAA	10	-	
T2	S/T	0.1	MA	4	DVB	0.2	-		TAA	10	-	
T3	S/T	0.1	MA	4	DVB	0.2	CB	3	TAA	10	-	
T6	S/T	0.1	MA	4	DVB	0.4	Hexane	3	TAA	10	-	
T11	S/T	0.18	MA	4	EGDMA	0.4	CB	3	TAA	10	-	
T12	Teric 18M5	0.2	MA	4	DVB	0.4	-		TAA	10	-	
T13	S/T	0.2	EA	4	DVB	0.4	-		DAA	8	HEXA	1.1
T14	CTAB	0.2	EA	4	DVB	0.4	CB	3	DAA	8	HEXA	1.1
T15	S/T	0.2	MA	4	DVB	0.4	-		DAA	8	HEXA	1.1
T16	CTAB	0.2	MA	4	DVB	0.4	CB	3	DAA	8	HEXA	1.1
T17	CTAB	0.2	MA	4	DVB	0.4	CB	3	MDAA	11	HEXA	1.1

(continued)

TABLE 8 (continued)

			Acid precursor phase						Amine phase[f]			
	Surfactant		Acid precursor		Crosslinker		Solvent and/or or diluent		Amine		Crosslinker	
Expt.	Type[b]	Amt (g)	Type[c]	Vol (ml)	Type[d]	Vol (ml)	Type[e]	Vol (ml)	Type[g]	Vol (ml)	Type[h]	Vol (ml)
T18	CTAB	0.25	EA	4.9	DVB	0.4	CB	3	MDAA	11	HEXA	1.1
T19	CTAB	0.1	EA	4.9	DVB	0.4	CB	3	TAA	10	-	
T26	CTAB	0.25	BA	6.5	DVB	0.4	CB	3	MDAA	11	HEXA	1.1
T37	S/T	0.6[i]	EA	4.9	DVB	0.4	CB	3	DAA	8	HEXA	1.1
T9γ-1	CTAB	0.1	MA	4	DVB	0.4	CB	3	TAA	10	-	
T9γ-2	CTAB	1.5	MA	60	DVB	6	CB	45	TAA	150	-	
T9γ-3	CTAB	1.5	MA	60	DVB	6	CB	45	TAA	150	-	
T9γ-4	S/T	1.5	MA	60	DVB	6	CB	45	TAA	150	-	
T14γ-1	CTAB	3.0	EA	60	DVB	6	CB	45	DAA	120	HEXA	16.5
T14γ-2	CTAB	3.0	EA	60	DVB	6	CB	45	DAA	120	HEXA	16.5
T14γ-3	CTAB	3.0	EA	60	DVB	6	CB	45	DAA	120	HEXA	16.5
T21	CTAB	0.25	EA	4.9	DVB	0.4	CB VA	2.55 0.45	MDAA	11	HEXA	1.1
T23	CTAB	0.25	EA	4.9	DVB	0.4	CB MMA	2.8 0.2	MDAA	11	HEXA	1.1

T24	CTAB	0.25	EA	4.9	DVB	0.4	CB MMA	2.55 0.45	MDAA	11	HEXA	1.1
T25	CTAB	0.25	EA	4.9	DVB	0.4	CB MMA	2 1	MDAA	11	HEXA	1.1
T31	CTAB	0.25	EA	4.9	DVB	0.4	CB VA	2.8 0.2	DAA	8.6	HEXA	1.1
T34	CTAB	0.25	EA	4.9	DVB	0.4	CB MMA	2.8 0.2	DAA	8.6	HEXA	1.1
W2	S/T	0.3	AAm	1.77	MBAAm	0.18	Water	2	TH	7.4	-	
W3	CTAB	0.3	AAm	1.77	MBAAm	0.18	Water	2	TH	7.4	-	
W4	S/T	0.3	AAm	1.77	MBAAm	0.18	Water	2	TE	8.2	-	
W5	CTAB	0.3	AAm	1.77	MBAAm	0.18	Water	2	TE	8.2	-	
T43	CTAB	0.25	EA	4.9	TMTA	0.5	CB	3	MDAA	11	HEXA	1.1
T44	CTAB	0.25	EA	4.9	TMTA	1.0	CB	3	MDAA	11	HEXA	1.1
T45	CTAB	0.25	EA	4.9	TMTA	1.5	CB	3	MDAA	11	HEXA	1.1
T29	CTAB	0.1	MA	4	DVB	0.4	-		TAA	10	-	
T30	CTAB	0.1	MA	4	DVB	0.4	-		TAA	10	-	
T39	HOEA		EA	4.9	DVB	0.4	CB	3	MDAA	8	HEXA	0.8
T40	CTAB	0.25	AA	3.1	DVB	0.4	n-heptane	5	MDAA	11	HEXA	1.1
T41	CTAB	0.25	AA	3.1	DVB	0.4	CB	5	MDAA	11	HEXA	1.1
T42	HOBA		BA	6.5	DVB	0.6	-	-	MDAA	8	HEXA	0.8

(continued)

TABLE 8 (continued)

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[a]Co^{60} irradiation was used to initiate the polymerizations in experiment numbers T9γ-1, T9γ-2, T9γ-3, T9γ-4, T14γ-1, T14γ-2 and T14γ-3 and the total dose was 1.2, 9.9, 9.9, 9.9, 1.6, 3.9, and 9.5 Mrad, respectively. T9γ-2 was irradiated at 45°C, all other irradiations were at $<$ 30°C. Experiment T29 was initiated by 2,2'-azobisisobutyramidinium dihydrochloride (Amido) by heating at 65°C for 21 hr. Experiment T30 was initiated by 2,2'-azobisisobutyronitrile (AIBN) by heating at 65°C for 21 hr. All other polymerizations were initiated by heating with a mixture of AIBN and amido at 65-70°C for 21 hr.

[b]Surfactants: S/T = Span 85/Tween 85, HLB 3.8; CTAB = cetyltrimethylammonium bromide; HOEA = poly-EA containing 10% HEMA; HOBA = poly-BA containing 10% HEMA.

[c]Acid precursors: MA = methyl acrylate; EA = ethyl acrylate; BA = n-butyl acrylate; AAm = acrylamide (amount shown is in grams); AA = acrylic acid.

[d]Crosslinkers (acid precursor phase): DVB = divinylbenzene as a 55% solution of DVB; EGDMA = ethyleneglycol dimethacrylate; MBAAm = methylenebisacrylamide (amount shown is in grams); TMTA = trimethylolpropane trimethacrylate.

[e]Solvents: CB = chlorobenzene; VA = vinyl acetate; MMA = methyl methacrylate.

[f]Except for experiments W2 to W5, this is the aqueous phase.

[g]Amines: TAA = 70% aqueous solution of triallylamine hydrochloride; DAA = 67% aqueous solution of diallylamine hydrochloride; MDAA = 53% aqueous solution of methyldiallylamine hydrochloride; TH = triallylamine salt of hexanoic acid; TE = triallylamine salt of 2-ethylhexanoic acid.

[h]Crosslinkers (amine phase): HEXA = 67% aqueous solution of 1,6-bis(N,N-diallylamino)hexane dihydrochloride.

[i]Plus Aerosil 200.

TABLE 9. Properties of Thermally Regenerable Ion-Exchange Resins Obtained by Polymerizing a Two-Phase Heterogeneous System

		Properties of hydrolyzed resin						
				Capacity from titration[b]			Thermally regenerable capacity[c]	
Expt.	Time of hydrolysis with 5N KOH at 87°C (hr)	Yield (%)[a]	Amine capacity from microanalysis (meq/g)	Amine (meq/g)	Acid (meq/g)	Acid/amine ratio	pH	Capacity (meq/g)
P10	65	58	2.70	1.44	6.0	4.16	6.8	0.0
T1	65	54	4.13	2.97	2.86	0.96	6.8	0.30
T2	65	61	3.34	1.94	4.89	2.5	6.8	0.20
T3	48	59	3.24	1.97	4.47	2.27	6.8	0.19
T6	40	68	3.04	2.0	4.33	2.16	6.8	0.22
T11	48	64	3.38	2.17	4.27	1.97	6.8	0.07
T12	48	60	3.11	2.17	4.27	1.97	6.8	0.03
T13	48	53	4.16	2.00	4.50	2.25	7.7	0.46
T14	48	63	4.30	2.86	3.81	1.33	7.7	0.78
T15	48	53	3.31	1.39	5.05	3.63	7.7	0.17
T16	48	65	3.59	2.94	3.78	1.28	7.7	0.31
T17	48	58	3.53	2.00	4.89	2.44	7.4	0.03
T18	48	59	3.30	2.30	3.59	1.56	7.4	0.94

(continued)

TABLE 9 (continued)

		Properties of hydrolyzed resin						
				Capacity from titration[b]			Thermally regenerable capacity[c]	
Expt.	Time of hydrolysis with 5N KOH at 87°C (hr)	Yield (%)[a]	Amine capacity from microanalysis (meq/g)	Amine (meq/g)	Acid (meq/g)	Acid/amine ratio	pH	Capacity (meq/g)
T19	65	71	3.49	1.02	3.68	3.6	6.8	0.76
T26	65	70	3.66	2.0	3.3	1.65	7.4	1.17
T37	48	58	4.43	1.24	2.94	2.37	7.7	0.56
T9γ-1	48	16	3.0	1.94	0.73	0.37	-	d
T9γ-2	48	79	3.74	2.56	3.38	1.32	6.8	0.53
T9γ-3	48	78	3.76	2.89	3.73	1.29	6.8	0.55
T9γ-4	48	81	3.66	2.67	3.55	1.33	6.8	0.72
T14γ-1	48	19	0.16	0.06	2.83	47	7.7	0.0
T14γ-2	48	42	2.38	0.91	7.22	7.9	7.7	0.08
T14γ-3	48	70	3.94	2.76	4.61	1.67	7.7	1.05
T21	48	77	3.56	3.50	2.50	0.74	7.4	0.79
T23	48	78	3.74	3.16	4.61	1.46	7.4	1.47
T24	48	63	4.13	3.34	1.18	0.35	7.4	0.96
T25	48	56	3.71	1.31	3.14	2.4	7.4	0.75

T31	48	67	3.97	1.21	3.49	2.88	7.7	0.88
T34	48	72	3.02	2.30	5.10	2.22	7.7	0.73
W2	48	45	5.84[e]	2.05	2.50	1.27	6.8	0.22
W3	48	44	5.85[e]	0.65	2.85	4.38	6.8	0.24
W4	48	43	6.89[e]	1.55	3.05	1.97	6.8	0.37
W5	48	44	6.67[e]	1.97	3.78	1.92	6.8	0.34
T43	90 + EtOH	-	3.50	2.30	4.12	1.79	7.4	0.13
T44	90 + EtOH	-	2.07	2.02	5.45	2.70	7.4	0.44
T45	90 + EtOH	-	1.55	1.11	2.65	2.39	7.4	0.0
T29	48	38	2.1	2.44	2.16	0.89	6.8	0.0
T30	48	31	2.7	1.04	4.76	4.58	6.8	0.0
T39	40 + EtOH	60	-	0.2	2.88	14	7.4	0.27
T40	-	-	-	-	-	-	-	-
T41	-	-	3.54	2.44	4.12	1.69	7.4	0.0
T42	80 + EtOH	-	-	0.23	8.83	38	7.4	0.0

[a] Yield based on total weight of monomers used and assumes complete hydrolysis of the acid precursor.

[b] Determined by shaking a sample of resin with 0.1 N NaOH for several days and then successively titrating an aliquot of the NaOH solution with 0.1 N HCl and 0.05 M $AgNO_3$.

[c] Measured on samples equilibrated at the given pH in 1000 ppm NaCl and regenerated at 80°C with water.

[d] Not determined.

[e] Includes some unhydrolyzed amide.

The initiating system for most of the experiments was a mixture of 2,2'-azobisisobutyronitrile (AIBN) and 2,2'-azobisisobutyramidinium dihydrochloride (amido). It was necessary to have one initiator in each phase. No polymer formed with just AIBN or just amido with chlorobenzene as solvent. In the absence of solvent, polymer formed with just one initiator, but the yield was less than when the two were used and the resins had no thermally regenerable capacity (T29 and T30) which may be explained by a lower degree of crosslinking, thus giving rise to a more flexible network and greater interaction. This, in turn, results in a greater degree of internal salt formation. T9 γ-1 to T9 γ-4 and T14 γ-1 to T14 γ-3 were initiated by γ-radiation.

All resins were usually obtained by hydrolysis with 5 N KOH under nitrogen at 87°C for 48 hr. In some cases, ethanol was added to facilitate the hydrolysis. The difficulty experienced in hydrolyzing some of the resins could usually be correlated with the degree of crosslinking and the type of crosslinker.

The most important factor affecting the thermally regenerable capacity is the acid to base ratio in the resin. The optimum value is about 1.3. This ratio is easily varied by varying the initial monomer composition (P10, T1, T2). Chlorobenzene or hexane (T3 etc., T6) generally had no significant effect on yield or capacity of the resins. The only exceptions to this were when only one initiator was used, in which case no polymer formed with chlorobenzene as solvent, or when acrylic acid (AA) rather than the ester was used (T40 and T41). No polymer formed with the AA/n-heptane combination, but polymer did form with the AA/chlorobenzene system. As expected, the resin from AA had no thermally regenerable capacity. The capacity is not very sensitive to the amount of DVB, but EGDMA instead of DVB as crosslinker adversely affected the resin (T11). Resins crosslinked with trimethylolpropane trimethacrylate (TMTA) were also inferior to those crosslinked with DVB (T43 to T45). As expected, as the amount of TMTA was increased, the resin became more brittle and the amine capacity decreased. The ease with which the ester groups could be hydrolyzed passed through a maximum at about 6 mole % of TMTA (T44) as did the thermally regenerable capacity. The surfactants Span 85/Tween 85 and CTAB gave similar products, but Teric 18M5 (T12) gave an inferior one. Although polymeric dispersants gave stable emulsions, the resins formed by using them (T39 and T42) had very low thermally regenerable capacities and extremely low amine capacities.

The properties of resins obtained from initiation by γ-radiation at ambient and elevated temperatures show that temperature is not an important parameter in determining these properties.

The thermally regenerable capacity of resin T14 as a function of pH is shown in Fig. 3. The thermally regenerable capacity is between 0.74 and 0.78 meq/g over the pH range 7.2 to 8.2. This

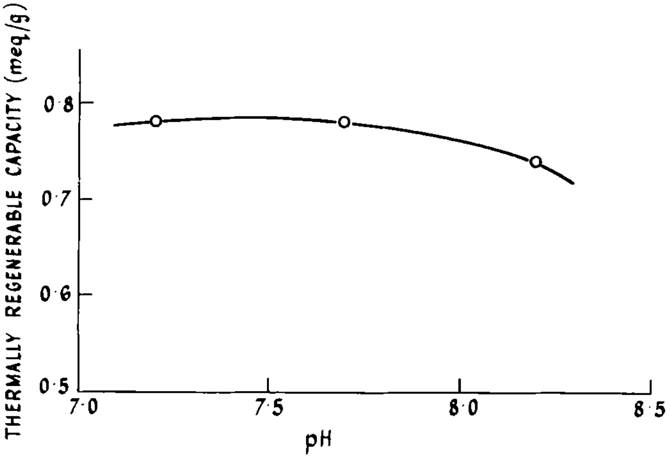

FIG. 3. Thermally regenerable capacity of resin T14 as a function of pH.

relative insensitivity of salt uptake to pH changes indicates the imperfect separation of the sites in the resin [9]. The difference between the amine capacities of the resins determined by microanalysis and by titration (Table 9) also indicates imperfect separation of sites [10].

The nature of the ester (MA or EA) and the amine (TAA, DAA or MDAA), is very important (c. f. T13 and T15, T14 and T16, T17 and T18). This is undoubtedly related to the relative solubilities of the amine in the ester or vice versa (see Fig. 2). The greater the solubility of the one in the other, the less distinct will be the separation of the acidic and basic domains in the resin, and therefore the greater the amount of internal salt formation and the lower the thermally regenerable capacity. Since CTAB promotes mutual solubility it is, from this point of view, not an ideal surfactant. The best thermally regenerable capacities were obtained with resins prepared from EA and MDAA. The order of increasing capacity is MA/TAA, MA/DAA, MA/MDAA < EA/TAA, EA/DAA < EA/MDAA, BA/MDAA.

The best thermally regenerable capacity was 1.5 meq/g (T23), which is for a resin prepared by using a small amount of MMA to separate the oppositely charged sites at what appears to be the optimum degree of separation. (MMA is not readily hydrolyzed by the conditions used in these studies for hydrolyzing the other acrylic esters).

No advantages are obtained by using a water-soluble acid precursor and an organic-soluble amine salt (experiments W2 to W5 in Tables 8 and 9).

Although the preparation of a resin by polymerizing the concentrated two-phase emulsions and then crushing the product is easy on the laboratory scale, novel scale-up would be needed to cope with the polymerization on a large scale. Therefore, the preparation of beads by polymerizing a suspension of the two-phase emulsion in a third phase was investigated.

Polymerizations in Three-Phase Systems

General Considerations. The third phase should ideally be one in which both acrylic esters and allylamine hydrochlorides are insoluble. However, because of the opposite solubility properties of these two monomers, one of them is invariably soluble in a given third phase. Table 10 lists the solubility of various compounds in different solvents. So far, no medium has been found in which both monomers are insoluble. It was thought that if one phase was dispersed in the second continuous phase, then that should shield the first phase from the third. However, when the two-phase system was added to a third phase, the two-phase emulsion immediately broke up. In most cases, the two-phase emulsions also disintegrate on heating, and so adding the two-phase emulsion to a heated third phase usually proved disastrous. The results of some attempts to carry out such polymerizations are shown in Table 11.

Water or Paraffin Oil as Third Phase. Table 11 shows that saturated aqueous solutions are useless as the suspending medium. Only very low yields of polyamine were obtained using amido as the initiator. Redox initiators for the MA/DVB system in the presence or absence of allylamines gave no polymer. A 70% yield of beads of EA/DVB was obtained using BO as initiator in the absence of allylamines, but EA did not polymerize with BO in the presence of MDAA or prepolymerized MDAA. Similarly, a 40% yield of EA/DVB beads was obtained by using the redox system lauroyl peroxide-Fe(II) caproate at 50°C, but no EA polymerized in the presence of prepolymerized DAA/hexa at 20°C.

It seems unlikely that beads can be prepared from an emulsion of monomers stabilized with Span/Tween or CTAB type surfactants since the emulsions are too unstable. Although a stable emulsion is necessary for the successful preparation of resin beads, it is shown below that it is not sufficient.

Prepolymerization. One way of stabilizing the emulsion is to carry out a prepolymerization of the two-phase emulsion; in effect, a polymeric dispersant is formed. In addition, prepolymerization increases the viscosity of the emulsion and also reduces the

TABLE 10. Solubility of Some Solutes in Different Solvents

		Solubility[a]								
Solvents	Solubility parameter δ	CB (δ = 9.5)	Hexane (δ = 7.3)	MA (δ = 8.9)	EA (δ = 8.6)	TAA[b]	MDAA[b]	DAA[b]	H_2O (δ = 23.4)	Fe(II) caproate
Freon $(CF_3)_2CHOH$		+		+	+	+	+	+		
Propylene carbonate	13.3	+	0	+	+	+	+	+	+	
Ethylene carbonate	14.7	+	0	+	+	+	+	+	+	
Sulfolane	13.4								+	
Paraffin oil	~ 6.5	+	+	+	+	0	0	0	0	
Ethanediol	14.6	0	0	0	+	+	+	+	+	0
Glycerol	16.5	0	0	0	0	+	+	+	+	
Propylene glycol	12.6	0		+	+	+	+	+	+	
Chlorobenzene (CB)	9.5	+		+	+	0	0	0	0	+
Fluorocarbons	~ 5.5									

[a] Solubility: + = soluble; 0 = insoluble.
[b] ~65% HCl in H_2O.

TABLE 11. Polymerization of Three-Phase Systems with Water or Paraffin Oil as the Third Phase[a]

Phase 1	Phase 2	Phase 3	Yield
MA/DVB/AIBN	TAA/Amido/Span 85	saturated aqueous $NaNO_3$	2% polyamine
MA/DVB/AIBN	TAA/Amido/CTAB	saturated aqueous $NaNO_3$	5% polyamine
MA/DVB/CoNap	TAA/Fe^{2+}/H_2O_2/S	saturated aqueous $NaNO_3$	< 5% polyamine
MA/DVB/CoNap	H_2O_2/S	saturated aqueous $NaNO_3$	no polymer
MA/DVB/AIBN	TAA/Am/CTAB	saturated aqueous NH_4Cl	5% polyamine
EA/DVB/BO	none	1% aqueous Poly AA	70% beads
EA/DVB/BO	Prepolymerized MDAA/hexa/Fe^{2+}/H_2O_2	1% aqueous Poly AA	20% polyamine
EA/AA/DVB/LO/FC	none	ethylene glycol (> 50°C)	40% beads
EA/AA/DVB/LO/FC	Prepolymerized DAA/hexa/Fe^{2+}/H_2O_2	ethylene glycol (20°C)	12% polyamine
Prepolymerized MA/DVB/AIBN	Prepolymerized TAA/Amido	paraffin oil	see discussion
MA/DVB/AIBN	TAA/Amido	paraffin oil + Span 80	see discussion
MA/DVB/AIBN	TAA/Amido	paraffin oil + Kemamine + octadecylamine	see discussion
MA/DVB/AIBN	TAA/Amido	plastic sheet	see discussion

[a] CoNap = Cobalt naphthenate; S = Span 85/Tween 85 of HLB No. 3.8; BO = benzoyl peroxide; LO = lauroyl peroxide; FC = ferrous caproate; prepolymerized = partly polymerized.

solubility of the ester and amine phases in the third phase. An emulsion of MA/DVB/AIBN and TAA/amido (Table 11) was therefore heated with stirring for a short time. Although there was no change in viscosity after about 20 min at 60°C, as soon as polymerization became evident the mixture gelled within 2 or 3 min, and therefore careful control of the conditions was needed in order to get a suitably viscous sample to add to paraffin oil as the third phase. When the viscous, partly polymerized mixture was added dropwise to hot paraffin oil, a dispersion of drops was obtained. However, after 2 hr, they had all coalesced to a soft layer which was still soft after 24 hr at 80°C. The addition of Span 80 or other oil-soluble surfactants to the paraffin oil prior to adding the partly-polymerized mixtures resulted in very little improvement. Spaghettilike threads of the partly polymerized mixture were extruded on to a plastic sheet which was then heated in an oven at 80°C, but the product remained soft and jellylike. The nature of many of the above polymerizations and prepolymerizations suggests that the allylamines polymerize first and that the residual allyl groups inhibit the ester polymerization.

Prepolymerization with Talc in the Third Phase. It seemed likely that more success would be achieved if a dispersion of the partly prepolymerized mixture could be more effectively stabilized in the third phase. The effect of adding solid dispersants such as colloidal silica and talc is shown in Table 12. Very good resin beads were formed under certain conditions. Part prepolymerization was essential for satisfactory bead formation. The nature of the product depended very much on a number of factors, including the stirring rate, the shape and material of construction of the stirrer, the potential acid to base ratio of the monomers, the nature of the solid dispersant and the nature of the acrylic ester and the allylamine. Unfortunately, because of the last condition, satisfactory resin beads could be obtained from only the MA/TAA and MA/DAA combinations, which are the combinations which give resins with the lowest capacity in the two-phase systems. The capacities of comparable resins prepared in a two- or three-phase system were similar.

Polymeric Dispersants. Although the procedure of partly polymerizing the two-phase system in order to stabilize the emulsion before adding it to the third phase could be satisfactorily controlled on the laboratory scale, it would be more difficult on a large scale. Another possible way of increasing the viscosity and especially the stability of the two phase emulsion would be to use polymeric dispersants. A polymeric dispersant made by copolymerizing a mixture of EA and 10% hydroxylethyl methacrylate (HEMA) was used to produce stable emulsions of EA, MDAA, initiators, crosslinkers and solvents. Generally, the emulsions were stable for at least 24 hr. The results of dispersing these emulsions in a third phase and polymerizing them are shown in Table 13. The benzoyl peroxide/dithionite

TABLE 12. Polymerization of Three-Phase Systems with the Use of Solid Dispersants in the Third Phase

					Capacity (meq/g)				
Expt.	Phase 1 and 2[a]	Type of emulsion	Phase 3	Results[b]	Amine (microanalysis)	Amine	Acid	Acid/ amine ratio	Thermally regenerable capacity (meq/g)
TA4	MA/TAA	w/o	paraffin oil + talc	+					
TA4H	hydrolyzed TA4			+	2.55	1.56	1.61	1.03	0.39
TA3	MA/0.5 DAA[c]	w/o	paraffin oil + talc	0					
TA6	MA/DAA[c]	o/w	paraffin oil + talc	+					
TA6H	hydrolyzed TA6			0	5.55	4.00	1.21	0.3	0.23
TA7	MA/DAA	o/w	paraffin oil + talc	0					
TA11	EA/DAA	o/w	paraffin oil + talc	0					
P69	EA/DAA	o/w	paraffin oil + Aerosil 200	0					
TA12	MA/DAA	o/w	paraffin oil + Aerosil 200	0					
TA13	MA/DAA	o/w	paraffin oil + Aerosil R972	0					
TA14	EA/MDAA	o/w	paraffin oil + talc	0					
TA15	EA/MDAA	w/o	ethylene glycol + talc	0					

[a] Plus the usual crosslinkers and initiators; partly prepolymerized.

[b] Results: + = satisfactory beads; 0 = poor beads or no beads.

[c] Half of the amount of DAA was used in TA3 as was used in TA6.

TABLE 13. Polymerization of Three-Phase Systems with the Use of Polymeric Dispersants to Stabilize the Two-Phase Emulsions

Expt.	Phase 1	Polymeric dispersant[a]	Phase 2	Initiators	Phase 3	Yield (total monomers) (%)	Amine capacity (meq/g)	Comments
TP1	MDAA/HEXA/H_2O	HOEA	EA/DVB/CB	Amido/AIBN	5% aqueous PVA	5	-	agglomerated, very soft
TP2	MDAA/HEXA/H_2O	HOEA	EA/DVB/CB	BO/dith[b]	5% aqueous PVA	21	1.1	large, soft, hollow beads
TP3	MDAA/HEXA/H_2O	HOEA	EA/DVB/CB	Amido/AIBN	5% aqueous PVA	28	-	large, soft, hollow beads
TP4	MDAA/HEXA/H_2O	HOEA	EA/DVB/CB	BO/dith + Amido	3% aqueous PVA	23	0.25	soft, sticky
TP6	HEXA/H_2O	HOEA	EA/EGDMA/ Toluene	BO/Amido	5% aqueous PVA	10	0.17	soft
TPC1	-	-	EA/DVB	BO/dith	5% aqueous PVA	29	-	soft, sticky
TPC2	-	-	EA/EGDMA	BO/dith	5% aqueous PVA	21	-	soft, sticky
TPC3	-	-	BA/DVB	BO + AIBN	5% aqueous PVA	80	-	good beads
TP9	MDAA/HEXA/H_2O	HOEA	EA/MMA/DVB	BO + AIBN	5% aqueous PVA	14	1.1	large hollow beads
TP8	MDAA/HEXA/H_2O	HOBA	BA/DVB	BO + AIBN	5% aqueous PVA	Emulsion unstable		
TP10	MDAA/HEXA/H_2O	DMAEA	EA/DVB	Amido/AIBN	paraffin oil & talc	-	-	soft, sticky mass

[a] HOEA = poly-EA with 10% hydroxyethyl methacrylate (HEMA); HOBA = poly-BA containing 10% HEMA; DMAEA = poly(dimethylaminoethyl methacrylate) containing 10% EA.

[b] Benzoyl peroxide, sodium dithionite; heat was needed.

TABLE 14. Diffusion of Amine Monomer into the Aqueous Phase[a]

	Amine diffused (%)	
Time (min)	Diffusion into 3% aqueous PVA[b]	Diffusion into saturated $NaNO_3$[c]
15	35	80
45	-	93
70	52	-
130	66	-

[a] At 20°C.

[b] Amine emulsion of MDAA/HEXA/H_2O/EGDMA/toluene/EA/HOEA.

[c] Amine emulsion of MDAA/H_2O/butanol/Span 80/Tween 80.

initiator system was inferior to AIBN/amido systems. Generally, greater than 3% of polymeric dispersant (based on the total volume) was required to achieve a stable emulsion. DVB appears to be the least compatible component of the emulsion with appreciable separation being apparent at greater than the 5% level. Chlorobenzene was the solvent used in most of these studies, but there had been some indications from the two-phase studies that this may not be a good solvent for polymerization. It was chosen largely because it has a density close to that of water and should therefore form a more stable emulsion. The substitution of toluene for chlorobenzene resulted in a less stable emulsion. The latter could be made stable by doubling the amount of polymeric dispersant. In these systems, the acrylate usually polymerized poorly and DVB was a poor crosslinker. However, the major obstacle to this approach was the fact that the amine monomer diffused out of the emulsion and into the aqueous third phase much more readily than it polymerized. Thus, the polymerized product consisted of hollow spheres. Table 14 gives an indication of the rate of diffusion of the amine monomer into the aqueous phase. Anything which is soluble in water would be expected to transfer into the external phase and stabilizers encourage this transfer. Also, the corresponding migration of water into the emulsion would be impossible to stop.

EXPERIMENTAL

Materials

The Span, Tween, and Brij surfactants (Atlas Chemical Industries Inc.), the Teric surfactants, and Vantoc CL were obtained from either ICI (Australia) or ICI (U. K.). Kenmat SA 17 (IPADBS) is a Beith Chemicals surfactant. Tergitol No. 2 is a product of Union Carbide Corporation Inc. CTAB is a BDH product.

The colloidal silicas Aerosil 200 and Aerosil R972 were gifts from Hoechst Australia Ltd. (Degussa Pigments Division).

The preparation or source of the allylamines, amido, and AIBN has been reported previously [11]. All amines were polymerized as their hydrochlorides. Acrylic esters and divinyl benzene were used without removal of inhibitors. Benzoyl peroxide (BDH), lauroyl peroxide (Fluka) and cobalt naphthenate (4.5% Co, obtained from Spartan Paints Pty. Ltd.) were used without purification.

Poly(ethylacrylate-co-10% hydroxyethyl methacrylate) was prepared by heating a degassed solution of ethyl acrylate (EA) (6 ml), hydroxyethyl methacrylate (0.68 ml), and AIBN (0.1 g) in toluene (14 ml) at 70°C for 65 hr, cooled, and poured into hexane. The precipitate was dissolved in toluene and the polymer again precipitated with hexane to yield 5.8 g (95%) of copolymer.

Poly(dimethylaminoethyl methacrylate-co-10% EA) was prepared by heating a degassed solution of dimethylaminoethyl methacrylate (3 ml), EA (0.34 ml), and AIBN (0.06 g) in ethanol (10 ml) at 70°C for 21 hr, cooled, and the solvent removed under vacuum to give 2.88 g of copolymer which was dissolved in 5.5 N HCl (3.7 ml).

Polymerization of Two-Phase Systems

The details for the preparation of thermally regenerable ion-exchange resins by polymerizing a two-phase system are summarized in Table 8. The following procedure for experiment number P10 is typical. An emulsion of MA (6 ml), DVB (0.3 ml), TAA (9 ml of a 70% aqueous solution of TAA.HCl), AIBN (0.15 g), amido (0.15 g) and a mixture of the surfactants Span 85 and Tween 85 of HLB number 3.8 was prepared by stirring in an Omnimix and then transferred to a reaction vessel. The emulsion was heated at 65°C for 21 hr with stirring at 240 rpm (until gelation). The cooled rubbery mass was broken up in a mortar and pestle and washed successively in a sintered glass column with acetone (resins containing secondary amines were washed with ethanol rather than acetone), 2 N HCl, pH 3 HCl, acetone, and dried to give 7.92 g (66%) of resin. After grinding and sieving, a 0.4 to 1.6 mm fraction (6.35 g) was heated with stirring at 87 °C under nitrogen with 5 N ethanolic KOH (50 ml, ethanol:water = 1:1) for 65 hr, cooled, and washed successively in a sintered glass funnel with 0.3 N NaOH (6 hr), 2 N HCl (4 hr), pH 3 HCl until the effluent was pH 3 and dried in vacuo at 50° C for 24 hr to give 5.2 g of resin. The properties of this and the other resins are listed in Table 9.

Capacity Measurements

The titration procedures used to determine the acid and amine capacities and thermally regenerable capacities have been described previously [10, 12].

Polymerization of Three-Phase Systems

The details for the experiments are apparent from the discussion and Tables 11, 12, and 13.

The following are typical examples of the procedure for the three-phase polymerizations with the use of paraffin oil containing talc as the third phase and a partly prepolymerized emulsion.

Experiment TA1. A mixture of cetyltrimethylammonium bromide (CTAB) (0.3 g), MA (12 ml), DVB (1.2 ml), AIBN (0.3 g), amido (0.17 g), and TAA.HCl (10 ml) was heated at 65°C under a nitrogen atmosphere for 20 min, and then an aliquot (4 ml) of this slurry added dropwise to a nitrogen-saturated slurry of paraffin oil (50 ml) and talc (1 g) at 77°C with stirring at 150 rpm and heating continued for 20 hr. The cooled mixture was washed in a sintered glass funnel with hexane, dried, and sieved to remove the talc. The product (2 g) was obtained as hard beads, 0.7 to 1.2 mm in diameter.

Experiments TA4 and TA4H. A mixture of CTAB (0.3 g), MA (12 ml), DVB (1.2 ml), AIBN (0.3 g), amido (0.17 g), and TAA.HCl (10 ml) was heated at 68°C under a nitrogen atmosphere for 20 min. DVB (0.21 ml) was added to this solution which was then added to a nitrogen-degassed slurry of paraffin oil (60 ml) and talc (1.2 g) at 79°C with stirring at 200 rpm, and heating continued for 20 hr. The cooled mixture was washed in a sintered glass funnel with hexane, dried and sieved to give a product (1.9 g) as hard beads, 0.25-1.6 mm diameter (TA4). The product (1.9 g) was washed with 2 N HCl and then hydrolyzed by heating at 88°C for 48 hr with 5 N KOH (20 ml) under nitrogen with slow stirring. The resulting resin was washed successively in a sintered glass column with 0.3 N NaOH, 2 N HCl, pH 3 HCl and dried in vacuo at 50°C to give 1.2 g of resin (TA4H). The amine capacity from microanalysis was 2.55 meq/g.

The amine and acid capacities from titration were 1.56 meq/g and 1.61 meq/g, respectively (acid to base ratio = 1.03). The thermally regenerable capacity of the resin (equilibrated at pH 6.8) was 0.39 meq/g.

CONCLUSIONS

Emulsions prepared from acrylic esters and allylamines using conventional surfactants are not very stable. Because of the acid/base ratio requirements in the final resin, unfavorable acid/base ratios for w/o emulsions have to be used. Polymeric dispersants gave much more stable emulsions.

The polymerization of the two-phase emulsions gave resins, some with very good strength and toughness, and thermally regenerable capacities as high as 1.5 meq/g, which is the highest value obtained for any thermally regenerable resins. However, the preparation of these resins in bead form was only partly successful. The only satisfactory beads were obtained by adding a partly prepolymerized emulsion to paraffin oil containing talc. The best beads were obtained from the MA/TAA and MA/DAA systems, the poorest systems as far as thermally regenerable capacity is concerned.

Since stabilization of the two-phase system by partial prepolymerization is impracticable on a large scale, an alternative method of stabilization of the two-phase system was required. This was achieved with polymeric dispersants. However, it appears the prepolymerization does more than stabilize the emulsion. It also insolubilizes the "monomers" and thus reduces their migration into the third phase. With polymeric dispersants monomer migration was too rapid to permit the preparation of satisfactory resin beads.

Because of the experimental difficulties which were experienced in attempting to obtain the resin in suitable bead form by polymerizing a mixture of monomers, it appears that the approach of incorporating resin plums in a matrix (to give "plum pudding" resins [12]) may be the best.

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