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Removal of Alkaline Catalysts from Polyols by Ion Exchange: Selection of an Ion-Exchange Resin

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ABSTRACT

Polyols, as commercially prepared, contain in their crude form various impurities such as alkali metal hydroxides which were employed as catalysts for their production. Most practical methods for removing these impurities involve acid neutralization of the alkali to form insoluble salts which are removed by filtration. A variety of commercial resins were evaluated in this work as ion exchangers for the purification of polyols. Amberlite 252, a macroporous cation exchange resin, was found to be the best resin. The loaded resin was regenerated efficiently. The results suggest that such a process is both technically and economically feasible.

Key Words: Ion exchange; Polyols; Organic media

INTRODUCTION

Polyoxyalkylene ether polyols, usually called polyols, are commonly used for the production of urethane polymers. These polyols react with polyisocyanate in the presence of a catalyst and other materials to produce different forms of urethane polymers such as rubberlike elastomers, flexible or rigids foams, etc. In order to obtain urethane polymers with the desired properties, it is important that the polyols to be reacted with the polyisocyanate are essentially free of impurities which may act as catalysts of undesirable reactions (1).

Polyols, as commercially prepared, contain in their crude form various impurities such as alkali metal hydroxides or metal salts which were employed as alkaline catalysts for the production of the polyols. The normal concentrations of the catalysts range from 1700 to 4000 ppm, and the desire is to reduce them to 5 ppm or less (2).

There are several known methods for the removal of these alkaline catalysts from polyols. Current commercial practices involve neutralization of alkaline catalysts with acids to form insoluble salts which are removed by filtration (3). Centrifugation of mixtures of polyol, water, and solvent can also be employed for the removal of residual catalysts (4). Adsorption with inorganic adsorbents such as bentonite, zeolites, or diatomaceous earth is a widely used and relatively inexpensive process (5). Cation-exchange resins have a high capacity for alkaline metals, but they do not work well in organic media. A major factor which contributes to their low exchange rate is the inhibition of mass transfer of polyether molecules through the pores of an ion-exchange resin bead so they may reach the active ion-exchange sites. This inhibition is directly related to the size of the molecule containing the catalyst impurity to be exchanged (6, 7).

The main objective of this work was to find a method for efficient removal of catalyst impurities (potassium and sodium) from polyether–polyols by ion exchange. It is known that different types of cationic ion-exchange resins can eliminate these alkaline impurities from polyols. However, it is of key importance to find a resin with a high exchange rate in order to reduce the concentration of alkaline metals to the accepted commercial specifications. Furthermore, an efficient and inexpensive regeneration method for reuse of the resin should be developed.

In summary, an ion-exchange resin for the removal of alkaline impurities must satisfy the following conditions: high chemical and physical strengths; high capacity and rate of exchange; suitable quality of the purified polyols; easy regeneration; low cost and steady supply.

In this paper we present experimental data for the recovery of alkaline impurities from polyols using a prewetted ion-exchange resin. Numerous ion exchangers were tested and improved by taking into consideration the above described conditions. Experimental breakthrough curves and regeneration procedures are presented to demonstrate the feasibility of the proposed process. Plant design considerations, regeneration conditions for the spent resin, equilibrium isotherms, and kinetics data will be reported in subsequent papers.

TABLE 1
Characterization of Polyols

Grade	Type	Average molecular weight	Density (g/cm^3), 40°C	Viscosity (cP), 40°C	C_K (ppm)
F-135	Flexible	4800	1.021	400	1348
F-148	Flexible	3500	1.010	300	2200
F-155	Flexible	3050	1.023	200	2450

EXPERIMENTAL

Polyol. Experiments were limited to the use of F-148, F-155, and F-135 grade polyols, made by REPSOL QUIMICA S.A. The products are characterized in Table 1.

Ion-Exchange Resins. A number of commercially available sulfonated polystyrene–divinylbenzene resins (one of them carbonated) have been used in this study. Their relevant properties are given in Table 2. The resins with XZS and XVS codes are characterized by an uniquely narrow particle size distribution, being referred by the manufacturer as "monosphere enhanced performance" resins. The rest of the resins cited in Table 2 have a broad particle size distribution which is typical of con-

TABLE 2
Resin Properties

Resin	Structure	Active group	Average particle size (mm)	Exchange capacity, q_0 (meq/g dry)	Maximum operating temperature (°C)	Water content (%)
Amberlite 200	Macroporous	$—SO_3H$	0.562	4.76	150	46
Amberlite 15	Macroporous	$—SO_3H$	0.718	4.89	120	46
Amberlite 252	Macroporous	$—SO_3H$	0.494	5.26	135	54
Lewatit S-100	Geliform	$—SO_3H$	0.539	5.21	120	45
Lewatit CNP-80	Geliform	—COOH	0.555	10.72	120	45
Dowex MSC-1	Macroporous	$—SO_3H$	0.667	4.64	150	44
Dowex CM-15	Macroporous	$—SO_3H$	0.554	4.80	150	43
Dowex XVS	Macroporous	$—SO_3H$	0.448	5.04	130	42
Dowex XZS-1	Geliform	$—SO_3H$	0.336	5.16	130	45
Dowex XZS-2	Geliform	$—SO_3H$	0.441	5.40	130	45

ventional commercial resins. The resin samples were used as supplied by the manufacturer, with no particle size classification, and conventionally treated in order to obtain normalized conditions of capacity and ionic form. The resins (each one from a single lot) were pretreated by repeated washes in a column with 1 N NaOH and HCl solutions, converted to the hydrogen form with 1 N HCl, and thoroughly rinsed with distilled-deionized water with a conductivity smaller than 1 μS (8, 9).

The total ion-exchange capacity of each resin (q_0, meq/g of dry resin) was determined by equilibrating resin samples in the hydrogen form with an excess of NaOH solution. The total capacity was determined by backtitrating the excess NaOH. Surface area, porosity, and apparent density were determined by using a Quantacrome Autoscan Porosimeter 2000 capable of operating to 60,000 psig, thereby measuring pores in the range of 20 to 5000 Å in radius.

Rate Experiments. Intraparticle diffusion dynamics were studied by measuring the rate at which alkaline metals were taken up by the resin in a well-mixed tank. Sufficient mixing energy was applied so that only diffusion within the resin particle was the controlling step. In a typical experiment, 35 g of the ion-exchange resin was mixed with 1000 g of polyol in a baffled glass mixing vessel. The mixture was then stirred for 4 or 5 hours. Small aliquots (3 g) of the polyol were periodically taken, and the potassium content was analyzed. The sample size was considered small enough not to change the polyol/solid ratio.

Breakthrough Experiments. In these runs, about 60 g of fresh resin was charged to a 22 mm i.d. 600 mm length tube. The polyol was then pumped through the resin bed at a fixed flow rate at 100°C. Samples of the effluent polyol were taken and analyzed for the potassium content.

Regeneration Procedures. After completion of a breakthrough curve, the spent resin bed was regenerated by consecutive flushing with solvents (methanol and water), contacting with an aqueous acid solution, and rinsing with water and methanol.

Sodium and Potassium Content. This was measured by atomic emission spectrometry in a Thermo Jarrel Ash (Smith Hiejfe II) atomic absorption spectrometer. The polyol samples were diluted with ethanol (1:5 by weight) to reduce their viscosity.

Acid Number. This was measured according to ASTM D2849-69 by automatic titration with an ethanolic solution of KOH. The acid number is defined as the amount of base, expressed as milligrams of KOH, required to titer the acidic components existing in 1 g of polyol sample.

Total Unsaturation. This was determined according to ASTM D2849-69 by reaction of a sample of polyol with an ethanolic solution of mercuric acetate and backtitration with an ethanolic solution of KOH. Total unsaturation is a parameter related to the number of side reactions that have taken place during polyol manufacture.

Color Test. This was determined according to ASTM D2849-69 by comparing the polyol sample with a color standard disk in a Lovibond Nessleriser Comparator, the results being expressed in Hazen units.

RESULTS AND DISCUSSION

A set of simple experiments was used to demonstrate the effects on the ion-exchange rate of prewetting of the resin beads and diluting the polyol with an organic solvent. As shown in Fig. 1, alcohol-wetted Amberlite 252 was more effective than a dried sample of this resin due to swelling of the resin matrix. Other investigators (10, 11) have shown, when investigating the elimination of nitrogen compounds from hydrocarbon oils, that prewetting the resin beads with a solvent miscible both with water and oil (CH_3OH, CH_2Cl_2) increases the rate of exchange. The prewetting of the ion-exchange resins with a miscible solvent was carried out as the initial step in all subsequent experiments done in polyol media.

It is interesting to observe (also shown in Fig. 1) that the polyol–methanol (1:20) mixture had the highest exchange rate due to its smaller viscosity. Nevertheless, the dilution of polyol was discarded as the industrial

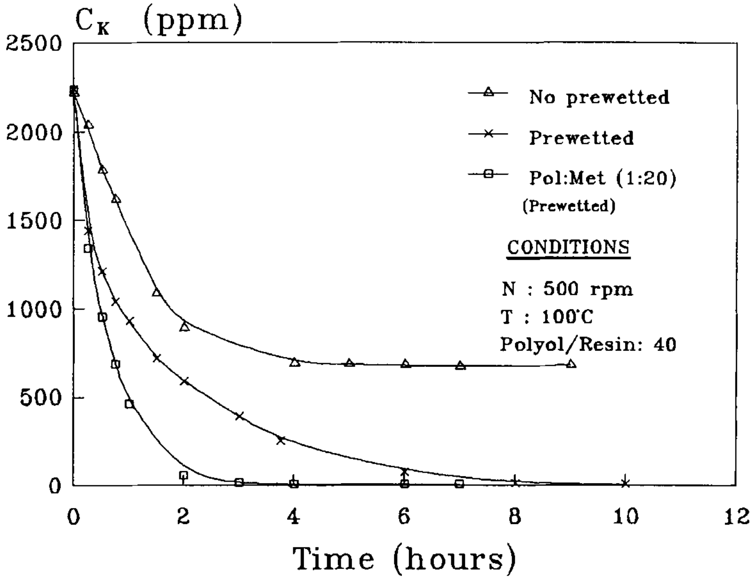


FIG. 1 Effect of prewetting of the resin over the ion-exchange rate.

operating method because the methanol solvent would have to be recovered by flash vaporization, which is an expensive operation.

In order to test which of four different prewetting solvents (methanol, ethanol, 2-propanol, and 1-butanol) had the strongest effect on the ion-exchange rate, a number of simple comparative experiments were made. Figure 2 shows the kinetic curves obtained, and methanol causes the biggest increase in the ion-exchange rate due to its greater dielectric constant and smaller viscosity. Methanol was therefore chosen as the solvent of choice for prewetting the resin beads.

The selection of the best resins was carried out in two steps: 1) a screening test by which the best ion-exchange resin was selected, and 2) by regeneration cycles to demonstrate the feasibility of using the selected resin under cyclic operation.

Screening Test

The first goal was to show that a number of preselected ion-exchange resins could withstand the chemical and physical attack of the polyol. A sample of 5–8 g of dry resin was placed with 20 g of polyol in a test tube for about 2 weeks at 100°C. None of the resins was damaged during the experiment.

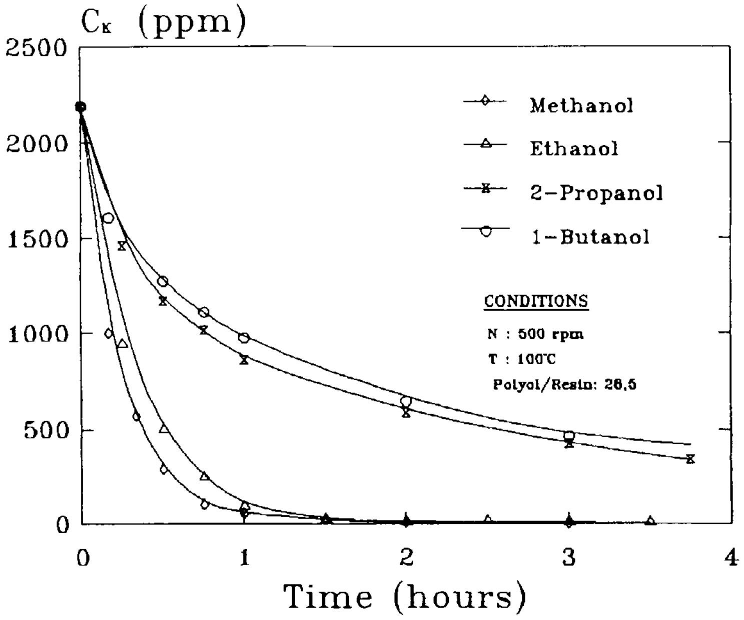


FIG. 2 Influence of prewetting solvent over ion-exchange rate.

Next, in order to compare the kinetic behavior of the preselected resins, the fractional attainment of equilibrium sorption was measured as a function of time under identical conditions.

Purification time is a critical parameter of this process. Thus, we established a criterion to select the best ion-exchange resins: the alkaline content had to be lower than 5 ppm after a contact time of 2 hours. The experimental kinetic results, presented in Table 3, show that Amberlite 252, Dowex XZS-1, and Dowex XZS-2 comply with this condition, and so they were selected as the best resins.

From the standpoint of the industrial application of this process, the discontinous kinetic curves obtained are sufficient to provide the essential information required for process design. However, bath kinetic data were also accurate and extensive enough to allow a more detailed theoretical analysis to explain the different behaviors of the exchange resins studied.

Since the ion-exchange rate was very slow and changed with the particle diameter, the ion-exchange rate seemed to be controlled by the intraparticle diffusion rate (12). Therefore, the ion-exchange rates of the batchwise test were represented by a homogeneous model which leads to a well-known equation (13–15):

$$F = \frac{C_0 - C}{C_0} = 1 - \frac{6}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{m^2} \exp -\left(\frac{m^2\pi^2 D_{\mathrm{eff}} t}{R^2}\right)$$

Intraparticle effective diffusivity values [D_{eff} (cm^2/s)] were obtained by matching the experimental data with the analytical solution of the kinetic curves (see Table 4). Figure 3 shows the excellent fit between the experimental data and the theoretical curves for the best ion-exchange resins.

TABLE 3
Alkaline Content at Different Contacting Times

	Alkaline content (ppm)		
Resin	1 hour	2 hours	4 hours
Amberlite 200	331	81	5
Amberlite 15	892	597	327
Amberlite 252	38	3	<1
Lewatit S-100	48	12	<1
Lewatit CNP-80	1126	832	607
Dowex MSC-1	622	258	15
Dowex CM-15	362	61	5
Dowex XVS	103	11	<1
Dowex XZS-1	11	3	<1
Dowex XZS-2	46	4	<1

TABLE 4
Effect of Resin Properties on Intraparticle Effective Diffusivity

Resin	$D_{\mathrm{eff}} \times 10^8$ (cm^2/s)	Surface area (cm^2/g)	Porosity (%)	Apparent density (g/cm^3)	Swelling (%)	
					H_2O	Methanol
Lewatit S-100	7.15	6.19	2.04	1.482	110.74	46.92
Dowex XZS-1	5.28	12.78	3.95	1.370	86.84	33.33
Dowex XZS-2	4.75	11.65	3.38	1.360	71.61	22.29
Amberlite 252	4.45	24.87	7.20	1.323	39.04	12.38
Dowex CM-15	3.04	14.39	15.73	1.167	30.56	10.19
Dowex XVS	2.74	39.73	18.98	1.120	22.97	8.14
Dowex MSC-1	2.66	39.52	27.78	1.038	17.85	6.66
Amberlite 200	2.45	62.69	31.75	0.881	12.93	5.88
Amberlite 15	2.25	78.12	31.12	0.898	11.62	4.65
Lewatit CNP-80	0.89	9.98	2.56	1.336	38.44	28.88

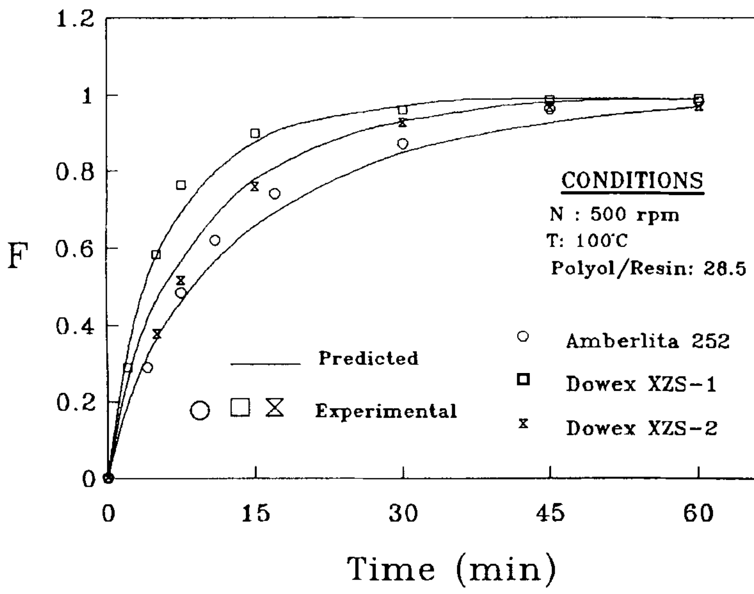


FIG. 3 Concentration profiles during the uptake of potassium with the best resins. Comparison of experimental and predicted profiles.

In order to interpret the different ion-exchange rates, a detailed experimental study of the ion-exchange resins was made. Resin porosity, apparent density, and surface area were obtain by mercury porosimetry, and the swelling of differents resins in water and methanol was measured under the microscope. All of these values are given in Table 4. It is well recognized that the DVB content of the resins is related to the matrix structure (10, 16). The surface area and porosity increase with DVB content (divinylbenzene), and the apparent density and swelling decrease.

As shown in Table 4, Dowex XZS-1, Dowex XZS-2, Lewatit S-100 (geliform), and Amberlite 252 (macroporous) have the highest values of swelling capacity and apparent density and the smallest values of surface area and porosity. It is therefore concluded that these resins have the smallest DVB content. The values of D_{eff} are consistent with the results obtained, since the other macroporous resins, which have higher DVB contents, show a smaller ion-exchange rate.

Lewatit S-100, a geliform strongly acid resin, showed the highest value of D_{eff}. However, the time required to reach complete polyol purification is longer due to its greater particle diameter. On the other hand, the performance of Lewatit CNP-80 was much poorer than that of the other resins because it is a weak cationic-exchange resin.

Similar results have been also obtained by other investigators in studies of the diffusion mechanism of large molecules in ion exchangers (10, 17, 18). They showed that the rate of intraparticle transport decreases substantially with crosslinking of the resin (% DVB).

After purification with the resins Amberlite 252, Dowex XZS-1, Dowex XZS-2, Dowex XVS, and Lewatit S-100, samples of polyols were analyzed in order to verify polyol quality. Figure 4 shows that the total unsaturation and acid number values obtained are better than the commercial specifications. Color analysis and foaming tests were also made using samples of these polyols, and the results were satisfactory. Finally, samples of polyol purified with Amberlite 252 and Dowex XZS-1 were examined by ^{1}H NMR, and compared with samples of polyol purified by neutralization with acids and subsequent filtration. As shown in Fig. 5, all the spectra obtained are identical, demonstrating that the properties and structures of polyols purified by both methods are identical.

Amberlite 252 was selected over Dowex XZS-1 and Dowex XZS-2 due to the greater physical stability of macroporous versus geliform resins (19). Furthermore, Amberlite 252 showed a high ion-exchange rate and the polyol obtained had good quality.

In order to validate the general applicability of this purification method to other polyol grades, we carried out two comparative experiments with

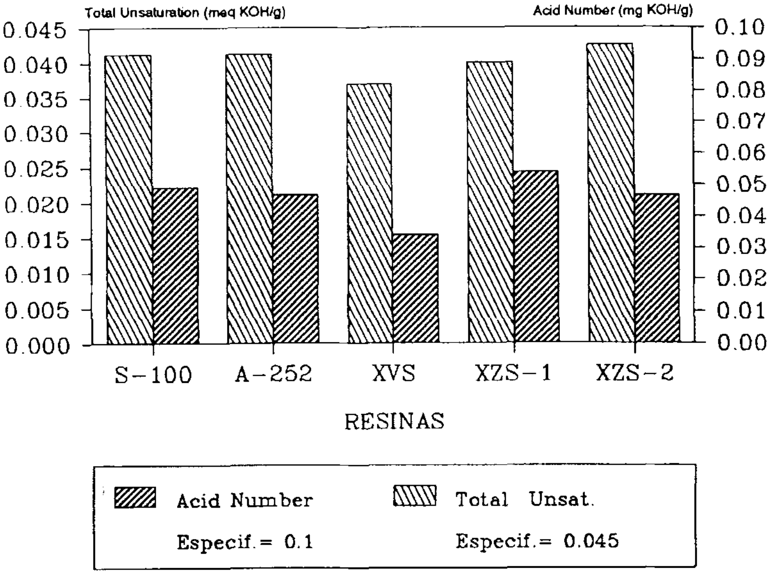


FIG. 4 Total unsaturation and acid number.

Grades F-155 and F-135. Figure 6 clearly confirms that an alkaline catalyst can be efficiently removed from flexible polyols by using Amberlite 252 resin and a contact time of 2 hours. The quality of these polyols compared to polyols purified by acid neutralization was quite satisfactory.

Regeneration and Recycle Operation

Before confirming the selection of Amberlite 252, the investigation focused on determining the regenerability of this resin.

To test the effectiveness of resin regeneration, a series of recycle runs was made by using an ion-exchange step and then an acid regeneration cycle. The polyol was pumped through a column of fresh resin (0.2 cm/s with 60 g of Amberlite 252 resin) to obtain the breakthrough curve shown in Fig. 7. The column was then flushed with methanol (a solvent miscible both with water and polyol), rinsed with water, treated with 0.5 M hydrochloric acid aqueous solution (until constant pH was reached), and subsequently flushed with water and methanol. The breakthrough curve was then repeated, and it is also shown in Fig. 7. It can be observed that the

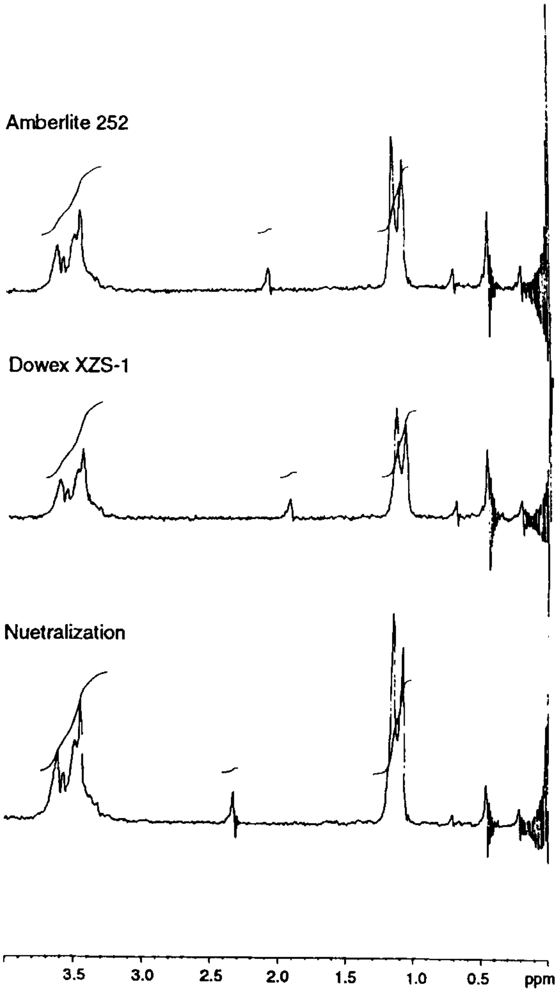
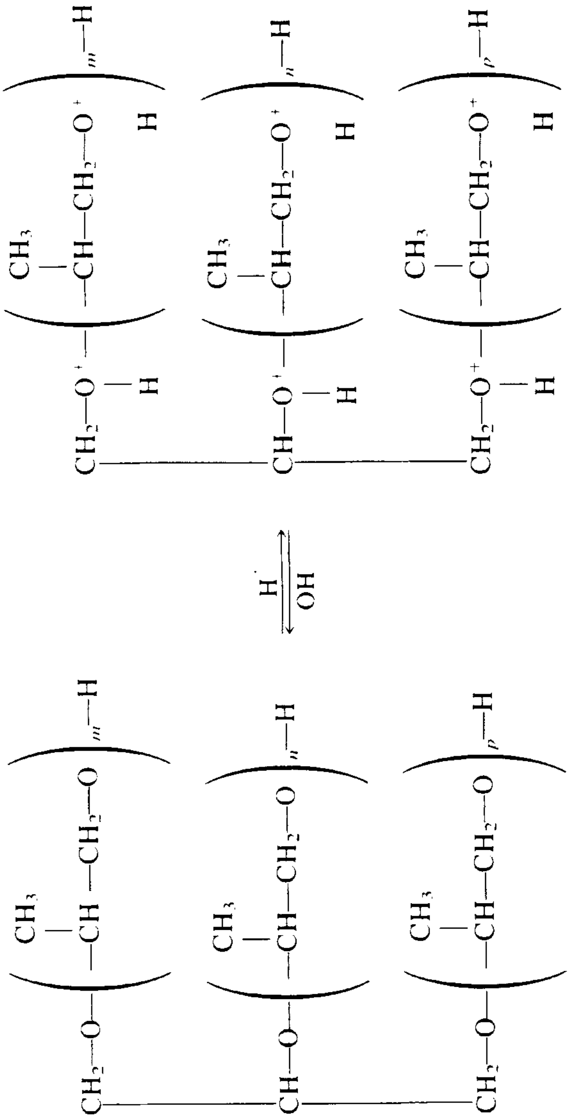


FIG. 5 Comparison of ^{1}H-NMR spectrum of the polyol purified by ion-exchange resins (Amberlite 252 and Dowex XZS-1) and by crystallization.

resin had not been satisfactorily regenerated. In order to determine an adequate method for ion-exchange resin regeneration, another series of regeneration runs was made using 4.5 M hydrochloric acid solution. The loading curves (Fig. 7) indicate that the resin was satisfactorily regenerated due to *O*-protonation of the polyol chain in a very strong aqueous acidic media: see page 136.



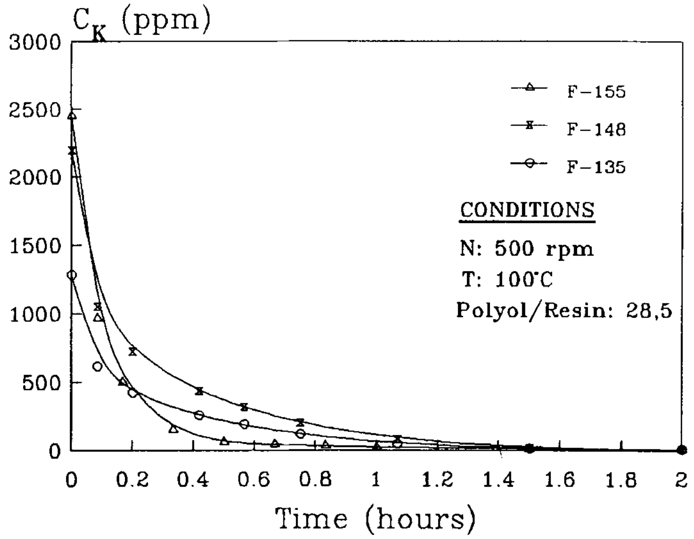


FIG. 6 Comparative experiments using different polyol grades.

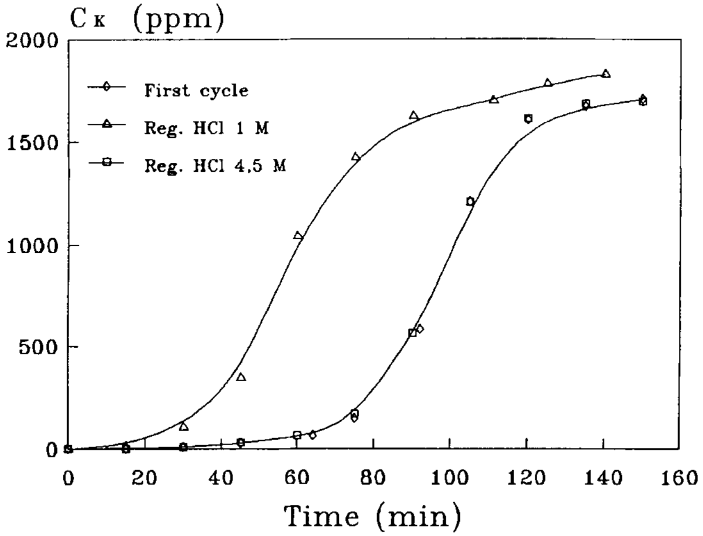


FIG. 7 Effect of regenerant concentration on Amberlite 252 regeneration.

Finally, in order to test the feasibility of using this method under cyclic operation, repeated experiments were carried out. As shown in Fig. 8, the breakthrough curves do not change after consecutive regeneration cycles. No cracks appeared within the resin particles. These results suggest that polyols, solvents, and strong concentrated acids do not harm the resin, and so the proposed method is technically feasible for removing alkaline impurities from polyether–polyols. Amberlite 252 would definitively be the resin of choice.

Scale-Up

Purification of polyols (F-148, F-155, and F-135) was carried out in pilot-plant equipment (a 50 L agitated and thermostated tank). The experiments were done at the same conditions as for the selection experiments, keeping constant the agitation power/volume ratio used in the laboratory tests. Under these conditions, 50 kg of purified polyol was produced.

The results obtained for the three polyol grades in the pilot-plant reactor were practically the same as those obtained in the laboratory, and the quality of the purified polyols was also satisfactory. These results indicate that the scale-up criterion used is valid, at least in the range used.

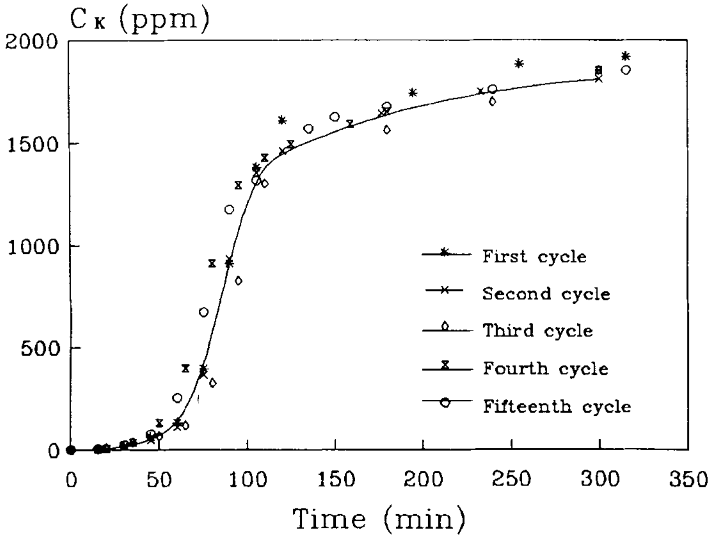


FIG. 8 Breakthrough curves for the series of recycle runs.

CONCLUSIONS

The removal of alkaline catalyst from polyols by ion exchange was investigated, and the following conclusions were reached:

The prewetting of resins beads with a solvent miscible both with water and polyol (methanol) increases the rate of exchange.

Amberlite 252, a macroporous strong cation-exchanger, is the resin selected for this process. This resin shows good chemical and physical strengths, high capacity, and a high rate of exchange. The loaded resin can be efficiently regenerated with a 4.5 M hydrochloric acid aqueous solution.

Polyols purified by this method show total unsaturation and acid number values which comply with commercial specifications. Foaming and color tests gave satisfactory results.

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