Organic Process Research & Development **1999**, *3,* 166–171

An Improved Method for the Purification of Polyether−Polyols Using Phosphoric Acid as Neutralization Agent

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Abstract:

The aim of this study was to develop a crystallization process for the removal of the alkaline catalyst (potassium hydroxide) from crude polyether−polyols. The process involves a first step of neutralization with an aqueous solution of phosphoric acid and subsequently the removal of water to reach supersaturation and crystal growth. Finally, the crystals formed are removed by filtration. Different amounts of phosphoric acid and water were investigated in order to establish a suitable recipe for this process. Different depressurization vs time profiles for the water evaporation were used to produce an uniform and narrow crystal size distribution with a large mean crystal size in this kind of experimental device.

Introduction

Polyethers made from epoxides are produced throughout the entire world according to the same basic process, namely, the polyaddition of basic structural units of epoxides (oxiranes), and in most cases according to an anionic mechanism. The discontinuous batch process is a common practice.[1]

These polyethers are reacted with polyisocyanate in the presence of an added catalyst and other materials to produce urethane polymers. Their principal application is in the production of rubberlike elastomers, flexible or rigid foams, and the like.

Potassium hydroxide is most often used as the basic catalyst in the polyol production. At the end of the polymerization process, most of the chains are terminated in hydroxyl groups, with only a small amount of alcoholate endgroups, due to the low quantity of catalyst added. The normal concentration of catalyst in the crude polyols ranges from 1000 to 4000 ppm, although a reduction to under 5 ppm is desirable.

One of the commercial practices for the removal of these impurities involves the acid neutralization of the alkali, forming insoluble salts, and the separation of them by filtration. Different kinds of inorganic[2,3] and organic[4,5] acids have been employed for neutralization with successful results. Nevertheless, all of them have the same technical problem: the filtration process is not always reliable because these batch crystallizers, used for a variety of polyol grades, do not incorporate any design features which would aid in producing the desired crystal size distribution, habit, and purity for a specific system. In general, the only parameters that can be varied in these batch crystallizers are the temperature and the vacuum level (which can often be only roughly controlled). Most manufacturing operations employ a trial and error procedure, varying these parameters until the desired filtration time and product specifications are obtained. Laboratory studies may help in the choice of the best conditions for batch crystallization.[6]

This experimental work was carried out in order to develop a crystallization procedure, taking into account the operational constraints of a constructed and working plant. Consequently, we had to carry out batch crystallization, since polyolether production is a discontinuous process. In the industrial process, there is no practical feasibility of including seed crystals; hence, this possibility was rejected. Finally, it should be noted that the interest of the company was basically to reduce the filtration time, and so that was one of the main targets in the experimental work.

Therefore, the main goal of this study was to obtain an adequate operation procedure for purifying polyethers using H_3PO_4 as neutralization agent. An initial operation protocol was successively modified in order to determinate the influence of the different operation conditions on crystal size distribution.

Experimental Section

Materials. The experiments were limited to the use of one flexible polyether−polyol grade, namely a glycerin-initiated block random copolymer of propylene oxide and ethylene oxide. The alkaline metal content, in crude form, is about 2200 ppm (potassium mainly, with less than 8 ppm of sodium). Its molecular weight distribution was determined by gel permeation chromatography (GPC). A weight-average molecular weight, $\overline{M}_w$, of 3550 with a polydispersity of 1.09 was obtained.

Phosphoric acid 87% (Fluka, analytical grade) was used as neutralization agent and Topanol (Fluka, 99% purity) as antioxidant.

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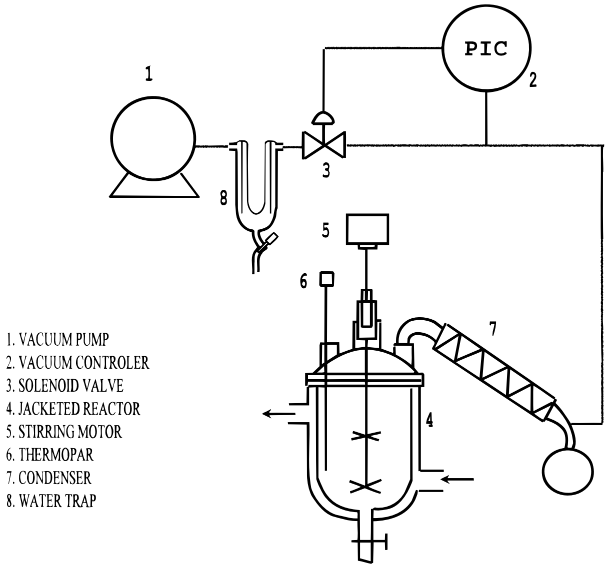

Figure 1. **Schematic of the laboratory scale crystallizer.**

Table 1. **Quality specifications for flexible polyols**

quality parameter	values	test methods
potassium content (ppm, max)	5	ASTM D 4668-87
water content (% by weight, max)	0.1	ASTM D 4672-87
acidity (mg of KOH/g of polyol, max)	0.1	ASTM D 4662-87
color (Hazen units, max)	50	ASTM D 4890-88

Crystallization Experiments. Batch crystallizations were carried out in a 2-L double-jacketed glass reactor, with digital control of stirring rate and temperature. An agitation device equipped with two Rusthon turbines having six vertical blades was used. Vacuum level was controlled by using a Divatronic DT digital vacuum indicator−controller, acting on a solenoid valve. The experimental setup is shown schematically in Figure 1.

Once the crystallization process had finished, the filtration process was carried out in a thermostated stainless steel cartridge, 10 cm i.d., and having a 2-L capacity at 130 °C and 245 kN/m^2, fitted with a Sartorius glass-fiber prefilter and a cellulose acetate filter with capability to retain particles greater than 1 μm.

Quality parameters related to the purification process of polyols were also measured. Table 1 shows the standard quality specifications required for these kinds of products. Potassium content was analyzed by atomic emission spectrometry in a Thermo Jarrel Ash (Smith Hiejfe 11) atomic absorption spectrophotometer. Water content of polyol was determined by the Karl Fischer method in a Metrohm KF-701 titroprocessor. Acidity was measured by automatic titration in a Metrohm 686 titroprocessor. Polyol colour was measured by using a Lovibond Nessleriser. Crystal size distribution (CSD) was determined by using a Sedigraph Micromeritics 5100 apparatus.

Because of the lack of data regarding the kinetics of nucleation and growth of potassium phosphate crystals in a dispersion of water in polyol, an initial operation scheme, summarized in Table 2, was devised on the basis of our previous knowledge of different industrial polyol processes:

First Step: Monomers Removal. Once the polymerization has finished, a small amount of unreacted monomers remains, contaminating the crude polyether−polyol, and they must be removed. Pressure was maintained at 7 mbar and temperature at 120 °C for 20 min, achieving the complete elimination of monomers.

Second Step: Neutralization. If the objective is the formation of crystals of potassium phosphates, then the second step must be the reaction of the potassium catalyst (polymer bonded) with the phosphoric acid solution, neutralizing the polyol. An aqueous solution of phosphoric acid, containing antioxidant, was added in order to neutralize the polyol, forming initially a water−polyol emulsion. The addition of this solution at its boiling point, 105 °C, produced a decrease of the bulk temperature, initially at 120 °C. Therefore, the temperature was maintained at 110 °C for practical convenience in this step. Pressure was maintained at 800 mbar for 20 min to avoid polyol splashing due to the vigorous ebullition of the bulk. A stirring rate of 140 rpm was initially used.

Third Step: Dehydration. The rate of water removal must be slow enough to allow the growth of crystals; consequently, pressure was fixed at 750 mbar during this step. Temperature set point was set at 140 °C, bringing about a progressive temperature increment until the mentioned value was reached. Initially, a duration of 2 h for this step was proposed. Small aliquots (5−8 g) of the suspension were taken periodically, and water content was measured by the Karl Fischer method.

Fourth Step: High-Vacuum Dehydration. Finally, a high vacuum level (<5 mbar) was maintained for 1 h in order to reduce the final water content of polyol under specifications (0.1% or less).

Fifth Step: Filtration. Once the crystallization process had finished, the filtration process was carried out. The polyol retained in the filter cake was washed out using a saturated solution of KH_2PO_4 in *n*-butanol. Then the crystals were collected and suspended in a solution of *n*-butanol and ethylene glycol to measure crystal size distribution. A nonionic surfactant, Triton X-100, was used for dispersing particles.

The bottleneck of the process is the time employed in the filtration step, which is logically governed by the crystal size distribution. Thus, the main criterion to select the best operating conditions was the time employed for the filtration of the bulk mixture, expressed as the average mass flow, G_m (kg/(m^2 h)). The following time criteria were proposed, by comparison with the mean times required for the filtration in several industrial polyol processes:

$$\textit{fast filtration}: \quad G_m > 2750 \text{ kg/(m}^2\text{ h)}$$

$$\textit{medium filtration}: \quad 2750 > G_m > 525 \text{ kg/(m}^2\text{ h)}$$

$$\textit{slow filtration}: \quad G_m < 525 \text{ kg/(m}^2\text{ h)}$$

Results and Discussion

Preliminary Experiments. Three identical experiments were initially carried out using the experimental procedure and conditions described above. A suitable filtration time,

Table 2. **Summary of experimental conditions in the initial experimental procedure**[a]

	time (min)				
	0	20	40	160	220
step	monomer removal	neutralization	dehydration	high-vacuum dehydration	filtration
temperature set point (°C)	120	110	140	140	130
pressure (mbar)	7	800	750	<5	2450
stirring rate (rpm)	140	140	140	140	

[a] Molar ratio K^+/H_3PO_4, 1; mass ratio H_2O/polyol, 0.06.

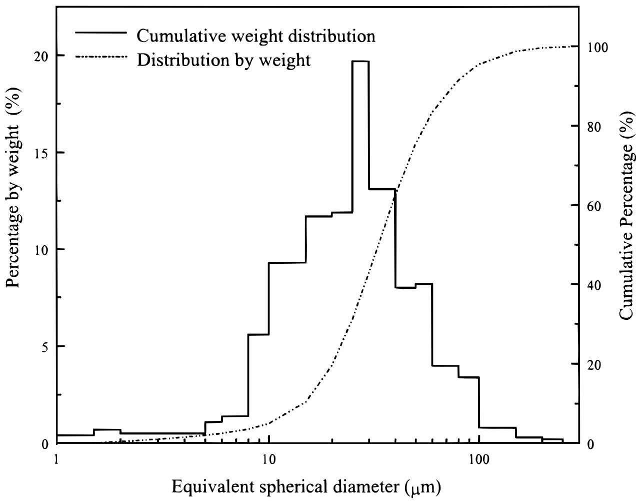

Figure 2. **Particle size distribution for the initial experimental procedure. Molar ratio K^+/H_3PO_4, 1; mass ratio H_2O/polyol, 0.06; stirring rate, 140 rpm; pressure (third step), 750 mbar.**

Table 3. **Influence of the stirring rate on the filtration process**[a]

stirring rate (rpm)	filtrability	concn H_2O (%)	concn K^+ (ppm)	acidity (mg of KOH/g)	color (deg Hazen)
100	fast	0.01	880		>70
120	fast	0.02	<2	0.077	40
140	medium	0.02	<2	0.067	35
160	slow	0.01	<2	0.050	30

[a] Molar ratio K^+/H_3PO_4, 1; mass ratio H_2O/polyol, 0.06; pressure (third step), 750 mbar.

about 20 min, with an average flow rate of 687 kg/(m^2 s) was reached. The final particle size distribution is shown in Figure 2. A mean particle diameter of 34 μm was obtained. The quality parameters of polyol complied with the commercial requirements and were basically the same for the three runs. The experimental data exhibited an acceptable repeatability.

Influence of Stirring Rate. To elucidate the optimal value for the agitation speed, several runs were carried out at different stirring rates between 100 and 160 rpm. No appreciable differences in CSD or filtration times were observed when the stirring rate was under 140 rpm, as shown in Table 3. Over 140 rpm, the stirring rate was too high, resulting in a smaller average size product. On the other hand, under 120 rpm, the contact between the immiscible phases was not good, and the neutralization of polyol was not achieved. Accordingly, the value of the final acidity obtained was meaningless. Another possible explanation for these poor results under 120 rpm is that, at very low stirring rates, a portion of the crystals formed did not remain in suspension and were abraded against the bottom of the vessel, favoring secondary nucleation and small average size product. Therefore, 120 rpm was selected as the agitation speed for the process. Taking into account the relationship between the power transmitted and the viscosity of the bulk for our stirring device, the corresponding value of power/unit volume applied is 0.0174 W/L.

Table 4. **Influence of the amount of phosphoric acid added for neutralization**[a]

molar ratio K^+/H_3PO_4	filtrability	concn H_2O (%)	concn K^+ (ppm)	acidity (mg of KOH/g)	color (deg Hazen)
3	medium	0.01	700		>70
2	medium	0.02	370		>70
1	fast	0.02	<2	0.077	40

[a] Mass ratio H_2O/polyol, 0.06; stirring rate, 120 rpm; pressure (third step), 750 mbar.

The oxidation of polyols is enhanced by both the presence of alkali metal alkoxides and the temperature. When the potassium extraction from the polyol phase is complete in the neutralization stage, the oxidation is avoided. Inadequate neutralization favors the oxidation reactions, and a dark polyol is obtained, as shown in Table 3 for 100 rpm.

Influence of the Amount of Neutralization Agent. Initially, the amount of phosphoric acid used was that stoichiometrically needed to form the potassium dihydrogen phosphate (molar ratio $K^+/H_3PO_4 = 1$). Therefore, the other two hydrogens of phosphoric acid could potentially be used for the neutralization. This could mean an important reduction of acid consumption.

Two runs were carried out using the stoichiometric amount of acid required to obtain K_2HPO_4 and K_3PO_4 salts; namely, a molar ratio K^+/H_3PO_4 of 2 and 3, respectively, was employed. The high final potassium levels in the filtered polyols obtained from these experiments (Table 4) show that only the first hydrogen of phosphoric acid is effective in the removal of potassium from polyols. Despite that, in these experiments the average flow rate was moderately high because the amount of crystals obtained was small, the major part of the potassium remaining unneutralized in the polyol phase. As in the previous case, incomplete neutralization leads to the oxidation of the product, and a dark polyol is obtained.

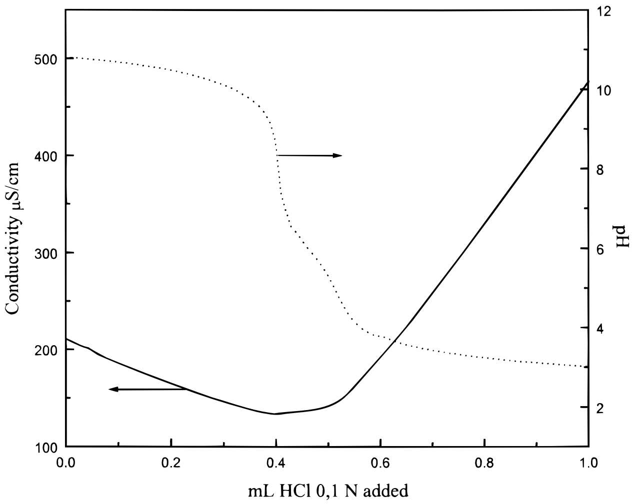

Figure 3. **Conductometric and potentiometric titration of crude polyol.**

As demonstrated by Lucas et al.,[7] potassium and polyol form an ionic pair, the polyol being in alkoxide form. The affinity of the alkoxide for the potassium is relatively high. Its behavior in a mixed aqueous−organic solution is quite similar to that of a relatively strong base, corroborating that this species is actually an alkoxide.

The basicity constants of potassium alkoxides were measured by conductometric and potentiometric titration with aqueous HCl, 0.1 N, to compare their values with the acidity constants of phosphoric acid. From the titration curve (Figure 3), it can be said that potassium alkoxide exhibits two acid−base constants. Based on the Henderson−Hasselbach theory,[8] the values of the basicity constants obtained for the polyol grade used in this work are $K_{b1} = 5.58 \times 10^{-3}$ and $K_{b2} = 6.46 \times 10^{-6}$.

Since the acid constants of phosphoric acid[9] are $K_{a1} = 7.52 \times 10^{-3}$, $K_{a2} = 6.23 \times 10^{-8}$, and $K_{a3} = 2.2 \times 10^{-13}$, it seems clear that only the first hydrogen of phosphoric acid exhibits enough acidity to displace the potassium of the alkoxide, forming only KH_2PO_4. X-ray diffraction (XRD) was used to verify that the crystal diffractogram agrees with that of high-purity KH_2PO_4.

Taking into account the previous findings, it can be stated that potassium is extracted from the polyol towards the dispersed aqueous phase, forming potassium dihydrogen phosphate, according to the following reaction:

$$R^-K^+(org) + H_3PO_4(aq) \leftrightharpoons RH(org) + KH_2PO_4(aq)$$

where R denotes the polyol chains and org and aq refer to the polyol and the aqueous phase, respectively. Later, the progressive removal of water produces the crystallization of the potassium salt.

Table 5. **Influence of the initial amount of water added for neutralization**[a]

mass ratio H_2O/ polyol	filtrability	final concn H_2O (%)	concn K^+ (ppm)	acidity (mequiv of KOH/g)	color (deg Hazen)
0.06	fast	0.02	<2	0.077	40
0.045	Fast	0.02	<2	0.065	40
0.03	fast	0.02	<2	0.050	40
0.01	slow	0.02	<2	0.066	35

[a] Molar ratio K^+/H_3PO_4, 1; stirring rate, 120 rpm; pressure (third step), 750 mbar.

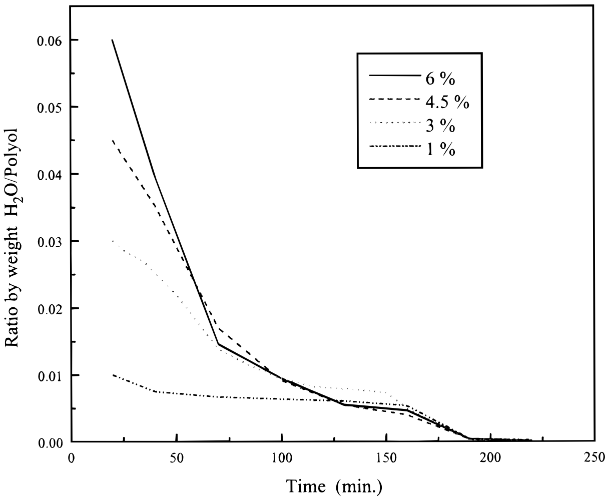

Figure 4. **Evolution of water content in the bulk during the crystallization process. Molar ratio K^+/H_3PO_4, 1; stirring rate, 120 rpm; pressure (third step), 750 mbar.**

Influence of the Water/Polyol Ratio. As indicated above, the evaporation rate of water will be the key problem, and the optimization of the water removal process will be the key factor to reach large crystals.

On the other hand, knowledge of the role that the water plays in the crystallization process is essential to explain the behavior of the system. The supersaturation degree in each stage and the water solubility in polyol will be the most influential factors.

Experiments employing different amounts of water in the neutralizing solution were done under essentially the same operating conditions. As expected, there is a critical value of water (3% with respect to polyol mass) under which the mean crystal size is too small for a suitable filtration process (Table 5). Therefore, 3% of water was selected as the suitable quantity for the rest of the experiments.

During these experiments aliquots of the bulk reaction were periodically taken off, and their water content was analyzed (Figure 4). Basically, two periods of time can be distinguished:

(i) Before 55 min, a dispersed phase of water can be observed, and crystals do not appear in either of the two phases.

(ii) At 55 min, the dispersed phase is removed, and incipient crystals can be observed at this point for the first time.

As shown in Figure 4, in those experiments using more than 3% of water, the curves obtained for different water concentrations, although different in their initial part, are

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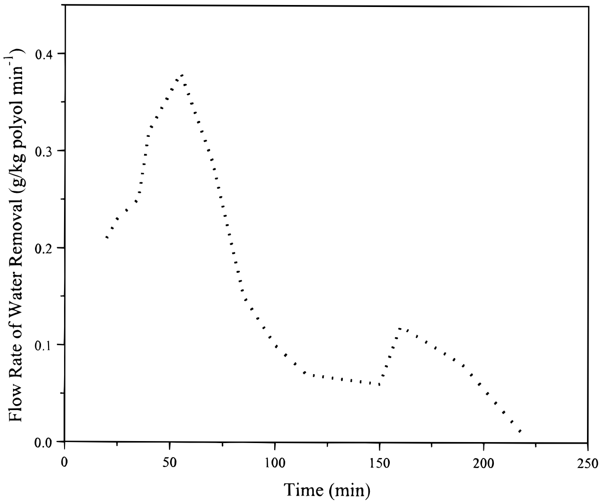

Figure 5. **Rate of water removal during the crystallization process. Molar ratio K^+/H_3PO_4, 1; mass ratio H_2O/polyol, 0.03; stirring rate, 120 rpm; pressure (third step), 750 mbar.**

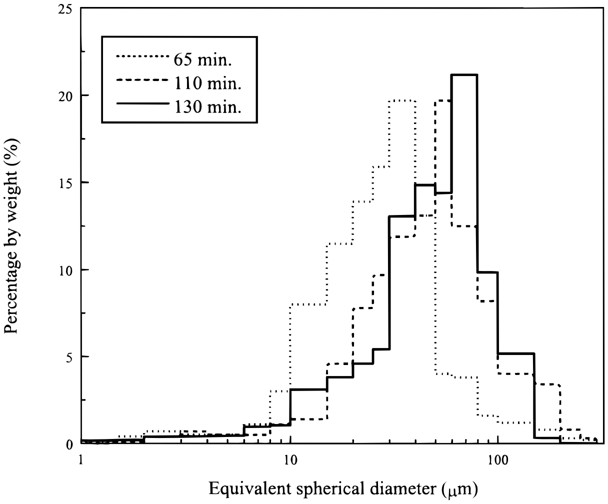

Figure 6. **CSD variation during the crystallization process. Molar ratio K^+/H_3PO_4, 1; mass ratio H_2O/polyol, 0.03; stirring rate, 120 rpm; pressure (third step), 750 mbar.**

basically coincident from 55 min. At that point, the level of water in the bulk decreases below the solubility value of water in polyol, about 1.5% at 120 °C, and the dispersed phase disappears. This can be seen as the water curves exhibit an inflexion point just at this point; namely, the rate at which water is removed from the bulk decreases markedly. Figure 5 shows the rate of water removal during the process for the mass ratio H_2O/polyol $= 0.03$. The curve exhibits a maximum value at 55 min and decreases sharply from this point. This fact indicates that, while the water of the dispersed phase is easily removed (under 55 min), the dissolved water ($<1.5\%$) is strongly linked to the polyol by hydrogen bonds, making difficult its elimination.

While the two phases exist, the aqueous phase contains the potassium salt due to its high solubility in water (51 wt %[10] at 100 °C). When the aqueous phase has been removed and a unique phase appears (a solution of water and KH_2PO_4 in polyol), the nucleation process starts. In this medium, the solubility of KH_2PO_4 might be very small, and therefore supersaturation is reached. Unfortunately, solubility values of KH_2PO_4 in polyol have not been reported in the literature, and therefore the supersaturation level could not be quantified.

As was mentioned in the Introduction, the use of seed crystals was discarded as a variable for this study. However, it is important to say at this point that the proper moment to introduce the seed crystal would be at 55 min. Before this time, the seed crystals would be dissolved in the aqueous phase, not exerting any appreciable influence on the process.

Absence of seed crystals always results in the spontaneous generation of nuclei, low growth rates, and small resultant CSD.[11] As water decreases slowly in that part of the process, the supersaturation is maintained, producing the growth of crystals until its final CSD is reached at about 130 min. Afterwards, changes in crystal size distribution are not observed, as shown in Figure 6. Water content of polyol is about 0.75% at this point.

A rough estimation of potassium dihydrogen phosphate crystals growth rate at 750 mbar was made by dividing the size of the largest crystal produced in the experiment by the time during which the growth occurs. By assuming that this particle was the fastest growing crystal in the batch, this simple calculation gives an estimate of the maximum growth rate that was attained in the batch crystallizer. For all the experiments, except for the run with 1% water, maximum growth rates ranged between 3.15 and 4.21×10^{-6} m/min. Note that these growth rates are of the same order of magnitude as those for crystal growth in aqueous media.[12]

Having selected the recipe for the neutralization process and a suitable operation mode, the main goal was to optimize the process conditions in order to reduce the dehydration time.

As commented above, no changes in particle size distribution are observed beyond 130 min. This means that the period of time necessary for the dehydration step can be reduced by half an hour, with the corresponding reduction of the total cycle time.

Influence of the Pressure during the Dehydration Step. To further investigate the effect of pressure during the dehydration, monopotassium phosphate crystals were grown under three different vacuum levels: 750, 700, and 650 mbar. As can be seen in Table 6, the filtration times increases as the pressure decreases. This fact indicates that a large amount of small nuclei are formed when the pressure vacuum is decreased; namely, the nucleation rate increases, resulting in the appearance of a large number of small crystals. Thus, 750 mbar was the pressure of choice for this step. A mean particle size of 71.65 μm with a quite uniform and narrow CSD was obtained using this operation procedure (Figure 6, 130 min).

Influence of Water Content on the Final Acidity of Polyol. Initially, 1 h was proposed for the high-vacuum step,

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Table 6. **Influence of vacuum degree during the dehydration stage on the filtration process[a]**

pressure (mbar)	filtrability	final concn H_2O (%)	concn K^+ (ppm)	acidity (mequiv of KOH/g)	color (deg Hazen)
750	fast	0.02	<2	0.050	40
700	medium	0.02	<2	0.053	40
650	slow	0.02	<2	0.030	40

[a] Molar ratio K^+/H_3PO_4, 1; mass ratio H_2O/polyol, 0.03; stirring rate, 120 rpm.

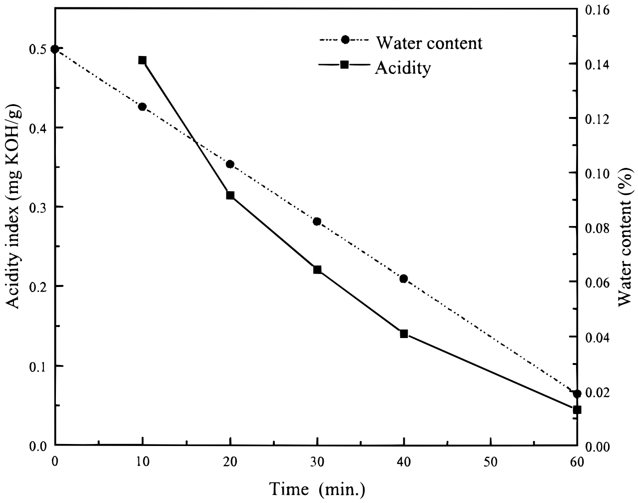

Figure 7. **Acidity index and water content profiles during the fourth step of the crystallization process (zero in time scale corresponds to the beginning of the stage). Molar ratio K^+/H_3PO_4, 1; mass ratio H_2O/polyol, 0.03; stirring rate, 120 rpm; pressure (third step), 750 mbar.**

reaching final water contents in the filtrated polyol under 0.02% in such a period of time. As the water specification must be under 0.1%, the time needed for this stage could be reduced. However, the water dissolved in the polyol allows the solubilization of a certain amount of KH_2PO_4, increasing the acidity of the polyol. Figure 7 shows the water content and acidity profiles during the high-vacuum step. As water content decreases, so does acidity, demonstrating that the water dissolved in the polyol enhances the solubility of monopotassium phosphate in this medium. At least 50 min is required in order to reach an acidity level under 0.1 mequiv of KOH/g. Obviously, a value far from the specification would be preferred for the industrial production, and at least 1 h must be taken for this stage. The final pressure and temperature profiles of the whole process are shown in Figure 8.

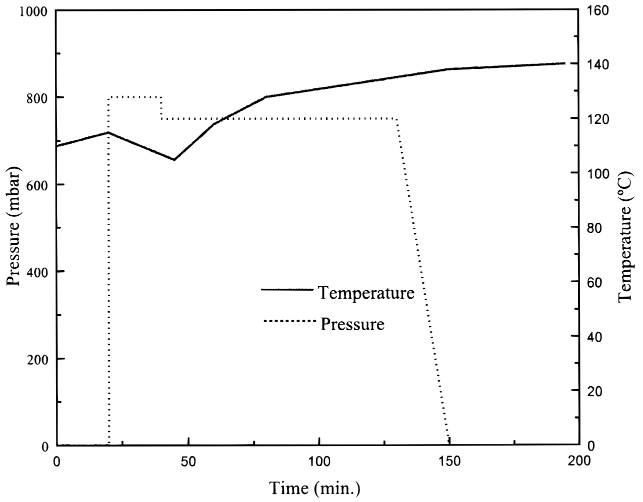

Figure 8. **Pressure and temperature profiles in the optimized experimental procedure. Molar ratio K^+/H_3PO_4, 1; mass ratio H_2O/polyol, 0.03; stirring rate, 120 rpm; pressure (third step), 750 mbar.**

Three batches of polyol were purified in the industrial plant using the method developed in this work. When the conditions of pressure and temperature, which could be controlled only roughly, were similar to those proposed, the filtration time for the batch was lower than the mean filtration time in the present process.

Conclusions

A crystallization method to purify polyether−polyol using phosphoric acid as neutralizing agent has been developed. A power per unit of volume of polyol of 0.0175 W/L is required for appropriate agitation of the bulk.

Only the first hydrogen of phosphoric acid is effective in the removal of potassium from polyols, forming KH_2PO_4. At least 3% of water with respect to the polyol mass is required in order to obtain crystals large enough to permit appropriate filtration rates.

Final acidity of polyols is directly related to the water content. A final content of water under 0.04% must be reached in order to obtain a polyol suitable for sale.

This crystallization process is very sensitive to any change in the operation conditions. Consequently, very accurate control of all the parameters related to the process will be necessary.

Acknowledgment

This investigation was supported by REPSOL QUIMICA S.A. through the Foundation for the Collaboration of University and Enterprise (FUE C-1170/90).

Received for review September 14, 1998.

OP980072Z