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Characterization of Reillex™ HPQ Polymer

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Characterization of Reillex™ HPQ Polymer

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CHARACTERIZATION OF REILLEX™ HPQ POLYMER

By D. D. Walker, J. W. Congdon, and J. E. Young

SUMMARY

This work examined the thermal stability of Reillex™ HPQ resin as part of a comprehensive plan to qualify that material for use in HB-line. No low temperature (<100 °C) exothermic reactions or volatile organic compounds occurred in various lots of as-received, chloride form Reillex™ HPQ polymer or the nitrate form polymer. The studies do not suggest any restrictions on purchase criteria for the resin nor any changes in planned use. Previously observed low temperature exotherms resulted from reaction of nitric acid with the aluminum sample holders used in the Differential Scanning Calorimetry (DSC) analysis.

INTRODUCTION

At the Savannah River Site, HB-Line uses columns loaded with ion exchange resin to extract and purify Pu and Np from acidic process streams. Several resins, including Dowex™ MSA-1, Dowex 21K, and Ionac A-641, have been used in this application at the Savannah River Site. Los Alamos National Laboratory tested and uses a new resin, Reillex™ HPQ polymer in small Pu-separation columns.[1-2] HB-Line Engineering proposes to switch to the new resin because of its availability, but the new resin also is more stable toward radiation and nitric acid. HB-Line Engineering and H-Area Technical Support personnel requested the Savannah River Technology Center qualify the Reillex™ HPQ polymer for use in HB-Line operations.

This report addresses thermal stability of the vendor supplied resin. The resin exhibited low temperature exotherms in the Differential Scanning Calorimetry (DSC) analysis during an investigation by M. L. Hyder in 1996. Researchers postulated that the exotherms may have resulted from reaction of nitric acid with solvent impurities remaining from manufacturing the resin. If true, a purchase specification on the solvent content of the resin might prove necessary to avoid the reaction during process operations. Although the previous work by Hyder was not documented, the authors located some of the earlier samples and analyzed them by DSC. The results were compared to similar analyses of recent samples of resin. In addition, portions of resin were submitted for Volatile Organics Analysis (VOA) by SRTC Analytical Development Section to identify any manufacturing solvents present.

This work fulfills a request from R. A. Vohden, "Qualification of Resin for use in HB-Line Phase II," Technical Task Request #TTR-97-NMPD/SEM-0081, March 23, 1998. The work complies with the following plan: B. W. Walker, "Technical Task Plan for HB-Line Resin Qualification," WSRC-RP-98-00551, Rev.0, March 17, 1998.

SAMPLES AND SAMPLE PREPARATION

Table I lists the samples of Reillex™ HPQ polymer analyzed for this program. The first sample listed was originally obtained in the chloride form from Reilly Industries by E. A. Kyser in 1989. During testing at SRTC, the entire batch was converted to the nitrate form. Sample 2 was from a second batch of chloride form resin obtained in 1995. Sample 3 was a free, 100 gram sample of chloride form Reillex™ HPQ polymer given to D. D. Walker by Reillex Industries in March 1998. Sample 4 was from the 50 kg drum purchased by W. R. Wilmarth in May 1998. This large batch is intended for HB-Line testing following conversion to the nitrate form. Samples 5 and 6 were remainders of samples analyzed by M. L. Hyder in 1996 that reportedly showed low temperature exotherms. Hyder obtained the resin from Kyser and thus Samples 5 and 6 presumably derive from the same source as Sample 1 or 2. No records other than the labels on the sample vials were available for the Hyder samples. Hyder investigated effects of irradiation on the resin, including the effect of cerium(IV) loading. Scanning electron microscopy (SEM) analysis of the two samples indicated Sample 5 contained cerium but Sample 6 did not. Neither sample contained chlorine.

Chloride form resins (~2 mL) were converted to the nitrate form by passing 8 M nitric acid (60 mL) followed by water (6 mL) through the resin in a glass column (1 cm diameter with fritted glass disk at bottom). Excess liquid was removed by blotting with filter paper. Resin samples were analyzed by DSC after drying at room temperature for several hours. Water content of the samples was not measured.

TABLE 1. Reillex™ HPQ Polymer Sample Origins

Sample	Lot #	Label Information or Origin
1	N/A*	"Reillex™ HPQ, old lot converted in 0.35 M HNO_3" (Sample obtained from E. A. Kyser, purchased 1989.)
2	50224AE	Chloride form (Sample obtained from E. A. Kyser, purchased 1995.)
3	80219MA	Chloride form (100 g sample obtained from Reilly Industries in March 1998.)
4	80302MA	Chloride form (50 kg drum, purchased by W. R. Wilmarth, from Reilly Industries in May 1998, drum dated 5/21/98.)
5	N/A*	Sample obtained from M. L. Hyder, contained Ce but not Cl, label reads "Reillex™ HPQ, 5/6/96"
6	N/A*	Sample obtained from M. L. Hyder, no Ce or Cl, label reads "Reillex™ HPQ, contacted with 8 M HNO_3"

*N/A = not available

ANALYTICAL METHODS

Resin samples, both chloride and nitrate forms, were analyzed by DSC. In addition, chloride form resins received from the vendor were analyzed for volatile organic compounds by gas chromatographic and mass spectral methods (GCMS).

For DSC analysis, approximately 5 mg of resin were placed in either an aluminum or gold sample pan. The sample temperature was increased at 10 °C/min from room temperature to 200 or 250 °C under a static air atmosphere in a TA Instruments (previously DuPont Instruments) Model 910 Differential Scanning Calorimeter.

Volatile organic analyses were performed by GCMS using a modification of the ADS method 2656 (Contract Laboratory Program SOW 7-93 for Volatile Organics). Samples were concentrated using an OI Analytical Model 4560A Dynamic Headspace concentrator (purge and trap), using a Corboxen 100™ microtrap. Volatile components were separated with a Hewlett Packard 5890 Series II gas chromatograph using a 60m x 0.75 mm VOCOL™ fused silica capillary column with 1 μm film thickness. The volatile components were identified using a Hewlett Packard Model 5970 quadrupole mass spectrometer.

RESULTS and DISCUSSION

Thermal Analyses

Table II lists the DSC analysis results for the chloride and nitrate forms of the samples in Table 1. Figures 1 through 4 provide the DSC traces.

None of the three batches of chloride form resin obtained from Reilly Industries (Table I, Samples 2, 3, and 4) show low temperature (<125 °C) exotherms (Figure 1) when measured in aluminum sample pans. Beginning at room temperature and continuing to 80-90 °C, the chloride form resins show an endotherm caused by evaporation of water from the damp samples. A small exotherm at approximately 170 °C occurred in two of the three samples.

The nitrate form resin samples converted with 8 M nitric acid show low temperature exotherms (<125 °C) superimposed on the water-evaporation endotherm (Figure 2, and Sample 6 in Figure 4) when measured in aluminum sample pans. When the DSC was repeated in gold sample pans, no low temperature exotherms occurred (Figure 2, and Sample 6 in Figure 4). The effect of pan metal on the response also occurred with 8 M nitric acid without resin. Nitric acid showed three low temperature exotherms between 80 and 120 °C when measured in aluminum pans but not in gold pans (Figure 2). This result suggests that the exotherms result from a reaction of nitric acid with the aluminum pans and not a reaction due to the resin. However, the nitrate form resins show exotherms at higher temperatures (150 and 200 °C) when measured in gold pans.

TABLE II. Summary of DSC Analyses

Sample*	Sample Form	Pan**	Results
1	Nitrate (0.35 M HNO_3)	Al	no exotherm below 150 °C; exotherm at 170 °C
		Au	no exotherms
2	Chloride	Al	no exotherms
2	Nitrate (8M HNO_3)	Al	strong exotherm at 85 °C
3	Chloride	Al	no exotherms
3	Nitrate (8 M HNO_3)	Al	strong exotherm at 85 °C
		Au	no exotherm below 125 °C; small exotherms at 150 and 200 °C
4	Chloride	Au	no exotherm below 240 °C
4	Nitrate (8M HNO_3)	Au	no exotherm below 125 °C; exotherms at 150 and 200 °C
5	Nitrate (with Ce)	Al	minor exotherms at 80 and 100 °C
		Au	exotherm at 85 °C
6	Nitrate (8M HNO_3)	Al	strong exotherm at 90 °C
		Au	no exotherm
	8 M HNO_3 solution	Al	exotherms at 80, 90, and 100 °C
		Au	no exotherms

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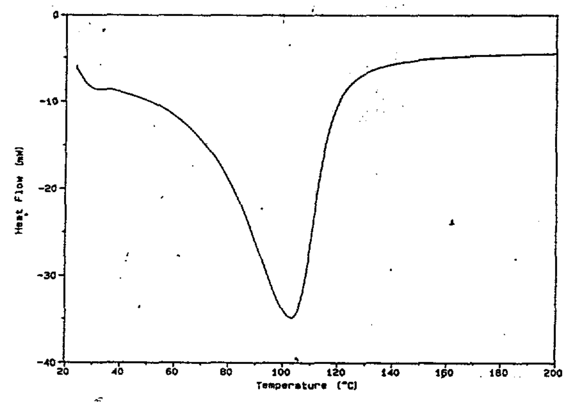
*See Table I for sample descriptions.

** Material of construction of the DSC sample holder.

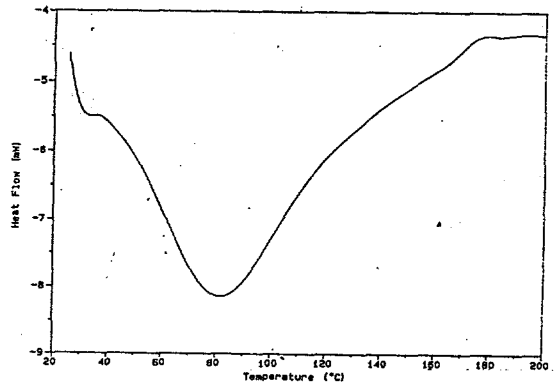
FIGURE 1. DSC Traces for Reillex™ HPQ Polymer Samples (chloride form)

Note: Scales of axes differ in graphs. Use caution when comparing samples.

**Sample 2 (Table I)
chloride form
Lot #50224AE**



**Sample 3 (Table I)
chloride form
Lot #80219MA**



**Sample 4 (Table I)
chloride form
Lot #80302MA**

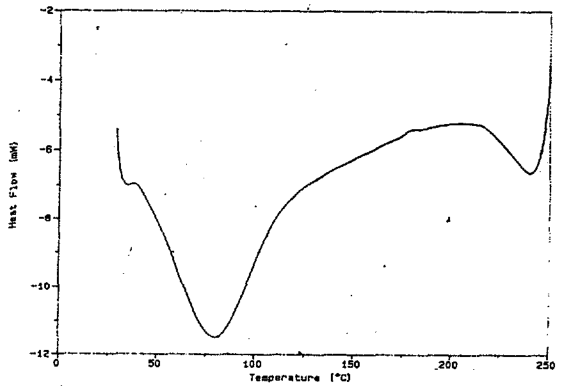
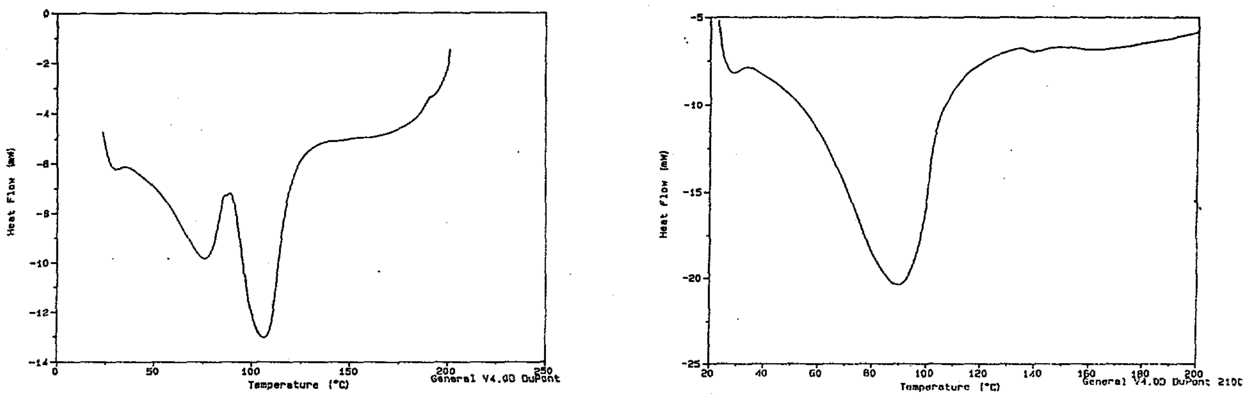


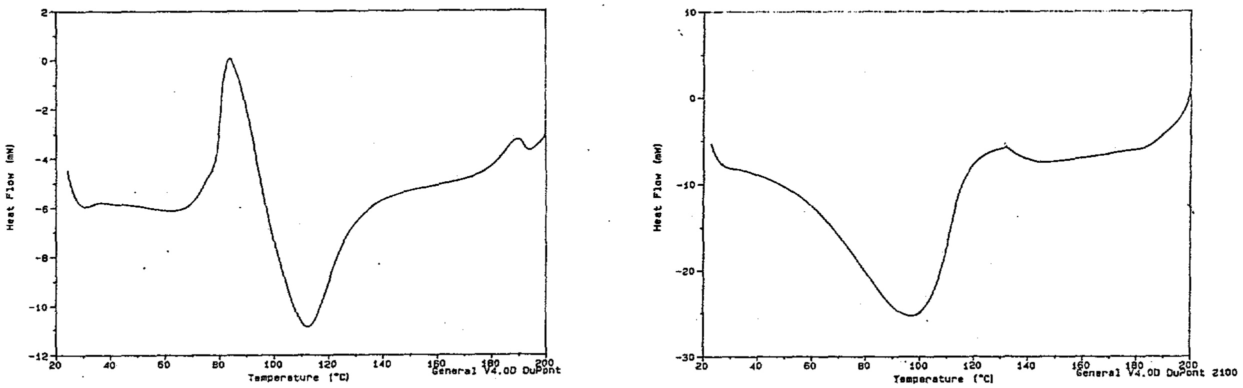
FIGURE 2. DSC Traces for Nitrate Form Reillex™ HPQ Polymer Samples and 8 M Nitric Acid

Note: Scales of axes differ in graphs. Use caution when comparing samples.

Sample 1 (Table I) treated with 8 M HNO_3


Aluminum pan
Gold pan

Sample 2 (Lot #50224AE) converted with 8 M HNO_3


Aluminum pan
Gold pan

Sample 3 (Lot #80219MA) converted with 8 M HNO_3

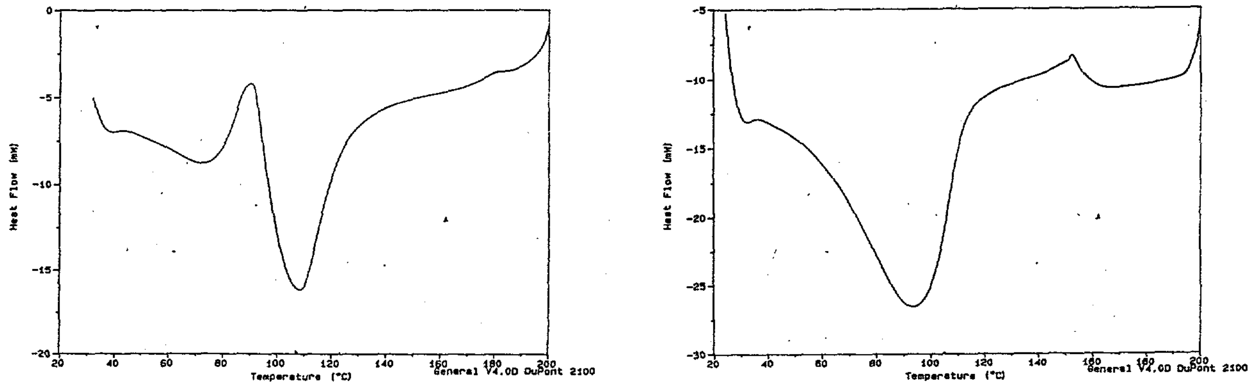
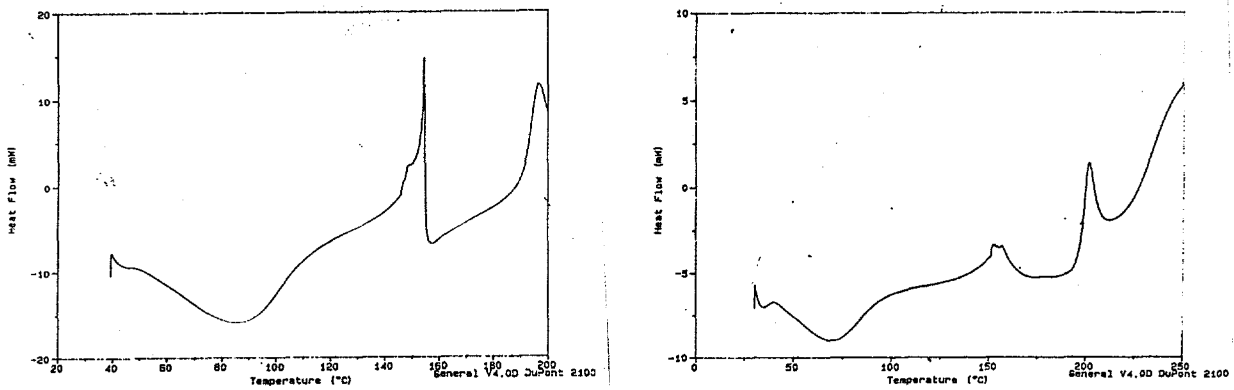

Aluminum pan
Gold pan

FIGURE 2. DSC Traces for Nitrate Form Reillex™ HPQ Polymer Samples and 8 M Nitric Acid (continued)

Note: Scales of axes differ in graphs. Use caution when comparing samples.

Sample 4 (Lot 80302MA) converted with 8 M HNO_3

Aluminum pan **Gold pan**



8 M Nitric Acid (no resin)

Aluminum pan **Gold pan**

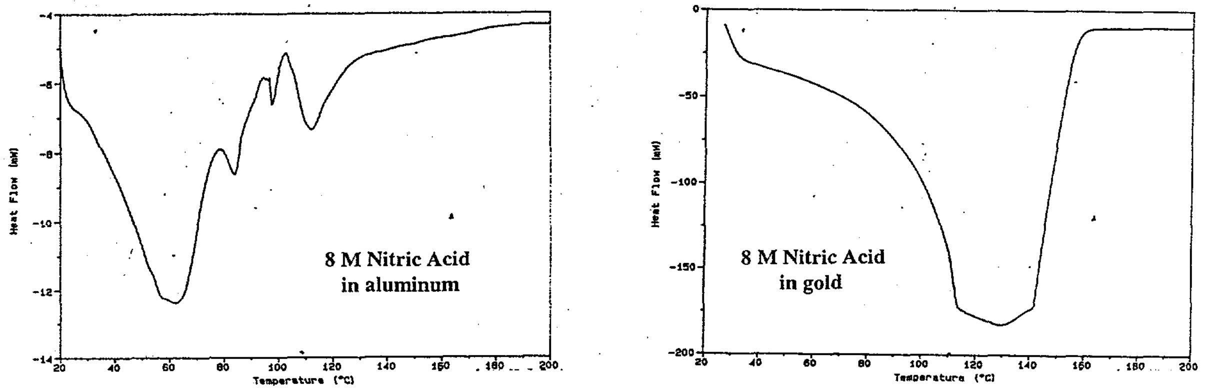
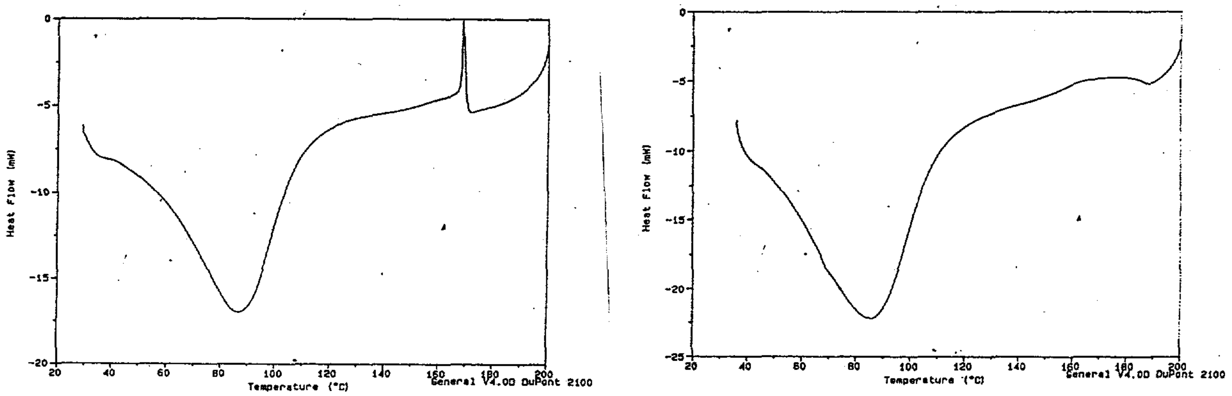


FIGURE 3. DSC Traces for Sample 1 (Table 1), Reillex™ HPQ Polymer Converted to Nitrate Form with 0.35 M Nitric Acid

Note: Scales of axes differ in graphs. Use caution when comparing samples.

Aluminum pan **Gold pan**



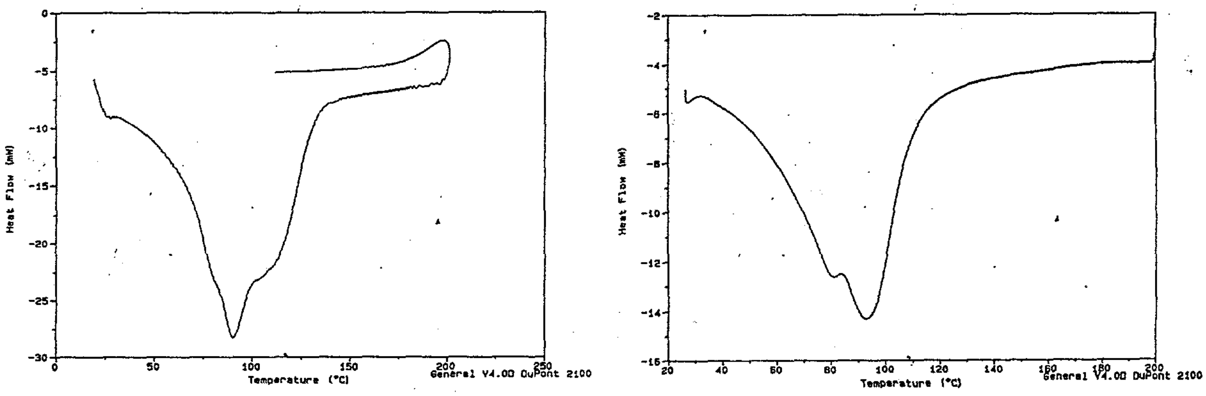
The low temperature exotherms appear to depend on the acid concentration. A low temperature exotherm was not present in Sample 1 (Table I) converted with 0.35 M nitric acid (Figure 3).

Repeat analyses on two samples from M. L. Hyder confirmed the low temperature exotherms previously reported (Figure 4). Sample 6 ("Reillex™ HPQ contacted with 8 M HNO_3") showed strong exotherms when measured in aluminum and no exotherm when measured in gold pans. However, Sample 5 ("Reillex™ HPQ, 5/6/96") showed small, low temperature exotherms in both aluminum and gold pans. The color of Samples 5 and 6 samples did not match the color of any of the other four resin batches in either chloride or nitrate forms. The original resin batches were off-white or tan, whereas Samples 5 and 6 were yellow (Sample 6, "Reillex™ HPQ contacted with 8 M HNO_3") or orange-yellow (Sample 5, "Reillex™ HPQ, 5/6/96"). In addition, Sample 5 contained cerium. Hyder investigated the affect of radiation and his samples in vials used for irradiations showed colors ranging from yellow to orange. The difference in thermal stability of Sample 5 is likely due to additional treatment steps involving cerium and probably Co-60 gamma radiation.

FIGURE 4. DSC Scans of Samples 5 and 6 (Table 1)

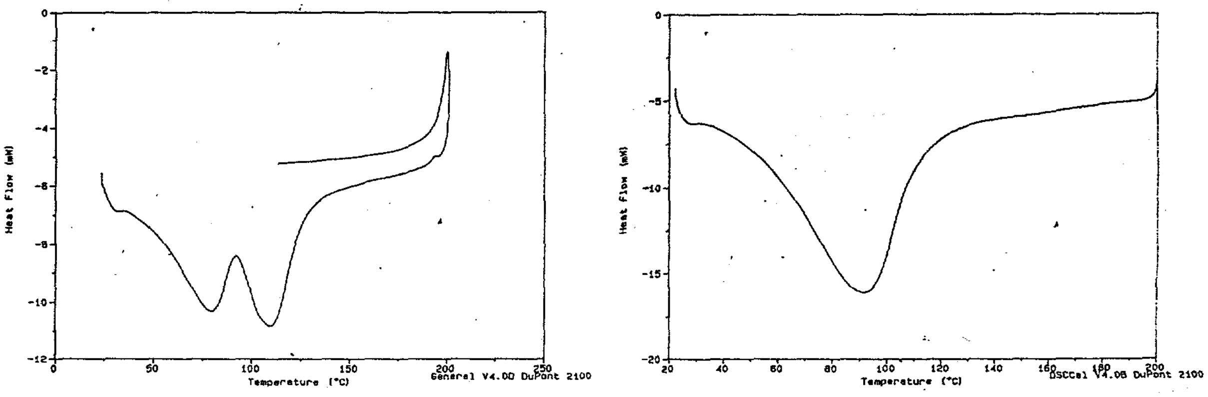
Note: Scales of axes differ in graphs. Use caution when comparing samples.

Sample 5 "Reillex™ HPQ, 5/6/96"



Aluminum pan **Gold pan**

Sample 6 "Reillex™ HPQ contacted with 8 M HNO_3"



Aluminum pan **Gold pan**

Volatile Organics Analyses

Samples of two batches of the chloride form resin were analyzed for volatile organic compounds. Table III summarizes the results. Methanol was the major volatile organic in the large batch of resin destined for use in HB-Line (Sample 4). The vendor indicated that methanol is used as a solvent in the preparation of the resin. The concentration of methanol is low (<0.1 wt %) and converting the resin to the nitrate form will likely remove some of the methanol. The other organic compounds found in these analyses occur at levels that do not pose a concern. Their concentrations are so low that their presence may result from exposure of the samples to laboratory air and containers or to chlorination of process water used in resin manufacture.

TABLE III. Summary of Volatile Organic Analyses

Sample*		Compound	Concentration (mg/kg of sample)
3	Chloride form resin, air dried	acetone	0.23
		chloroform	0.025
		2-butanone	0.022
		toluene	0.021
4	Chloride form resin, wet	methanol	870.
		chloroform	0.0021
		toluene	0.00082
		pyridine derivative**	0.00066
		bromodichloromethane	0.00054
		o-xylene	0.00047
		m-xylene	0.00046
		methylethylbenzene or propylbenzene	0.00023
		2-hexanone or 4-methyl-2-pentanone	0.00012
		p-xylene	0.00006

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* See Table I for additional sample information.

**Based on mass spectrum similarity to 4-pyridinamine.

RECOMMENDATIONS

The previously reported low temperature exotherms (<125 °C) were artifacts of the analytical procedure or presence of cerium and are not a characteristic of Reillex™ HPQ polymer as received from the manufacturer or from conversion to the nitrate form. No purchase specification is needed to address the potential for low temperature exothermic reactions. However, the small, low temperature (~80 °C) exotherms observed in the presence of Ce(IV) suggest that further testing of loaded resin is warranted.

The manufacturer synthesizes the resin using methanol as a solvent and a sample obtained from the vendor contained 0.087 wt % methanol in the wet resin. Conversion to the nitrate form will likely remove much of the residual methanol. We recommend establishing an appropriate limit on the methanol content of resin used in HB-Line to avoid flammable vapor mixtures, product or waste stream contamination, and reaction with nitric acid. This limit could be imposed on purchases of chloride form resin from the manufacturer or on the chloride-to-nitrate conversion step.

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