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Subject: RECOVERY OF PERFLUOROCTANOIC ACID (FC-26)  
BOTTOMS (FZ-155)

Date: SEPTEMBER 4, 1981

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**I. INTRODUCTION:**

A method for recovery of perfluorooctanoic acid from Antwerp distillation bottoms is described. The procedure involves a single one-plate distillation to obtain a main cut. This material is stabilized, followed by a fractional distillation, resulting in overall yields of 52% and 95% purity C<sub>7</sub>F<sub>15</sub>COOH. Adaptation of this processing sequence to production is expected to be straightforward, as there is much experience with fluorochemical acids. Economics on this recovery project should be significant, since the bottoms have been of no value up to now.

**II. RESULTS AND CONCLUSIONS:**

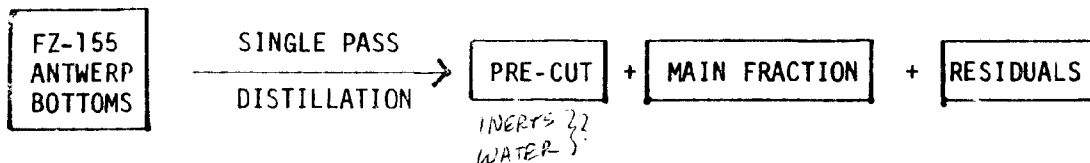
- A) A one-plate distillation of the "Antwerp bottoms" efficiently yields a main cut (67%) from the metal contaminated pot residues. A 20% pre-cut is discarded. *? WHAT'S IN PRECUT*
- B) An ammonium hydroxide and sulfuric acid cycle is effective in stabilizing the main cut.
- C) Fractional distillation in the lab, using a Vigreux column, yields an 80% main fraction as C<sub>8</sub> acid. A 1% pre-cut is not saved.
- D) Direct fractionation of the "Antwerp bottoms" gives C<sub>8</sub> acid of unacceptable purity. A second fractionation offers no improvement. A stabilization step is needed.
- E) This three step lab process gives 52% overall yield of perfluorooctanoic acid with APS values of <0.2% and 95% purity.
- F) Based on the recovery rate in "E", there is a potential for reclaiming \$300,000 of C<sub>8</sub> acid from "no-value" bottoms.
- G) All lab work was done using FZ-155 lot 2301 sampled from drum 26.
- H) Scale-up was demonstrated at the Gemolite pilot plant.



### III. EXPERIMENTAL AND DISCUSSION:

#### A) Distillation

The first of a three step sequence to recover C<sub>8</sub> acid from Antwerp distillation bottoms (FZ-155) is described below.



#### 1. FZ-155 Starting Material

GLC analysis shows 88% as C<sub>8</sub> acid.  
Dark greenish black in color.  
Contaminated with metal ions.

#### 2. Results

Out of 400g of bottoms, 20% by weight is collected as a pre-cut and 67% as the main fraction with the remaining weight (~13%) as residuals.  
Analytical on Main Cut:

APS Consumption: >0.3%  
Equivalent Weight: 423.3 (expect 414 ± 5)  
GLC - 91% as C<sub>8</sub> acid

#### 3. Procedure

A 500 ml round bottom flask is equipped with a stirrer, Therm-o-watch and a single pass take-off condenser. The first fraction (pre-cut) is collected at 25 inches (water aspirator vacuum) and a head temperature of 45-50°C, with the pot temperature taken to 110°C. Some batch foaming is observed, but not excessive, if the pressure is reduced in a careful manner. For the main cut the apparatus is rearranged to accommodate a manifold and vacuum pump. A 16 inch Vigreux column is used to collect the main-fraction at 10 mm pressure and a head temperature of 85-90°C. The pot temperature is taken up to 130°C before terminating the distillation.

#### 4. Discussion

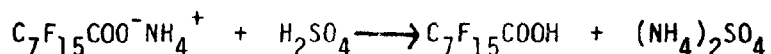
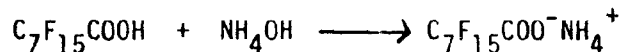
The purpose of this first step is to separate the main-fraction from the pot residues of metal contaminated "high boilers" and the pre-cut "lower boilers." The pre-cut consists mainly of water and inerts, but with enough lower homologs of the fluoro-acid to probably cause a surface effect. This could explain the foaming problem observed during the pre-cut. However, in the lab, this problem is minimized by using a single pass take-off condenser instead of the Vigreux column. A nitrogen sweep is helpful.

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Later lab work, in conjunction with pilot plant work, showed that a single pass take-off condenser could be used to separate the pre-cut and main fraction without using a Vigreux column at all. Results were similar. The temperature and pressure differentials are sufficient for separating the two fractions (pre-cut and main cut) in a facile manner, allowing simpler equipment to be adaptable. This is especially important on scale-up.

#### B) Base-Acid Cycle (Stabilization)

The main fraction from the first distillation step was treated, as follows:



##### 1. Charges

	<u>Mol. Wt.</u>	<u>Moles</u>	<u>Wt.</u>
Main Fraction of C <sub>8</sub> Acid (assume 100% C <sub>8</sub> Acid)	414	0.25	103.5g
Water			103.5
Ammonium Hydroxide (28% as NH <sub>3</sub> )	17	0.30	18.2
Sulfuric Acid	98	0.50	49.0

##### 2. Results

Material balance was quantitative. No analytical work was done on this step.

##### 3. Procedure

In a 500ml round bottom flask fitted with a stirrer, Therm-o-watch, and an addition funnel is placed the pre-melted charge of the main fraction of the C<sub>8</sub> acid. Next, the water charge is added. With no heat applied, ammonium hydroxide is charged using the addition funnel. An exotherm to 45°C is noted. The mixture is stirred at 45°C for 2 hours. Some foaming occurs. With the heat off, sulfuric acid is added dropwise over 15 minutes. The reaction is allowed to exotherm to 55°C. This temperature is maintained for 2 hours with stirring. The contents are transferred to a separating funnel and there is a clear sharp separation as long as the temperature is 55°C. The bottom product phase is taken to the next step.

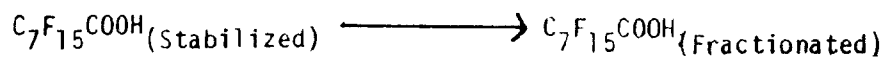
##### 4. Discussion

Attempts to take the main cut from "A" and fractionally distill it again gave unacceptable material. A base-acid cycle step (stabilization) is needed.

Early work on this project by G.R. Shirey showed that collection of all distillable material followed by stabilization and fractionation resulted in poor quality product.

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This base-acid cycle procedure is essential for removing color contributing impurities.

C) Fractionation



<u>1. Charges</u>	<u>Wt.</u>	<u>Mol. Wt.</u>
Stabilized C <sub>8</sub> Acid	~104g	414

2. Results

85g collected for an 82% recovery  
GLC showed 95% C<sub>8</sub>  
Equivalent weight conformed.  
APS consumption: 0.1 to 0.2% (FC-126 spec. is >0.2%  
FC-143 spec. is <0.2%)

3. Procedure

The same equipment and conditions described in the distillation (part A above) with the Vigreux column, is used for this step. A pre-cut of about 1% is discarded.

4. Discussion

Although the Vigreux column is appreciably less efficient for a given length than the packed column, it has the advantage of less hold-up and pressure drop. Further, Vigreux has a relatively large cross-section for vapor flow; hence, it is particularly suited for high temperature and low pressure distillations. A bubble-cap column is not a good choice because of difficulties distilling a material that solidifies (m.p. ~40°C). Freezing and plugging of the lower sections invariably occurs, if not well insulated. The high heat input needed to prevent this could cause product degradation and severe flooding when the plug melts. The Vigreux was selected as the best choice for demonstrating this process in the lab.

D) Overall Yields

An overall yield through the 3 process steps calculated to be about 52% by weight. This is based on:

1st step distillation - 67% main cut  
2nd step stabilization - assume 100%  
3rd step fractionation - 82% product @ 95% purity

E) References

1. J.W. Eberlin Technical Notebook: 56462 - 7,8,31,32,53,54,55  
57330 - 29,33
2. G.R. Shirey Technical Notebook: 54852 - 20

#### IV. CHEMOLITE PILOT PLANT WORK

##### A) Process Work

Pilot plant work by A.M. Fisch is independently documented in a report to D.M. Sanderson, dated 8/31/81, and titled Antwerp Still Bottoms.

The three step process were assigned the following F-numbers:

F-6737 - Single-Pass Distillation

F-6738 - Stabilization

F-6739 - Fractional Distillation

##### B) Concurrent CCD Lab Work

The following work in our lab was done in conjunction with the pilot plant program. With completion of the single-pass distillation (F-6737), a retain sample was stabilized, and then fractionated following the procedures described in this report. The overall yield was 50% with 77% across the fractionation step. As determined by CCD Analytical, an APS consumption value of "zero" was obtained. The CRDPP stabilization (F-6738) was completed and a retain sample was fractionated in our lab. The lab yield was 73% for this last step, slightly low. The APS value was >0.25%.

#### V. ECONOMICS

The unofficial cost savings for recovery of prefluorooctanoic acid from Antwerp distillation bottoms (FZ-155) is estimated on a conservative basis. About 20,000 lbs. of FZ-155 is available at "zero-value." As shown in this report, at least 50% can be recovered as useable product. Antwerp acid (FMZ-3256) is valued at about \$30 per lb. for these calculations. Based on this, about \$300,000 worth of C<sub>8</sub> acid (FC-26) can be reclaimed.

#### VI. FUTURE WORK

- A) It is recommended that this process be taken directly to production, based on lab and pilot plant work. There is much plant experience with fluoro-chemical acid distillations and the proper equipment is available.
- B) A decision would be needed for which direction to route the fractionated acid i.e. FC-26, FC-126 or FC-143. No product would be lost and the APS quality would determine use.

*J. W. Eberlin*  
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