3. Measurement of Residual C-8 Fluorosurfactant Levels on Various Products - C. S. COPE

Following the report from 3M Company that "Fluorad" FC-143 (C-8 APFC) surfactant had been found teratogenic in tests with laboratory animals, we received several company requests for analytical determination of residual C-8 concentrations in various [redacted] products. Included were two types of [redacted] felt produced by F&F Department's Fairfield, Conn., plant, a sample of [redacted] glass cloth manufactured by [redacted] (submitted by R. J. Cavanaugh of Research), and two samples of TE-9724-J [redacted] PFA baked powder (prior to extrusion) manufactured at [redacted] (analysis requested by P. Thistleton of the Technical Department).

[redacted] As a reference point concerning residual levels of C-8 APFC on our products, it may be noted that the Customary Advisory Letter issued to our customers on 4-1-81 by the Sales Division stated: "With the exception of aqueous dispersions, there is no significant residual FC-143 in any of the fluoropolymer resins which we sell." This statement is not inconsistent with the fact that very low levels, of the order of 1-5 ppm, of residual C-8 APFC have been detected (using a method which is not specific for C-8) in the past on [redacted] fine powders and granular resins, the main products we sell in dry, bulk form in the unextruded condition. (Extruded resins should contain even lower levels of residual C-8.)

Analyses of all these samples were performed by boiling the samples in a dilute aqueous solution of phosphoric acid in the presence of a nonvolatile, nonionic detergent ("Triton" X-100). Perfluorocaprylic acid is sufficiently volatile at 100°C that it steam-distills off under these conditions. The C-8 in the distillate is then analyzed by the chloroform/Azure A (a blue dye) colorimetric method, sensitive to about 2-3 micrograms. The method is nonspecific for C-8, and other ionic surfactants can, in principle, interfere.

In no case among the recent samples was a residual C-8 concentration above the range typically found on [redacted] fine powder detected. For the F&F felt samples, values of 3.5 ppm (unbleached felt XT-7700) and 0.7 ppm (bleached felt XT-7800) were obtained. For the [redacted] fabric, we found 0.35 ppm (equivalent to 3.95 ppm based on [redacted] solids present). For the TE-9724-J samples, concentrations of 2.8 and 1.0 ppm were found. Results have been transmitted in writing to those who requested the analyses.

The most recent analyses of residual C-8 APFC on fine powder were obtained in March on a set of three samples of [redacted] 64 submitted by E. H. Stueber of the Technical Department. Two of these samples were from lots which had performed poorly in wire-coating at [redacted] while the third was a control which performed normally. Technical's request for C-8 analyses was prompted by a desire to test, in the absence of any clear-cut distinctions in the normal characterization data, whether possible differences in residual C-8 level might account for the differences in fabrication behavior. The two unsatisfactory lots, with residual C-8 levels of 4.2 and 2.5 ppm, were found to be somewhat above the control (1.5 ppm) in this respect, but by no means enough so to be considered unusual. Furthermore, tests done years ago showed that

the paste extrusion performance of fine powder was not significantly affected either by removing the last traces of residual dispersing agent (by extraction with a solvent) or by depositing dispersing agent back onto the dry polymer (by deposition from solution, followed by evaporation of the solvent) to the (relatively high) level present on the polymer before drying. We were, therefore, unable to encourage Technical that the differences in wire-coating performance were likely to stem from this source.

Samples of the three [redacted]64 fine powder lots have been submitted to ESL for confirmatory analyses using the GC method developed there which is specific for C-8.

4. C-8 Fluorosurfactant Analyses on Samples Received from the FEP Area - C. S. COPE

Requests were received from Technical Department personnel in the FEP Area for C-8 fluorosurfactant analyses on several polymer and water samples. The polymer samples were taken from the [redacted] Dryer and associated equipment at a time when dryer performance was being questioned. The water samples were taken as part of the program to establish a material balance on C-8 distribution in the FEP Area.

In all cases, the C-8 was recovered from the samples by distillation in the presence of dilute aqueous phosphoric acid. Indications are that this treatment is relatively effective in separating out any "in situ" dispersing agent from the C-8 APFC. With the polymer samples, a nonvolatile, nonionic detergent ("Triton" X-100) was added to promote wetting. Analyses of the distillates from the polymer samples happened to be carried out by titration with cetyltrimethylammonium bromide, whereas with the distillates from the aqueous samples (run at a later date), the chloroform/Azure A method was employed. Results of the analyses are presented in Table II-CSC.

The measured C-8 concentrations on the polymer samples provided few surprises, it having been established earlier that the [redacted] Dryer serves to remove most of the C-8 from the (wet) feed entering from the [redacted] Press. Since the C-8 removed from the polymer discharges through the dryer vent line leading to the water scrubber, a polymer plug in this line would be expected to contain more C-8 than the dry polymer exit the dryer. Dry polymer removed from the rotor of the dryer would be expected to have a C-8 content comparable with that of the dryer product. Two earlier measurements of C-8 level on the dryer product gave values of 6 and 34 ppm, bracketing the value of 17 now obtained on the polymer scraped from the dryer rotor.

The concentration of 1950 ppm (0.195%) found on the sample taken from the lid of the screw conveyor now located between the discharge of the [redacted] Press and the entrance to the [redacted] Dryer was much higher than at first expected, based on previous measurements on [redacted] Press product samples, which had equivalent C-8 concentrations of 0.042% and 0.066%. The differences are even greater when differences in water content are taken into account (the dispersing agent is expected to be predominantly adsorbed on the polymer, rather than in the aqueous phase). The recent sample contained 70% water (total basis), vs. 24.5% and 14.8%, respectively, in the earlier samples, making the relative C-8 concentrations, expressed on a water-free basis, different by about an order of magnitude. We postulate that this difference is attributable to back-leakage of C-8-containing vapor from the dryer during the period when dryer performance was unsatisfactory. The C-8 would be expected to have condensed out on cool surfaces, such as the screw conveyor lid, the top of which was exposed to the ambient atmosphere.

TABLE II-CSC

C-8 FLUOROSURFACTANT ANALYSES ON SAMPLES FROM THE FEP AREA

(Submitted by A. R. Behnke and J. R. Evitts, Technical Department)

Sample Identification	Date Submitted	Measured Concentration of Equivalent C-8 APFC, ppm (Based on Initial Weight)
Polymer Samples (Analyzed by CTMAB Titration)		
Polymer scraped from rotor of [redacted] Dryer	3/30/81	17
Sample of plug found in vent line of [redacted] Dryer.	3/30/81	170
Dust sample from lid of Screw Conveyor feeding [redacted] Dryer (70% H_2O, total basis)	4/2/81	1950
Water Samples (Analyzed by $CHCl_3$/Azure A Method)		
[redacted]100 Coagulator Effluent (Batch 21-4111)	4/27/81	260
[redacted]100 PK (First) Rinse Water (Batch 21-4111)	4/27/81	15 (0.12% polymer solids present)