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TELOMER PRODUCTS - SURFACTANTS

ABSTRACTS

[ ]: Thermal Degradation

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pTFE and FEP dispersions containing fluorosurfactants are typically "cured" on coated substrates (frying pans, etc) at 400°C in an oven. Thus, the thermal behavior of [ ] was investigated at this temperature, and compared to the thermal behavior of "C8" (3M's FC-143) under identical conditions. Results are discussed.

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[ ]: Thermal Degradation

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Objective

To gain some level of understanding of the differences in behavior of [ ] and Perfluorooctanoic Acid ("C8") at 400°C.

Status

In response to a request by Fluoroproducts Technical Service, we sought to provide them with data in order to understand the thermal behavior of [ ] at these temperatures (in particular, relative to 3M's "C8," the current fluorosurfactant in use). We therefore took samples of C8 (3M's "FC-143") and [ ] (both 100% active ingredient), and heated each sample in an Acclerating Rate Calorimeter to 400°C, and held them at temperature for a half an hour, then cooled them back to room temperature. Two samples of each were then collected: any gases were collected from the ARC sample by venting to a cylinder for analysis, and the remaining condensed material was sampled from

the ARC bomb. Summary findings (all data collected and supplied by D. P. Cobranchi and J. R. Valentine) follow.

Vapor Pressure of FC-143 ("C8"). Cobranchi reports: "The material does not appear to be stable at temperatures above 130°C. The ln(press) vs 1/T plot shows a distinct break at this temperature. In addition, the self-heat rate data indicate an endothermic process occurring at the same temperature. The data below 130°C were, therefore, fit to a Clausius-Clapeyron model which resulted in the following function:"

$$VP(psi) = e^{-3500/1.987/T(K)+6.02}$$

Vapor Pressure of [redacted] Cobranchi reports: "The vapor pressure of the [redacted] has been determined between approximately 85 and 160°C. The vapor pressure is found to obey the Clausius-Clapeyron equation:"

$$VP(psi) = e^{-8803/19.87/T(K)+13.08}$$

GC/MS Identification of FC-143 Thermal Degradation Products. The vapor sample represented ca 10% of the total sample weight; the remaining 90% was liquid/solid at room temperature. Far and away the major peaks observed were from CO2 and C7F15H (four separate isomers-- one predominant). Other species observed in trace amounts were:

F-(CF2)6-H	CF3CFHCF2H
F-(CF2)5-H	CF3H
F-(CF2)4-H	CH4
F-(CF2)3-H	(CH3)3SiF
F-(CF2)2-H	CH3CF2H

(note: the presence of Silicon Fluorides is indicative of the presence of HF, and are produced by the reaction of HF with the GC column's stationary phase)

GC/MS Identification of [redacted] Thermal Degradation Products. The vapor sample represented ca 5% of the total sample weight; the remaining 95% was liquid/solid at room temperature. Again, CO2 was the major peak in the vapor spectrum, with several other species observed in much lower but roughly similar amounts:

F-(CF2)6-H	O=C=S
F-(CF2)5-H	CH3SiF3
F-(CF2)4-H	(CH3)2SiF2

F-(CF2)3-H
F-(CF2)2-H
CF3H

(CH3)3SiF
CH3CF2H
CH4

(note: the presence of Silicon Fluorides is indicative of the presence of HF, which are produced by the reaction of HF with the GC column's stationary phase)

Notably, no SO2 or SO3 was detected, although given the small amounts of volatiles produced and the relatively large number of components, we cannot completely rule out peak coelution as a possibility. The only sulfur-based volatiles observed were O=C=S and very, very small amounts of CS2 (detected, but well below threshhold).

The liquid/solid sample proved to be much more intractable, and eventually dissolution in CFC-113 was required in order to ensure that a sample representative of the container was obtained for analysis. Compounds detected were as follows:

F-(CF2)6-CH2CH3
F-(CF2)6-CH=CH2
F-(CF2)5-H
F-(CF2)6-CH2F
F-(CF2)6-CH2CH2SO2F
F-(CF2)6-CH2CH2SO2CH2CH2C4F9
F-(CF2)8-CH2CH3

Additionally, species with molecular weights greater than that of [redacted] itself, and containing an S=O, were also detected, but unidentifiable.

Path Forward

Tha ARC data for C8 is most definitive; it clearly shows an endothermic process (beginning at 130°C), consistent with decomposition via decarboxylation as suggested by the accompanying GC/MS data. In contrast, the ARC data suggests that loss of material through simple volatilization is more likely with [redacted], as no significant endotherms/exotherms were seen, and no SO2 or SO3 was picked up in the GC/MS analyses.

By copy of this summary, we will share this data and our interpretation with the Fluoroproducts SBU.