AR226-1655

C. FC-143 in Teflon® Products - S. S. Shelburne

Objective: Determine levels of FC-143 in the Teflon® process and the conditions for removal of and identification of byproducts of thermal treatment.

Status: Heating of FC-143 ammonium salt/Triton X-100 mixtures at 175°C and analyzing off gases by IR show that decarboxylation, with CO_2 and a perfluoromonohydride as byproducts, occurs in FC-143 thermal treatment. Although the FC concentration on I yarn is too low to use IR for positive identification of perfluoro byproducts, heating the yarn to 200 or 250°C and measuring the decrease in off gas absorbance by IR does confirm previous work that thermal treatment is an effective means of removing the FC. There is no evidence of evaporation, but the IR scan does show the presence of unidentified compounds. Mass spec will be necessary to identify these.

A study of the decarboxylation reaction shows two possible products, (1) the perfluoromonohydride or (2) the perfluoroolefin (Ref. 1, 2).

$$CF_3(CF_2)_6\overset{O}{\overset{\|}{C}}-O-M^+ \xrightarrow{\Delta} \textcircled{1}\ CF_3(CF_2)_5CF_2H + CO_2$$

$M^+ = NH_4^+, Na^+$

$$\textcircled{2}\ CF_3(CF_2)_4CF = CF_2 + CO_2$$

The monohydride is observed in the IR as a peak at 3010 cm^{-1} (C-H Stretch, Figure I, SSS). There is no evidence for the perfluoroolefine which would absorb at ∿ 1790 cm ($CF = CF_2$). The spectra shows evidence of other compounds binds the monohydride, probably from the Triton. If it is necessary to identify these, mass spec analysis must be run in Wilmington.

Samples were run by heating them from 125-175°C in a Teflon® column in a GC. The GC allowed the use of controlled N_2 purge and temperature. The evolved gases are carried to a 10 cm IR cell through tubing. All samples are heated at 125°C for 30 minutes to remove water.

The Nicolet FTIR is used in a repetitive scan mode, usually with a 5 minute scan time. Yarn samples were run initially, but the low FC concentration caused a change to FC/Triton liquid mixture. To emphasize the IR peaks, the solutions were run at 5:1 Triton/FC ratio rather than the actual 50:1 ratio.

The NH_4 salt scans show CO_2 and CF_2 absorbance peaks as early as 150°C, but the hydride peak does not appear until after 5-6 minutes at 175°C. This is due to its low mass and probably low absorptivity. This time cannot be compared to earlier kinetics work because of low purge flows and thus, the time necessary to displace the volume of the tubing and cell (∿ 11 minutes).

Ref. 1 - LaZerte, JD; JACS:75, 4525 (1953)
Ref. 2 - PCRD 58-131 - R.G. Meschke

The low purge is necessary to prevent excessive dilution in the IR cell. However, Teflon® "I" yarn samples, which contain the sodium salt, heated at 200°C showed a decrease in the CO_2 and CF_2 peaks after 25 minutes, indicating that the decarboxylation was complete. At 250°C, the same peaks start to decrease after ∿ 8 minutes. (Table I-SSS) These do confirm that the temperatures in the previous work were correct.

Work is continuing to quantity the degree of decarboxylation with the sodium salt and to trap the off gases for better identification.

FIG I 555

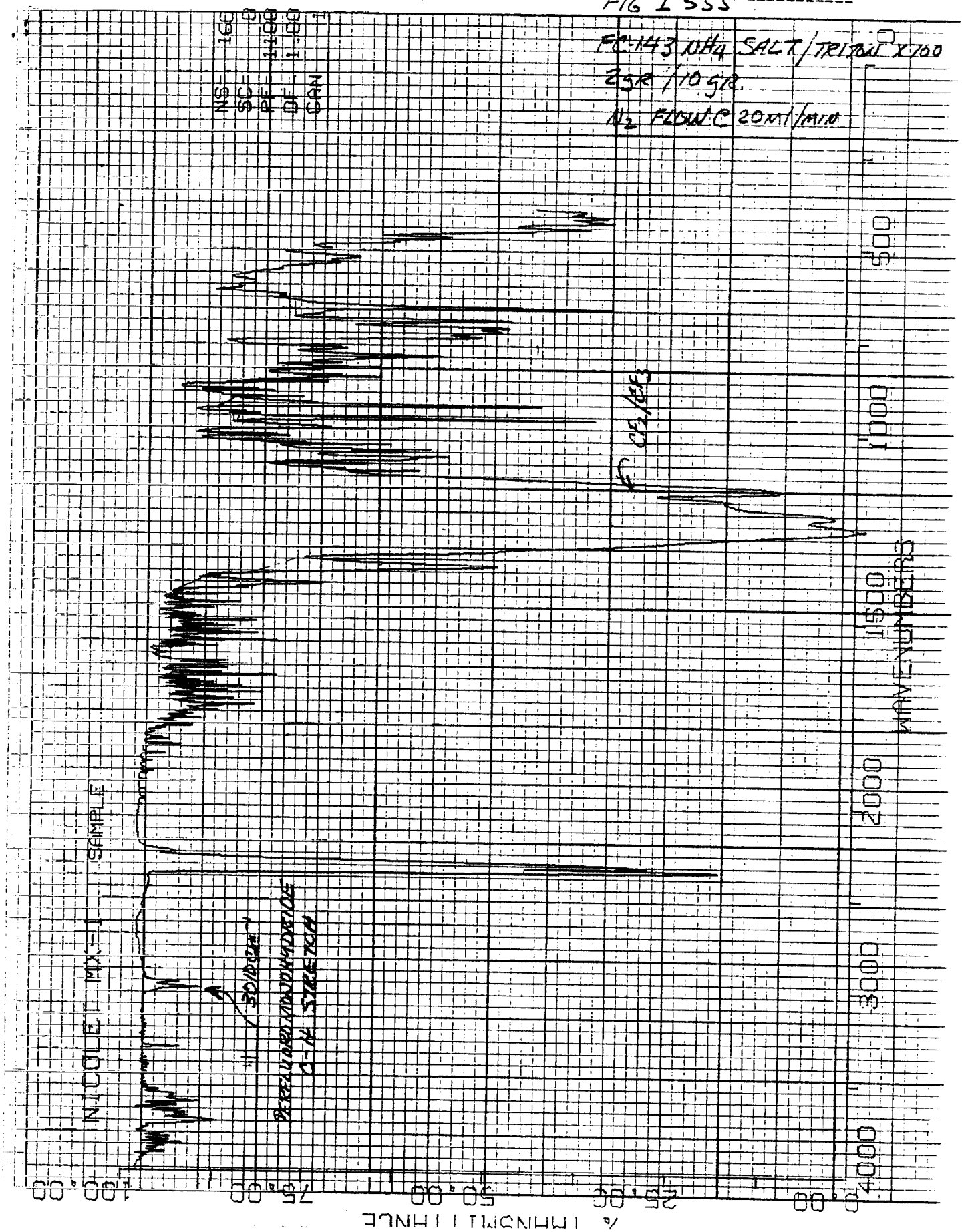

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TABLE I-SSS

FC-143 OFF GAS IR ANALYSIS

N_2 Flow 20 ml/min.

Time for Volume Displacement - 11 Minutes

	Sample	Temp.	Time Min.	% Chart C-H-3010 cm^{-1}	% Chart CO_2-2340 cm^{-1}	% Chart CF_2-1250 cm^{-1}
I.	NH_4FC143/Triton 2g/10 gr.	150	-	-	3	4.5
	Temp. Increase 8°/min.	175	0	-	7	11
		"	1	-	10	15
		"	5	1	26	29
		"	8	2	36	38
		"	13	5	50	44
		"	25	10	82	99
II.	Teflon® I Yarn	200	0	Non-detect	2	10
	3.5 gr.	"	2	"	3	12
	Heat Time	"	10	"	11	19
	125-200°C	"	16		19	21
	6.5 min.	"	21		18	21
		"	25	"	18	23
		"	30	"	12	18
III.	Teflon® I Yarn	250	0	Non-detect	14	31
	3.65 gr.	"	8	"	18	16
	Heat Time 125-250°C	"	16	"	16	8
	10.5 min.	"	21	"	16	5
		"	26	"	12	4
		"	31	"	11	-