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FC-143 IN THE [redacted] PROCESS

M. A. Forte

Period: July, 1978 - March, 1979

Reference: Notebook No. SA-154

Previous Related Reports: None

Textile Fibers Department
Spruance Research
Analytical Research Group
E. I. DuPont de Nemours & Co., Inc.
Richmond, Virginia

INTRODUCTION

Based on information supplied by the 3M Company[1], DuPont became aware that elevated organic fluoride levels were detected in the blood of 3M workers exposed to certain fluorinated surfactants. Entry of the surfactant was felt to be related to exposure to airborne dust. A fluorinated surfactant is employed at Spruance in the [redacted] process. It is a component of [redacted] dispersion which is purchased from PP&R Department. Based on FC-143 physical properties, the possibility existed for worker exposure at Spruance. Therefore, this study was undertaken to determine the extent of exposure, if any, and the ultimate fate of FC-143 in our process due to potential customer or environmental impact.

OBJECTIVES

- To determine the fate of FC-143 in the [redacted] process.
- Establish the extent, if any, of worker exposure to FC-143.
- To develop an accurate analysis for FC-143 in air, water and [redacted] product/ingredients.

SUMMARY AND CONCLUSIONS

FC-143 was not detected in operator breathing zones. Limit of detection was 50 ppb based on sample volume. Therefore, use of FC-143 in [redacted] dispersion is felt to lead to low, if any, airborne exposure of personnel. FC-143 was found to be 0.43 ppm in process wash water and less than 0.5 ppb in stack gas based on level in condensate. Therefore, the environmental impact is considered small with present production levels. It appears that 80-90% of FC-143 is tightly bound in [redacted] during polymerization at PP&R. FC-143 was detected at low levels in "I" Product, but was not detected in other [redacted] products.

FC-143 was measured by Gas Chromatography of the methyl ester with an electron capture detector. Esters of ether extracts were prepared with methanol/BF_3 rather than with diazomethane as recommended by 3M. Air samples were taken, as recommended by 3M, by scrubbing with methanol. Aqueous samples were extracted with ether and yarn samples were extracted with methanol.

PATENT ACTION

No patent action based on this work is planned at present.

PUBLICATIONS

There are currently no plans to publish any of this work.

CODE LISTING

FC-143: Ammonium perfluoro octanoate.

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TABLE OF CONTENTS

I. [redacted] PROCESS MEASUREMENTS

a. Background

[redacted] colloidal dispersion is mixed with viscose in the manufacture of [redacted] fiber. The viscose is regenerated in an acid bath in spinning and acts as a matrix to bind the [redacted] particles prior to sintering. Surfactants such as FC-143 and Triton X-100 are added to the colloidal [redacted] dispersion to prevent agglomeration of the particles.

b. Fate of FC-143 in the Manufacture of [redacted]

FC-143 is added to dispersion at the 2200 ppm level by PP&R in polymerization. During polymerization most of it is apparently irreversibly absorbed on or incorporated in the [redacted] particles. This hypothesis is based on measurements of FC-143 in raw dispersion and on supernatant liquid from the PP&R polymerization. In order to understand the hypothesis, a brief description of the polymerization is necessary. [redacted] monomer (35%) is polymerized in water (∿ 65%) in the presence of FC-143 and other surfactants. The solids are increased to ∿ 60% by decanting water off. If no other physical phenomenon were involved, one would expect to find 2200 ppm FC-143 in the water associated with the remaining [redacted] dispersion and in the decantation water. This is not the case as can be seen from the data in Table I.

TABLE I

[redacted] LEVEL OF FC-143 IN DISPERSION PROCESS SAMPLES FROM PP&R

Sample	Conc. ppm
Supernatant Liquid	220
Raw Dispersion - 35% Solids	100
Concentrated Dispersion	120

There is additional supportive information for the absorption hypothesis[2]. Analysis of other surfactants used in polymerization at Parkersburg had given low recoveries.

Attempts at analysis of FC-143 in [redacted] process and yarn samples do not lead to a materials balance based on amount added at PP&R. A schematic representation of the process is given in Figure 1 to show the path of [redacted] dispersion. The pertinent sample results are given in Table II.

I. [redacted] PROCESS MEASUREMENTS (Cont'd)

b. Fate of FC-143 in the Manufacture of [redacted]

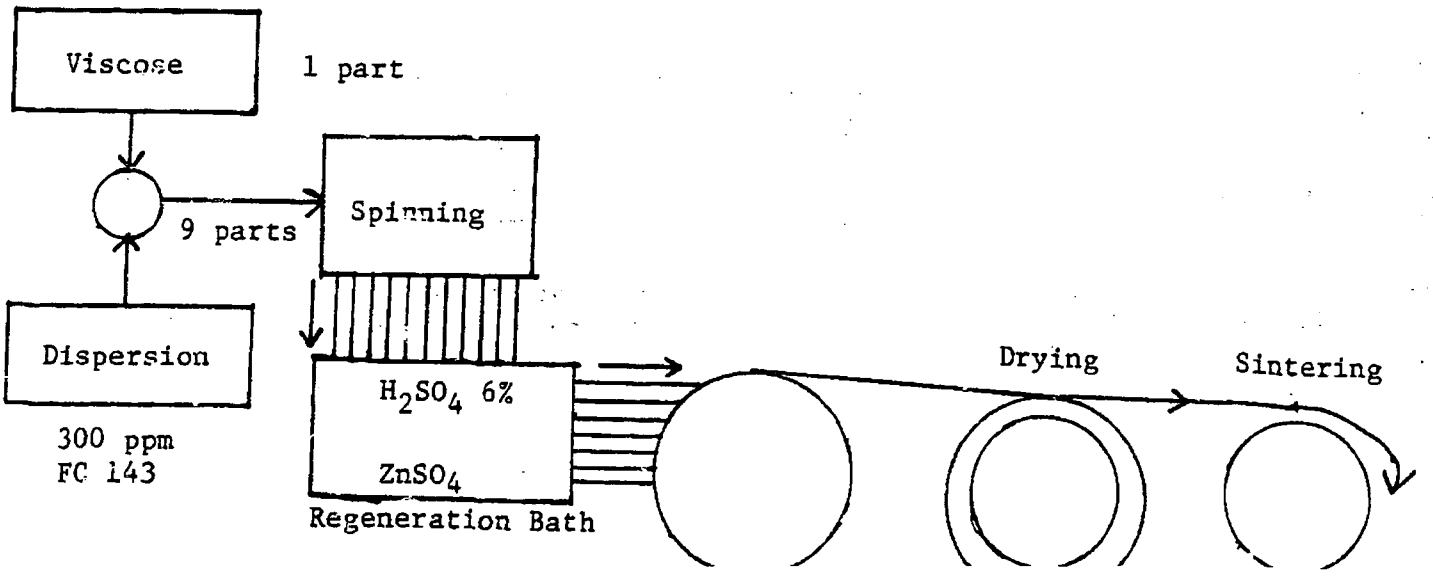
TABLE II

FC-143 IN [redacted] PROCESS

Yarn Samples	Conc. ppm
After Wash Reel	1.2
Dried Yarn	0.3
Sintered Yarn	Not Detectable
Aqueous Samples	
Regeneration Bath	Not Detectable
Wash Reel Water	0.43

FIGURE I

[redacted] YARN PROCESS



I. [redacted] PROCESS MEASUREMENTS (Cont'd)

b. Fate of FC-143 in the Manufacture of [redacted]

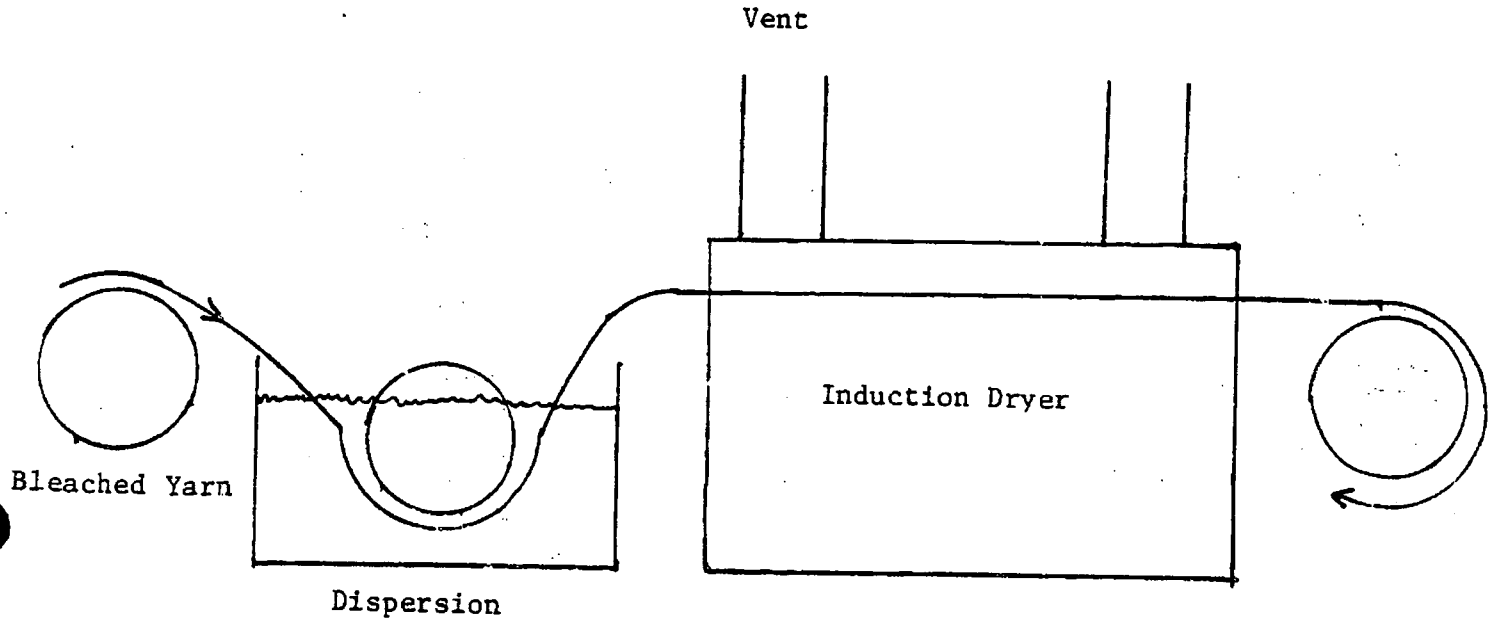
Based on the ratio of wash water to yarn, the level of 0.43 ppm is equivalent to ∿ 70 ppm in yarn. Therefore, the majority of FC-143 must remain with yarn.

Based on colloid chemistry, the FC-143 molecule would orient at the surface of the [redacted] particle. pH of dispersion is adjusted with NaOH which converts the ammonium salt to the sodium salt. The sodium salt would be converted to a carboxylic acid group in the Regeneration Bath. The carboxylic acid would undoubtedly be decomposed in Sintering.

Dispersion is also used to coat [redacted] yarn for pump packing end-use. As can be seen from Figure 2, dispersion is added to bleached yarn and dried in a dielectric oven. Thermogravimetric measurements made on FC-143 indicate it begins to volatilize at 120°C. There was some likelihood for FC-143 to volatilize in the oven. As can be seen from the data in Table III, this occurs on only a slight degree, probably due to its conversion to the sodium salt at pH adjustment.

FIGURE 2

"I" YARN PROCESS



I. [redacted] PROCESS MEASUREMENTS (Cont'd)

b. Fate of FC-143 in the Manufacture of [redacted] (Cont'd)

TABLE III

FC-143 IN INDUCTION DRYER SAMPLES

Sample	Conc. ppm
Coated Yarn Before Dryer	5
Coated Yarn After Dryer	5
Vent Residue	8
Powder on Dryer Floor	117

Calculated on the basis of dispersion on the coated yarn, the level of FC-143 is ∿ 10 ppm. This compares with 200 to 300 ppm on aqueous dispersion. Yarns were extracted with methanol in which FC-143 is very soluble. Apparently, FC-143 became "locked" in dried dispersion.

II ENVIRONMENTAL MEASUREMENTS

Since it is difficult to prove the hypothesis of FC-143 entrapment in [redacted] a materials balance cannot be obtained. Since FC-143 acid is volatile at process temperatures, the possibility existed for FC-143 entry into the air. The possibility was considered low, however, since studies[3] conducted in the past on the degradation products from sintering have not revealed the presence of any fluorinated hydrocarbons.

a. Air Sampling in Spinning and Winding

[redacted] yarn is heated to remove cellulose in a sintering operation. To ensure no exposure was taking place, air samples were taken in operator breathing zones. The results of this study given in Table IV show that operator exposure is very unlikely. The level of 50 ppb is based on detection limits of FC-143 and volume of air sampled. Air samples were also taken at the dryer exit and above the dryer in the "I" process. These too showed less than 50 ppb FC-143. This is in part due to FC-143 conversion to the sodium salt.

TABLE IV

AIR SAMPLES TAKEN IN SM-3 AREA

Location(1)	Approximate Temperature °F	Level of FC-143 PPB
Roll 2	250	< 50

II. ENVIRONMENTAL MEASUREMENTS (Cont'd)

a. Air Sampling in Spinning and Winding (Cont'd)

During a visit[4] and examination of the "I" production facility, J. M. Morgan of Haskell Laboratory noticed that some of the equipment had a small amount of white dust on it. Since the material might conceivably have contained FC-143 from mechanical introduction into the air, dust samples were taken and tested for FC-143 level. The dust sample testing showed that there was less than 1.5×10^{-10} FC-143 g/liter of air based on the detection limits.

b. Process Effluents

There are two process effluents which could contain FC-143. As was mentioned earlier, wash reel water was found to contain 0.43 ppm FC-143. This would eventually wind up in the James River. The other effluent which could contain FC-143 is oven exhaust. Measurements made on the condensate showed FC-143 level to be less than the detection limit of 0.5 ppb V/V.

III. METHOD DEVELOPMENT

a. Background

The procedure for analysis of FC-143 in air (in Appendix II) was supplied by 3M. Their procedure was based on methyl ester preparation with etheral diazomethane followed by gas chromatography and electron capture detection. We ultimately found their G.C. conditions and trapping method to be useful. Their ester preparation method was considered unsafe due to literature accounts of spontaneous explosions of highly toxic diazomethane. The literature[5] indicated that methyl esters are easily formed by two minute reaction in methanol/BF_3. This reagent is available commercially from Supelco, Inc.

b. G.C. Analysis

A quantity of the methyl ester of FC-143 was prepared by refluxing one gram of the material in 100 ml. of methanol to which 5 ml. of concentrated HCl had been added. Upon addition of water, the ester separated as a heavy oily liquid. The ester product was confirmed by IR analysis as shown in Figure III. This material was employed as a standard to evaluate G.C. columns, for retention time measurements, for detector linearity determination, and for partitioning studies. The retention time of the methyl ester was given as 11.1 minutes on the 20% DC-20, 10% Bentone 34 on Anakrom ABS column recommended by 3M.

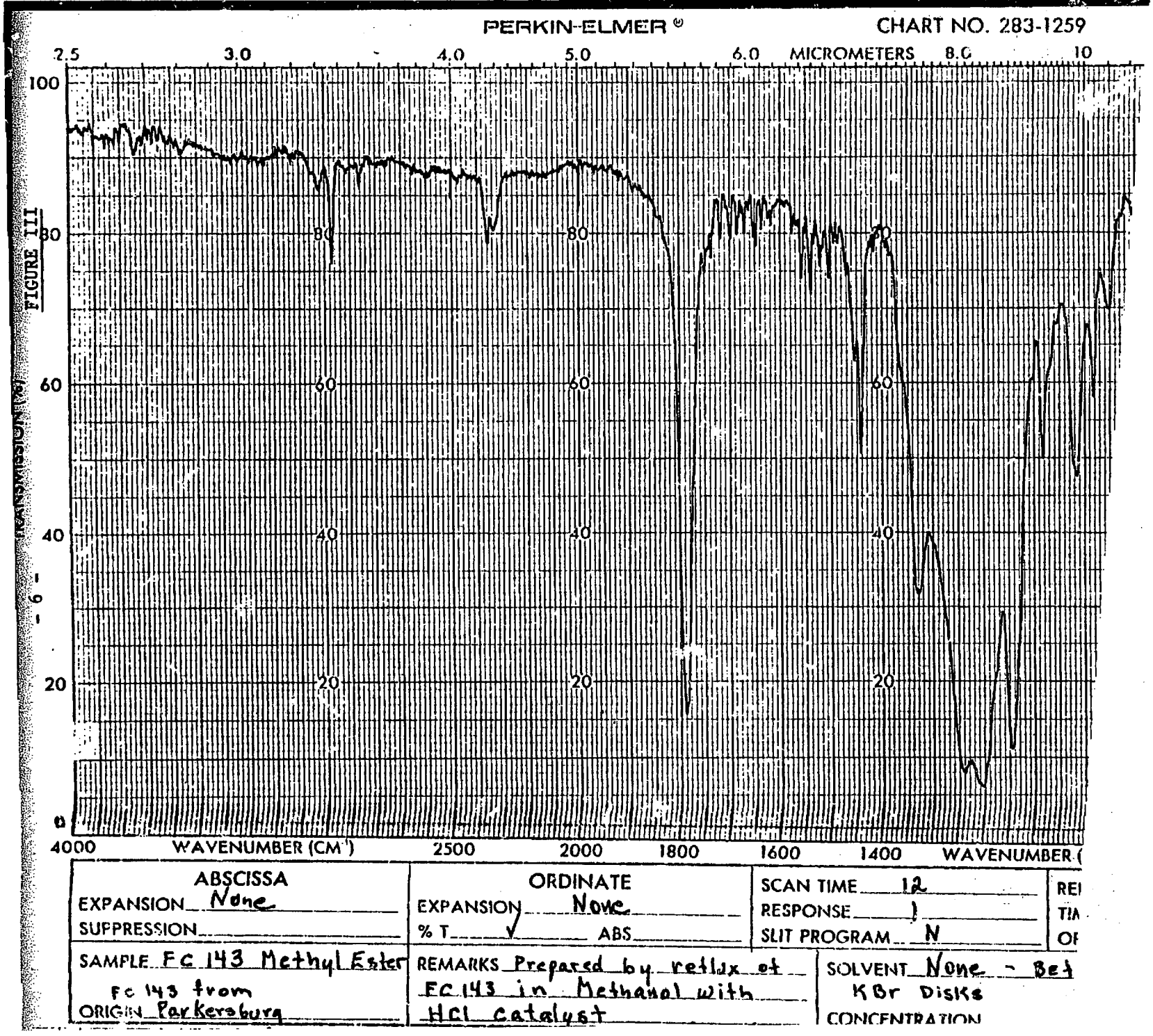


FIGURE III

- 6 -

Company Sanitized. Does not contain TSCA CBI

III. METHOD DEVELOPMENT (Cont'd)

b. G.C. Analysis (Cont'd)

Through suitable adjustments of initial temperature and temperature program, retention time on the 20% DC-20, 10% Bentone 34 was reduced to ∿ 7.0 minutes. Due to its high liquid loading, this material is sticky and difficult to pack in a glass column. I found that chilling the material and using a vibrator enabled us to pack a 10' glass column.

The electron capture detector is linear in response over only a specific range. Above a certain concentration no additional signal is obtained. The detector on the Hewlett Packard GC was found to be linear in the range of 600 to 31,000 ppb of FC-143 ester in ether. A plot of integrator counts vs. concentration is shown in Figure IV. The linearity study was made under the following conditions:

Carrier gas - Argon/methane - 95/5
Injection port - 150°C
Detector temperature - 250°C
Column SP 1000 - 10' glass
Column temperature - 80°C for 4 min. then prog. at 8°C/min to 180°C
Pulse interval - 150

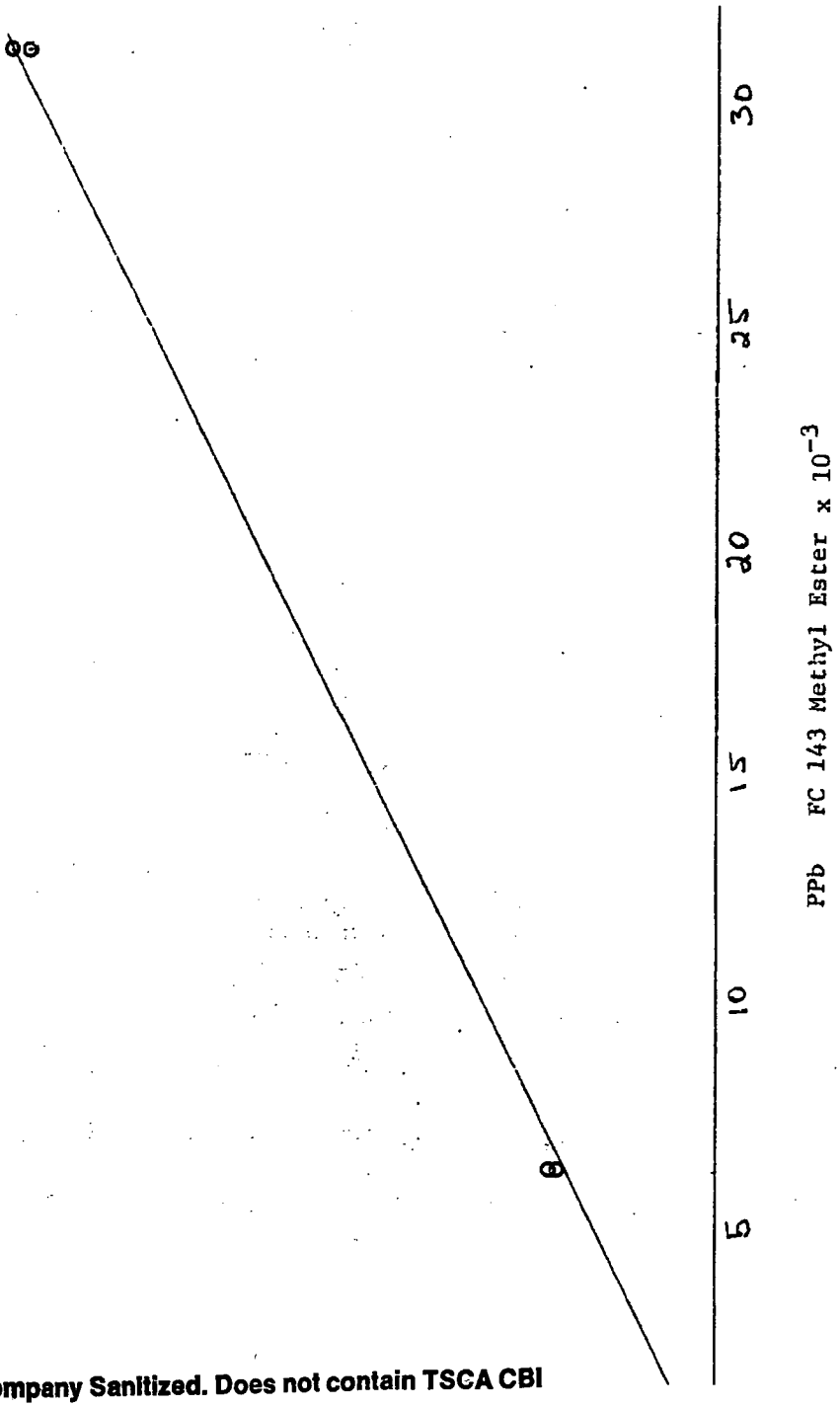
Response is also a function of detector temperature. It was found that at 250°C there was little change in response with temperature.

c. Preparation of Esters

Pesticide grade methanol/BF_3 was employed to prepare the FC-143 ester. The recommended procedure was to react the acid with methanol/BF_3 and then add water to stop the reaction. Normally aliphatic acid esters could then be extracted with Freon or some other chlorinated solvent. Of course, in this case, a chlorinated solvent would flood the electron capture detector. Ether was found to be partially soluble in the water/methanol/ester mixture so a good separation could not be obtained. It was found that a mixture of 80/20 cyclohexane/ether separated well if saturated KCl was employed instead of water. A partitioning experiment showed that the FC-143 methyl ester went completely to the ether cyclohexane phase.

With these reaction conditions, 5 ppm of FC-143 could be detected in the extracts. Solid samples were extracted with methanol. Liquid samples were acidified with HCl if the FC-143 was present as the ammonium salt. Ether or methanol extracts were evaporated almost to dryness in a 70-80°C water bath with a stream of N_2 before reaction with methanol/BF_3.

FIGURE IV



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1. Rogers, L. B. - "Fluoro Surfactants in Blood", Employee Information Bulletin, July 12, 1978.

2. Hall, Linda - Parkersburg Analytical Research, Telephone Conversation, February 21, 1979.

3. Sarasohn, I. M. - [redacted] Off-Gas Analysis", Letter to Author, June 23, 1975, Appendix III.

4. Morgan, J. M. - Visit to [redacted] Manufacturing Facility, March 20, 1979.

5. Metcalfe, T. D. and Schmitz, A. A. - Analytical Chemistry, Volume 33, No. 3, March, 1961, pages 363-364.

E. I. DU PONT DE NEMOURS AND COMPANY
Incorporated

Appendix Ia
Section
Method

Page 1

Textile Fibers Department
Industrial Fibers Division

PROCESS CONTROL - OPERATING PROCEDURE

SPRUANCE

PLANT: SPRUANCE FIBERS
RICHMOND, VIRGINIA

SUBJECT: ANALYSIS OF FC-143 IN AIR

CHANGES: NEW METHOD

APPROVED BY:

Prepared By: M. A. Forte

I. INTRODUCTION

FC-143 is absorbed in methanol in a Telmatic air sampler. Methanol is evaporated off and the methyl ester is prepared through reaction with methanol/BF_3. The ester is measured by GC with an electron capture detector. Detection limit is 0.05 ppm v/v based on a 40 liter air sample.

CAUTION: The physiological properties of FC-143 methyl esters are unknown - handle with care to avoid exposure.

II. REAGENTS AND EQUIPMENT

A. Gas chromatograph equipped with an electron capture detector (Hewlett Packard 7620A with 3385A integrator).

B. Telmatic air sampler - Taylor Parker Co., Norfolk, Virginia, Cat. No. 158.

C. Batteries, nickel-cadmium, 8.4 volts - Taylor Parker Co., Cat. No. 84TA.

D. Methanol/BF_3, pesticide grade in glass ampoules - Supelco, Cat. No. 3-3041.

OPERATING INSTRUCTIONS	SAFETY INSTRUCTIONS
II. REAGENTS AND EQUIPMENT (Cont'd)	
F. Chromatography Column 10' glass packed with: DC-200 20%, Bentone 34 10% on 100/120 mesh Anakrom ABS - Supelco.	
G. FC-143 Methyl Ester Standard	
1. Weigh 1.0 g. of FC-143 into a round bottom flask. Add 100 ml of dry methanol, 5 ml of concentrated HCl and a few boiling beads.	Perform these operations in a hood.
2. Connect flask to a reflux condenser and gently reflux for two hours.	
3. Cool the flask to room temperature, then pour the contents into a 500 ml. separating funnel which contains 300 ml. of DI water.	
4. Stopper and shake. Allow the phases to separate. FC-143 methyl ester separates as an oily liquid.	
5. Drain this liquid into a serum stoppered vial.	
H. GC Standard	
1. Fill a 10 µl syringe with 3 µl of FC-143 methyl ester. Weigh the syringe and its contents on a micro balance to 0.000001 g.	
2. Add 5 ml. of ether/cyclohexane 20/80 to a 10 ml volumetric flask. Inject 1.0 µl of FC-143 methyl ester into ether/hexane.	
3. Reweigh syringe to 0.000001 g. Dilute to the mark with ether/cyclohexane and label Solution "A". Make a 1:10 dilu-	

III. PROCEDURE

OPERATING INSTRUCTIONS	SAFETY INSTRUCTIONS
A. Air Sampling	
1. Add 15 ± 0.2 ml. of methanol made basic to methyl red with 0.1N methanolic KOH to a 25 ml. impinger tube.	
2. Connect to Telmatic air pump with gum rubber tubing.	
3. Set sampling rate at 2.0 liters per minute.	
4. When ready to sample, turn air pump on and set timer to 20 minutes.	
5. After sample has been taken, remove impinger and transfer contents with methanol rinse to a 150 ml. beaker.	
B. Sample Preparation	
1. Evaporate the beaker contents almost to dryness on a steam bath.	Perform sample preparation steps in a hood.
2. Transfer the beaker contents with methanol 10% concentrated HCl rinsings to a 15 ml. tapered centrifuge tube. The tube contents should be acid to methyl red, add methanol 10% HCl dropwise. Place the tube in a 70 ± 5°C water bath and evaporate the tube contents to about 1/2 ml. with a stream of N_2.	
3. Remove tube from bath, dry and add 1 ml. of methanol/BF_3 from a freshly opened glass ampoule.	
4. Stopper the centrifuge tube and put it back in 70 ± 5°C water bath.	
5. Remove the tube after 2 ± 0.1 minutes and quickly unstopper it. Cool to room temperature or slightly below.	
6. Add 2 ml. of ether cyclohexane fol-	

III. PROCEDURE

OPERATING INSTRUCTIONS	SAFETY INSTRUCTIONS

B. Sample Preparation (Cont'd)

7. Allow the layers to separate until a clearly defined top layer of ether/cyclohexane appears or centrifuge to speed the separation.

8. Prepare 15 ml. of an external standard containing 50 ppm of FC-143 in methanol the same way.

C. Gas Chromatographic Analysis

- Column glass 2 mm i.d. x 10' packed with DC-200 20%; Bentone 34 10% on 100/120 mesh Anakrom ABS.
- Injection port temperature - 150°C.
- Argon/methane 95/5 flow rate: 30 ml/min.
- Detector Settings:

Pulse Interval	150
Temperature	250°C
Range	10^3

- Oven temperature

Isothermal	100°C 4 min.
Program	8°C/min to 180°C

- Integrator 3385A

Attenuation	2^6
Slope Sensativity	0.50

4 min. reset baseline at all valleys

NOTE: If air (oxygen) has entered the EC detector, it must be conditioned for two days at 100°C with column installed and 15-20 ml. of argon/methane flowing.

III. PROCEDURE

OPERATING INSTRUCTIONS	SAFETY INSTRUCTIONS
D. Sample Analysis 1. Inject a 2 µl sample of Standard "B" to check response and retention time. The FC-143 methyl ester should come out between 7 and 8 minutes. 2. Inject a 2 µl sample of external standard. 3. Record area counts for external standard. 4. Inject a 2 µl sample of prepared air sample. 5. Record area counts for air sample.	

IV. CALCULATIONS

Let A = Sample peak area

B = External standard peak area

C = ppm v/v in external standard = 1.0

V = Volume of air sampled = 40 liters

$$\text{ppm FC-143 v/v} = \frac{A}{B} \times C$$

$$= \frac{A}{B}$$

Example:

A = < 3483

B = 69660

$$\text{ppm} = < \frac{3483}{69660}$$

ppm = < 0.05

E. I. DU PONT DE NEMOURS AND COMPANY
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Textile Fibers Department

Section Appendix Ib
Method

Page 1

PROCESS CONTROL - OPERATING PROCEDURE

SPRUANCE

PLANT: SPRUANCE FIBERS
RICHMOND, VIRGINIA

SUBJECT: ANALYSIS OF FC-143 IN ETHER OR METHANOL EXTRACT

CHANGES: NEW METHOD

APPROVED BY:

Prepared By: M. A. Forte

I. INTRODUCTION

Liquid samples are acidified with 6N HCl followed by extraction with ether. Solid samples are extracted with methanol. Extracts are evaporated almost to dryness and the residue is reacted with methanol/BF_3 to generate methyl esters. The level of FC-143 methyl ester is measured by G.C. with an electron capture detector.

CAUTION: The physiological properties of FC-143 methyl esters are unknown - handle with care to avoid exposure.

II. REAGENTS AND EQUIPMENT

A. Gas chromatograph equipped with an electron capture detector - Hewlett Packard 7620A with 3385A integrator.

B. Methanol/BF_3, pesticide grade in glass ampoules - Supelco, Cat. No. 3-3041.

C. Vials, glass stoppered, tapered 15 ml. - Fisher Scientific.

D. Chromatography Column - 10' glass packed with: DC-200 20%, Bentone 34 10% on 100/120 mesh anakrom ABS - Supelco.

E. FC-143 methyl ester standard - Prepare as in Appendix Ia II.C. 1-5

III. PROCEDURE

OPERATING INSTRUCTIONS	SAFETY INSTRUCTIONS
A. Sample Preparation	
• Dispersion	
1. Pipet 1/2 ml. of dispersion into a 15 ml. tapered vial.	
2. Pipet 1/2 ml. of 6N HCl into the vial and mix.	
3. Pipet 3 mls. of ether into the vial, stopper and shake well.	
4. Add 10 ml. of saturated KCl solution and shake well.	
5. When the ether layer has separated, remove one ml. with a disposable pipet and put it into a graduated vial.	
6. Place the vial in a 70°C ± 5°C water bath and evaporate almost to dryness with a gentle stream of nitrogen.	
7. Remove the vial from the bath and cool to room temperature.	
8. Pipet 1 ml. of methanol/BF_3 into the vial and stopper.	
9. Put the vial in the 70°C bath and react for 2.0 ± 0.1 min.	
10. Remove the vial from the bath and loosen the stopper slightly to prevent a vacuum.	
11. When the vial has cooled to room temperature add 2.0 ml. of 80/20 cyclohexane/ether and swirl to mix.	
12. Add 9 ml. of saturated KCl, stopper and shake well.	

III. PROCEDURE

OPERATING INSTRUCTIONS	SAFETY INSTRUCTIONS

A. Sample Preparation (Cont'd)

Solid Sample

- Methanol Extract

1. Add one drop of 30% NaOH to 200 ml. of extract to insure basic conditions.
2. Evaporate almost to dryness on a steam bath.
3. Cool and add two drops of concentrated HCl.
4. Transfer the extract to a 15 ml. tapered vial with two 1/2 ml. washings of dry methanol.
5. Evaporate to 0.25 ml. with a stream of Nitrogen.
6. Pipet 1 ml. of methanol/BF_3 into the vial and stopper.
7. Follow Steps 9-13 of dispersion preparation.
8. Prepare 15 ml. of an external standard containing 50 ppm of FC-143 in methanol the same way.

B. G. C. Analysis

Follow Steps III C and D, Appendix Ia for G.C. checkout and sample analysis.

IV. CALCULATIONS

Let A = Sample peak area

B = External standard peak area

V = Volume of Teflon® dispersion ml.

W = Weight of solid sample grams.

III. PROCEDURE

OPERATING INSTRUCTIONS	SAFETY INSTRUCTIONS

IV. CALCULATIONS (Cont'd)

$$\text{Dispersion ppm FC-143 Weight/Volume} = \frac{3 \times A \times S \times M}{V \times B}$$

$$\text{Solid ppm FC-143 Weight/weight} = \frac{A \times S \times M}{B \times W}$$

Example:

A = 10,000 counts

B = 15,000 counts

S = 50 ppm

M = ml. of external standard

3 = Volumetric factor

$$\text{Dispersion ppm FC-143 Weight/Volume} = \frac{3 \times A \times S \times M}{V \times B}$$

$$\text{Solid ppm FC-143 Weight/Weight} = \frac{A \times S \times M}{B \times W}$$

Example:

A = 10,000 counts

B = 15,000 counts

S = 50 ppm

M = 15 ml.

W = 5.0 g.

$$\text{Solid ppm} = \frac{10{,}000 \times 50 \times 15}{15{,}000 \times 5.0} = 100$$

Appendix II

Interoffice Correspondence

Subject:

Routing copy:
J. W. Feuk - Med. - 220-2E
J. A. Pendergrass - Med. - 220-2E
F. A. Ubel, M.D. - Med. - 220-2E

June 23, 1978

TO: R. A. PROKOP - COMMERCIAL CHEMICAL - 236-3B

FROM: D. F. HAGEN - CENTRAL RESEARCH - 201-1W
S. D. SORENSON - (3-7058) - MEDICAL - IND. HYG. SERV. - 220-2E

Attached is the sampling and analytical procedure for FC-143 as per your request.

Please call if there are any questions.

DFH/SDS
/mm

Mr. R. A. Prokop June 23, 1978

FC-143
Sampling Procedure

I. Filter Method:

A. Equipment

1. Battery operated pump capable of drawing 2-2.5 lpm through filter. Examples: MSA Model S, or Bendix Super Sampler.
2. Three piece cassette filter holder.
3. Nuclear Pore® 0.8 um pore size filter media.

B. Preparation

1. Pump flowrate should be calibrated using bubble meter, wet test meter or similar method using standard industrial hygiene calibration techniques.
2. Assemble cassettes using filter support or screen under filter. It is desirable to wrap the cassette with vinyl tape (electrical tape).

C. Procedure

1. Remove colored plugs from both ends of filter holder cassette. Attach cassette to end of sampling hose so that airflow is in right direction, e.g. filter support, or backup screen must be on pump side of filter.
2. If a breathing zone or personal sample is desired, attach the cassette assembly to employees' lapel so that the inlet orifice is in a downward position.
3. The pump can be attached to the employees' belt, generally in the back.
4. Turn on pump - record time.
5. Check to see that the pump is at the desired flow-rate. Recheck periodically.
6. Record time at end of sample period.
7. Replace colored plugs in ends of cassette.

II. Impinger Method, Alternate Method

A. Equipment

1. Battery operated pumps as described above.
2. All glass midget impinger.
3. Methanol. G.C. grade preferable, reagent grade can be used.
4. Transport vials - glass with teflon lined caps

B. Preparation

1. Flowrate should be calibrated.
2. Fill impinger with 15 ml methanol.

C. Procedure

1. Sample at 2.0 liters per minute for 20 minutes Slower rate may be used for longer periods; at least 40 liters of air should be sampled.
2. Hand hold impinger in employees' breathing zone.
3. At end of sample period, the impinger and stem should be rinsed with methanol. The rinse should be added to the sample for analysis.
4. Transport vials should be tightly capped and sealed with tape.

Analysis Procedures

Trace analysis for FC-143 are performed via gas chromatography after formation of the methyl ester derivative. Dust samples which have been collected on filters are extracted with [redacted] cc of 0.1 N HCl. The acid solution is then extracted with three 2 cc portions of diethyl ether. The diethyl ether extracts are combined in a 10 cc volumetric flask. Two cc of diazomethane reagent* are added and the esterification allowed to proceed at room temperature for 25 minutes.

WARNING - Diazomethane is extremely toxic and its solutions have been known to explode. All work should be carried out behind safety shields and in efficient hoods. Precautions, as outlined by Aldrich Chemical Company, should be taken when using this reagent.

This solution is then placed under a dry air jet to drive off the excess diazomethane as evidenced by the loss of the yellow coloration. The solution is then brought up to the 10 cc volume prior to analysis. Aliquats of this solution are injected into the gas chromatograph using the conditions outlined below.

In the alternate method, impingers containing 15 cc of methanol solvent can also be used for air sampling applications. In this case, the methanol in the impinger after sampling is transferred quantitatively to a 25 cc volumetric flask and diluted to volume. A 10 cc aliquat is made basic with 1 N KOH and evaporated to near dryness under a stream of nitrogen. Five cc of distilled water is added and 1 N HCl is added dropwise to obtain a pH between 1 and 2. the resultant acidic solution is extracted with three 2 cc portions of diethyl ether. The ether extracts are combined in a 10 cc volumetric flask.

G. C. Conditions

Column: 12' (1/8" O.D. SS) 20% DC-200 + 10%
Bentone 34 on 100/110 mesh ABS
Oven Program: 70°C (4 minutes) to 180°C at 5°C/min.
Detector: Electron Capture - HP. 5840
Carrier: Argon/Methane (95/5) at 45 cc/minute

Preparation of Diazomethane Reagent

*The method for preparing the diazomethane regent is given in the DIAZALD^R literature from Aldrich Chemical Company, Inc.; 940 West St. Paul Avenue; Milwaukee, Wisconsin.

The Aldrich Chemical Company's procedure for "Preparation of Ethereal-Alcoholic Solution of Diazomethane" from DIAZALD is detailed below.

1. Preparation of ethereal-alcoholic solutions of diazomethane: Ethanol (95%, 25 ml) is added to a solution of potassium hydroxide (5 g) in water (8 ml) in a 100 ml distilling flask fitted with dropping funnel and an efficient condenser set downward for distillation. The condenser is connected to two receiving flasks in series, the second of which contains 20-30 ml ether. The inlet tube of the second receiver dips below the surface of the ether, and both receivers are cooled to 0°C.

   The flask containing the alkali solution is heated in a water bath to 65°, and a solution of 21.5 g (0.1 mole) of Diazald^R in about 200 ml of ether is added through the dropping funnel in about 25 minutes. The rate of distillation should about equal the rate of addition. When the dropping funnel is empty, another 40 ml of ether is added slowly and the distillation is continued until the distilling ether is colorless. The combined ethereal distillate contains about 3g of diazomethane and must be stored in the freezer compartment of a refrigerator (shelf life is about 2 weeks or until weakly yellow).

   Diazomethane is not only exceedingly toxic, but its solutions have been known to explode quite unaccountably. Hence, ALL WORK WITH DIAZOMETHANE, regardless of how it is generated, SHOULD BE CARRIED OUT BEHIND SAFETY SHIELD IN EFFICIENT HOODS. Use TEFLON sleeves on all ground glass joints.

APPENDIX III

cc: R. G. Parrish
J. Trotman
File PE-3

R-12004 REV. 8-65

DUPONT
ESTABLISHED 1802

E. I. DU PONT DE NEMOURS & COMPANY
INCORPORATED
WILMINGTON, DELAWARE 19898

TEXTILE FIBERS DEPARTMENT
Pioneering Research Division

Experimental Station
Wilmington, Delaware
June 23, 1975

TO: M. A. Forte
Spruance Plant
Richmond

FROM: I. M. Sarasohn

[redacted] OFF-GAS ANALYSIS

The purpose of this memorandum is to summarize our data concerning analysis of off-gases from a sintered Teflon® yarn submitted by you to this laboratory a number of weeks ago (M. A. Forte to I. M. Sarasohn, memorandum, May 8, 1975).

This pyrolysis experiment was carried out in a hot quartz tube in flowing air. The sample was heated rapidly from room temperature to 305°C (~20-30 min); the temperature was then slowly increased to 315°C over a two hour period in a simulation of your process. The resulting effluent was swept into a collection trap at -78°C and the stripped air was collected in a Saran® gas bag which was sampled at the end of the run and analyzed by mass spectrometry to insure the absence of significant quantities of an untrapped gas; only air and CO_2 were detected in the gas bag.

Condensed liquid from the cold trap was injected into a gas chromatograph for separation prior to mass spectroscopic analysis, G.C. conditions being chosen to emphasize lower molecular weight materials. The effluent from the G.C. column was split into two streams, one going to the flame ionization detector (FID) for rough quantitation, the other going directly into the mass spectrometer using suitable pressure-dropping and enriching devices. Concentration levels were estimated from FID peak areas using the measured response factor for n-heptane. These levels are reported at the bottom of each table in terms of µg n-heptane/µl injected and µg n-heptane for the entire trap assuming unit density for the trap

contents. Apparently, the trap and side arm condensate contained at least 90% water, based on these figures. Except for water, CO, CO_2, and formaldehyde which exhibit no FID response, calculated amounts should be in error by no more than a factor of 5 or 10 depending on the nature of the specific material in question and can be reasonably estimated from published values of FID response factors by consulting the literature. Measured weight gain of the trap is recorded in Table I, but some material condensed in the gas transfer line upstream of the trap (i.e., trap side arm), preventing precise quantitative measure of material evolved by the sample. The condensation collected from the trap side arm was analyzed separately (Table II).

This work was charged to 8416-05502-2210-002.

IMS:rkc
attachments

TABLE I

Sample: [redacted] Yarn
Sample Wgt.: 1.6676g
Sample Wgt. Loss: 0.0938g
Trap Wgt. Gain: 0.0159g
Temperature: R.T. to 305° (1/2 hr)
305° to 315° (2 hr)
Air Flow Rate: 6 ml/min

Tentative Identification	G.C. Area	% (A/A)
Water, CO, CO_2, Formaldehyde	N.R.	—
Methanol	.06	.8
Acetaldehyde	.66	9.1
Ethanol	.03	0.5
Acrolein	.05	0.7
Acetone	.34	4.6
Acetic Acid	.02	0.3
Propionaldehyde	.01	0.2
1,3-Dioxolane	.04	0.6
Methyl Vinyl Ketone?	.05	0.7
Biacetyl?	.24	3.4
Mixture: 2-Methyl-1,3-Dioxolane + Crotonaldehyde or 2,5-Dihydrofuran	.25	3.4
p-Dioxane	1.09	15.0
Methylfuran	.04	0.6
Furfural	3.41	47.5
Furfural Methyl Ketone	.09	1.3
5-Methyl-2-Furaldehyde	.53	7.4

Total G.C. Area 7.244 mv-min (1.6 µl inj)
Organic Equiv. 40.8 µg/µl or 649 µg (entire trap)
1 Peak Unidentified 1-2% (A/A)

TABLE II

Side Arm Condensate
15 µl Recovered

Tentative Identification	G.C. Area	% (A/A)
H_2O, CO, CO_2, Formaldehyde	N.R.	—
Acetaldehyde	.02	.4
Formic Acid	Trace	.1
Pyruvaldehyde	.13	1.9
Acetic Acid	2.02	29.9
Hydroxy-2-Propanone	.25	37

Total G.C. Area 6.770 mv-min (1.4 µl)
Equiv. Organics 43.6 µg/µl or ≈1300 µg (entire sample*)
11 Peaks Unidentified 1-18% (A/A)

* Assumes 50% recovery of side arm condensate

INDEXING APPENDIX

Abstract

A survey of potential exposure sites for FC-143 in the [redacted] Manufacturing facility is presented. The fate of the fluorosurfactant in the [redacted] process is also shown. It was concluded from the study that employee exposure to the material is negligible. Analytical method development for measurement of FC-143 via gas chromatography of methyl esters and detection by electron capture detector is discussed. Methods for FC-143 in air, on solids and in [redacted] dispersion are given.

Indexing Subjects

1. Perfluorooctanoic acid (FC-143) in air.
2. Perfluorooctanoic acid (FC-143) physical properties.
3. Gas chromatography of perfluorooctanoic methyl ester with electron capture detection.

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