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TO: J. P. YUK
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FROM: C. S. COPE *C. S. Cope*
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CONCENTRATION LEVEL OF C-8 FLUOROSURFACTANT
IN
[REDACTED] TE-3311 DISPERSION

INTRODUCTION

We spoke by telephone about two weeks ago concerning the level of C-8 fluorosurfactant present in TE-3311 dispersion transferred from our Department to yours for use in making **[REDACTED]** fibers by the viscose process. At about the same time, I also had telephone discussions with A. A. Wright and M. A. Forte of your Department on the same subject. My understanding from these discussions is as follows:

- Analyses at Spruance of the measurable C-8 levels in TE-3311, primarily by extraction followed by esterification and G. C. analysis, have shown about 200 ppm (100-300 ppm range) to be present.

- Since the level of C-8 used in the recipe for preparing TE-3311 would lead us to expect about 1200 ppm to be present, it has been concluded that the unaccounted-for portion of the C-8 is inaccessibly held ("trapped") within the PTFE polymer itself. Attempts at Spruance to locate the "missing" C-8 elsewhere in the spinning process or on the final product have been unsuccessful.

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These findings were not in accord with our general experience with regard to C-8 in PTFE dispersions, although no specific data were available along these lines for TE-3311 in particular. Accordingly, I set about determining the level of C-8 in TE-3311, using analytical techniques we have applied and found reliable in the past.

DISCUSSION

The TE-3311 sample used in the following analyses was from a recent lot, [REDACTED]

Analytical Procedures

None of the methods of C-8 assay available to us can be applied directly to "Triton" - stabilized PTFE dispersions. It is first necessary to separate the C-8, for which purpose the technique of adding a strong, non-volatile acid (phosphoric acid) and water to the dispersion and distilling over the volatile C-8 acid (with water) was employed. A detailed description of this procedure is appended.

The distillate fractions, containing successively lower concentrations of C-8 until essentially no further carry-over of C-8 was taking place, were analyzed by a variety of complementary methods:

- NaOH titration
- Chloroform/methylene blue analysis
- Cetyltrimethylammonium bromide titration.

NaOH Titration

Titration with NaOH (0.1 N) to a phenolphthalein pink end-point gives results, when expressed as equivalent C-8 APFC (eq. wt. = 431), which are known to be high by this method, presumably because of the presence of small amounts of other volatile acids carried over in the distillation.

Chloroform/Methylene Blue Analysis

The chloroform/methylene blue analysis, regarded as the preferred method of assay in this case, is based on formation of a neutral complex between the cation of methylene blue hydrochloride and the C-8 anion. The blue-colored complex is then partitioned between fixed amounts of water and chloroform. The greater the level of C-8 present, the more intense the blue coloration in the chloroform layer. Measurement of the absorbance maximum at about 633 nm in the visible region by spectrophotometer serves as a measure of C-8 assay, the relationship between absorbance and concentration being established by measurement of prepared standard solutions of known C-8 APFC concentration. It has been demonstrated that "Triton" X-100 and citric acid (used at low levels in TE-3311 for chelation of any iron adventitiously present) do not interfere in the analysis of distillate samples by this method. A description of the chloroform/methylene blue method is appended.

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(Incidentally, as you are no doubt aware, chloroform is now designated as a Suspect Carcinogen, and we would therefore prefer to avoid its use. However, a brief study of methylene chloride and "Freon" 113 as possible substitutes indicated that neither was suitable.)

Cetyltrimethylammonium Bromide Titration

The titration analysis using cetyltrimethylammonium bromide (CTMAB) solution (0.100% w/v) is based on the finding in this Department that the cation of CTMAB forms a neutral 1:1 molar complex with the C-8 anion. This complex is not surface-active. Hence, [redacted] raw dispersion may be used as an "indicator" for the titration; when the equivalence point is needed, the C-8 is no longer effective as a surface-active agent to keep the polymer particles dispersed, and they settle out as a flocculent gel, leaving the aqueous phase clear. Actually, raw [redacted] FEP dispersion (HFP/TFE copolymer) is preferred as indicator, since it contains less C-8 to begin with and also happens to give a perfectly clear aqueous supernate when the equivalence point is reached.

The CTMAB method, like the chloroform/methylene blue method, is relatively specific for C-8, though "Triton" X-100, if present, would certainly be expected to interfere. A disadvantage of the CTMAB method, insofar as your possible use of it would be concerned, is that raw FEP dispersion has a short shelf-life and is difficult to ship without coagulation occurring. A description of the CTMAB method is appended.

Analytical Results

A summary of our analytical results on the TE-3311 sample tested is given in Table I. Expressed as equivalent C-8 APFC, the results obtained are:

<u>Method Used</u>	<u>ppm C-8</u> (based on total dispersion)
NaOH Titration	1950
CHCl ₃ /Me Blue	1140
CTMAB Titration	960

Recognizing that the NaOH titration results were expected to be high, the agreement among the different results is considered good. The indicated concentration of C-8 is at the level expected from our previous general experience, and several-fold higher than that obtained by extraction/GC analysis. We conclude that the C-8 present can be recovered and accounted for, and that little or no C-8 is located within the PTFE particles themselves, which, incidentally, are known to be solid and very highly crystalline. We do know that there is an equilibrium between C-8 adsorbed on the surface of the particles and C-8 dissolved in the aqueous phase. At room temperature, the majority of the C-8 is adsorbed.

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Note the high sensitivity of the CHCl_3 /methylene blue method, which permits reliable determination of C-8 in amounts as low as 10 micrograms. For this reason, dilution of distillate samples (typically by 20-fold) was required prior to C-8 assay by this method.

One of the main attractions of the analytical procedures just described is that they should be applicable as well to determination of residual C-8 in the PTFE fiber products you produce at

[REDACTED]

One point we should like to emphasize with respect to the C-8 analysis is that, although we have now apparently succeeded in accounting for the C-8 expected to be present, the result does not directly answer the question as to how accessible this C-8 is in terms of contact by personnel, e.g., by skin contact, or by inhalation of vapors evolved on heating during fabrication operations. Information on this subject could come only through more extensive testing of a more direct nature.

Program

I hope in the near future to "close the balance" on C-8 in the production of TE-3311 dispersion by measuring, using the same methods given here, the C-8 concentration in the supernatant layer which is produced (and discarded) during the thermal concentration step in which raw dispersion (45% solids known C-8 content) is treated with "Triton" X-100 and raised to the 60% solids content of TE-3311. When these results are in hand, I shall let you know.

CSCope/ld1

Attachments: 1 Table
3 Analytical Methods (Spruance copies only)

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