

APPENDIX 2

ANALYTICAL TECHNIQUE USED TO DETERMINE C-8 CONCENTRATION IN AQUEOUS SOLUTION

The basis for the analytical technique used to determine the C-8 concentration in an aqueous solution was Polymer Products Department method Code No. T 212.2000 (revised 8-7-81). The referenced method is for the determination of equivalent C-8 dispersing agent in FEP aqueous dispersion. By using the method with and without the addition of an aliquot of an unknown C-8 sample, it was possible, by difference, to determine the concentration of the unknown C-8 sample.

The following is a description of how the method was adapted for use.

A 'large' source of aqueous FEP dispersion was obtained for use in this analysis. The dispersion was stored in a plastic container until needed. When used, the dispersion was gently mixed and then filtered through 'cheese cloth' to remove large pieces of coagulated dispersion. The filtered dispersion was used for all samples for the day's analyses.

For purposes of this technique, 10 +/- 0.01 grams of FEP dispersion were used, made up to 100 ml with demineralized water using a graduated cylinder.

The equivalent C-8 concentration in the FEP dispersion was determined using Method T 212.2000. This concentration was considered the 'blank'. In actual usage, only the volume of CTMAB (cetyltrimethylammonium bromide, 1.0 gm/liter) required to coagulate the FEP dispersion was recorded.

A second measurement was made, similar to the first, but where a measured volume of the unknown C-8 solution was added to the FEP dispersion. In the second measurement, additional CTMAB would be required to complex with the additional C-8 present before the FEP dispersion would coagulate. By difference (the amount of CTMAB required for the unknown sample relative to the 'blank'), the quantity of the unknown additional C-8 could be determined and, hence, its concentration.

The theory upon which the method is based is that each mole of CTMAB will complex with a mole of equivalent C-8 and that the complex will have no dispersant properties. When sufficient C-8 has been removed from the solution, the FEP dispersion will be destabilized and coagulate. The supernate will be clear after the dispersion 'breaks'.

This method requires the laboratorian to determine the point when enough CTMAB has been added to the dispersion sample so that the liquid above the coagulated dispersion is clear. This point was not always easy to determine and at times varied between laboratorians. However, within a single day using the same experienced laboratorian, the results appeared to be internally consistent.

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Below is the equation used in this technique:

$$Cx = \frac{(Vx - Vb)}{Vcx} \times 1000 \times \frac{431}{364.48}$$

- here Cx Concentration (in mgm/l) of the unknown C-8 solution.
- Vx Volume (in mls) of CTMAB solution required to coagulate the FEP dispersion and the aliquot of unknown C-8 solution.
- Vb Volume (in mls) of CTMAB solution required to coagulate the FEP dispersion without any added C-8 solution.
- Vcx Volume (in mls) of the aliquot of unknown C-8 solution.
- 1000 Concentration (in mgm/l) of CTMAB standard solution.
- 431 Molecular weight of C-8 (as ammonium perfluorooctanoate).
- 364.48 Formula weight of CTMAB.

Typical results are shown below:

$$Cx = \frac{(22.6 - 8.9)}{4.0} \times 1000 \times \frac{431}{364.48} = 4,050 \text{ mgm/l}$$

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Polymer Products Department

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TEFLON* FEP FLUOROCARBON RESIN, AQUEOUS DISPERSION .

Equivalent C-8 Dispersing Agent

I. Scope and Applications

This method is applicable to determining the equivalent C-8 dispersing agent in FEP dispersion.

II. Principle

Percent C-8 is determined by titrating FEP dispersion with a solution of cetyltrimethylammonium bromide.

III. Interferences

IV. Sensitivity, Precision, and Accuracy

The precision (σ) of this test based on five runs made on one sample is 0.0005 with an $\bar{X}$ of 0.1254% C-8.

V. Apparatus

VI. Reagents

1. Cetyltrimethylammonium bromide (CTMAB), 1 g/liter (RC 190.127)

VII. Operating Conditions

VIII. Safety and Health Precautions

As dispersion or coagulation effluent can contain C-8, contact with dispersion should be avoided by wearing the proper gloves. The current allowable exposure limit for C-8 is below 1 ppb and C-8 is suspected of being teratogenic.

IX. Procedure

1. Weigh 25 ($\pm$ 0.01) g FEP dispersion into a 600-ml beaker.
2. Add 200 ml (grad cyl) demin water to the dispersion.
3. Stir the beaker using a magnetic stirrer until the dispersion and water are mixed (about 30 seconds).
4. Fill a buret with 1 g/liter CTMAB solution. Record the reading.

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5. Using the buret, add CTMAB solution to the dispersion slowly, with constant magnetic stirring. As CTMAB is added, polymer will begin to coagulate. When it appears that most of the polymer has coagulated, stop adding CTMAB and then stop agitation a few seconds later.
6. Allow the bulk of the polymer to settle out and observe the supernatant liquid. If it is cloudy, resume agitation and add 0.2 to 0.5 ml of CTMAB.
7. Stop agitation and allow to settle.
8. Repeat steps 6 and 7 until the supernatant liquid is perfectly clear. A clear supernatant liquid is the end point of the titration.
9. Record the buret reading.
10. Find specific gravity of the dispersion and percent solids, using Method T 202.804.
11. Calculate % C-8 and g C-8/g FEP.

X. Calculations

1. Calculation of % C-8

mL CTMAB = (step 9 - step 4)

$$\% \text{ C-8} = \frac{\text{mL CTMAB} \times 0.1184}{\text{wt of dispersion, g}}$$

$$0.1184 = \frac{[0.0275(\text{Normality of CTMAB})] \times [431(\text{M.W.})] \times 100(\%)}{1000 (\text{mg/g})}$$

2. Calculation of g C-8/g FEP

% FEP = % solids (step 10)

$$\% \text{ C-8 from step 1. Calculation } \frac{\text{g C-8}}{\text{g FEP}} = \frac{\% \text{ C-8}}{\% \text{ FEP}}$$

Report two significant figures, i.e., .091%.

XI. Calibration

XII. Notes

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XIII. References

1. Couture, M. J., Washington Works Technical Laboratory
Notebook No. 1026, pp 88-89
2. Plastics Department Laboratory Test Method T 202.8040
3. Original Method, Washington Works Technical Laboratory, 3-11-71
4. First Revision, Washington Works Technical Laboratory, 2-16-76

Revised to reflect the use of C-8 instead of C-9 in FEP polymerization.

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