D. Rozzi
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Inter-Office Memo

TENNECO CHEMICALS, INC.

To H. B. Carr At Burlington Date November 4, 1969

From F. W. Kanzler At Burlington Copy to H. H. Duhamel
E. Farber
J. C. Fisher
A. P. Gallmayer
E. J. Hourihan
E. L. Kanyok
D. Johnson
C. W. Johnston
M. K. Rosen
M. C. Spalding
P. R. Scarito
W. D. Wesely
M. W. Williams
Burlington P. E.

Subject Technical Memorandum
Infra Red Analysis of Bound
Acetate in Vinyl Chloride/Vinyl
Acetate Copolymers

SUMMARY

1. An infra red method has been developed for the analysis of bound acetate in vinyl chloride/vinyl acetate copolymers.

2. The analysis is accomplished by scanning a dissolved copolymer sample in a sealed cell from 5.55 μ (1800 cm^{-1}) to 6.06 μ (1650 cm^{-1}) on the Perkin-Elmer 700 infra red spectrophotometer. The absorption of the carbonyl group at 5.75 μ (1740 cm^{-1}) is utilized as the analytical point for comparing the absorbances obtained for samples to that of known concentration standards.

   B.A.C.M. #200 is attached to provide a detailed outline of the analysis.

3. Correlation studies with the A & E Laboratory indicate excellent agreement (Table 1). A "t test" of significance at 95% confidence performed on this data showed that the results from the two laboratories are statistically similar.

4. The return time for this analysis is approximately 2 hours.

RECOMMENDATIONS

1. Correlation studies with the A & E Laboratory should be continued at a periodic frequency.

2. The method should be introduced as a grading method for copolymer resins.

3. The data should be utilized to establish copolymer plant process capability and to assure consistency between lots.

4. A program should be initiated to study in-lot variations of the bound acetate level.

DISCUSSION

1. Selection of the Analytical Point

Several analytical points for quantitative estimation of bound acetate in vinyl chloride/vinyl acetate copolymers are discussed in (1.). Attempts were made to calculate the ratio of the bands at 7.0μ (1430 cm^{-1}) and 7.5μ (1335 cm^{-1}) versus the band at 7.3μ (1370 cm^{-1}) for different concentrations. The accuracy was found to be very poor since the levels of the bound acetate could only be estimated. This method also had the disadvantage of requiring the casting of a thin film (ca. 0.001") from solution which is not a practical step in a routine laboratory analysis. A method described by Weinberger, Kagarise (2) was attempted next. Since this method also employed a cast film it was dismissed for the above mentioned reasons.

To eliminate the requirement of thin film casting, a sealed cell was constructed from sodium chloride crystals and spacers to obtain an approximate thickness of 0.1 mm. The exact thickness of the cell was determined from the interference pattern of the empty cell to be 0.112 mm. Considering the excellent resolution and the freedom from interfering absorbances, the band at 5.75μ (1740 cm^{-1}) was selected as the analytical point. Standards of known bound acetate levels were used for calibration purposes.

2. Operating Parameters

Sample size: 4.0 gm of copolymer
Solvent: Tetrahydrofuran, reagent grade, 100 ml
Scan: 5.55μ (1800 cm^{-1}) to 6.06μ (1650 cm^{-1})
Analytical point: 5.75μ (1740 cm^{-1})
Cell: Sodium Chloride crystals, 0.112 mm thickness

3. Calibration

Initially a standard copolymer provided by the A & E Laboratory with a known level of bound acetate was used for

calibration purposes. Since this level was in the 10% bound acetate range and the pen speed on the Perkin-Elmer 700 is not adjustable, a multi level standardization was decided upon to compensate for nonlinearity of the instrument response. Due to lack of availability of a high level bound acetate standard, a blend of a vinyl chloride homopolymer and a vinyl acetate homopolymer was prepared. The blends were made up in levels of 5%, 10%, 15% polyvinyl acetate in polyvinyl chloride. The standards were individually prepared for each series of samples run.

Initial correlation data with the A & E Laboratory showed good agreement in the levels of about 9.5% to about 12.0% bound acetate (Table 2). However, almost all high level (13% to 15%) data showed a considerable amount of disagreement between laboratories. (Memo to H. B. Carr from F. W. Kanzler, dated February 17, 1969). Subsequent investigations of various possible sources of error led to the following steps:

a. Pen Speed
   As mentioned above, it was determined that the constant pen speed of the P & E 700 resulted in an overshoot on low absorbances and undershoot on high absorbances. For this reason, calibration standards that cover the entire range of targeted bound acetate are required for meaningful analyses.

b. Base line
   For the calculation of the bound acetate levels, the absorbance of a sample is compared with the absorbance of a standard. This absorbance is read at 5.75μ (1740 cm^{-1}) and is measured as the distance from the maximum transmittance to the minimum transmittance of the carbonyl band. To find a reproducible point at maximum transmittance, a base line is used. Initially, in Burlington, the base line was drawn from the maximum transmittance at 5.62μ (1780 cm^{-1}) to the maximum transmittance at 5.95μ (1680 cm^{-1}). A study to compare the above type of base line with a base line drawn as in Flemington from a point at about 5.62μ (1780 cm^{-1}) parallel to the transmittance lines on the chart paper was made. The results shown in Table 3 show a better agreement with the Flemington Laboratory when using the latter base line.

C. Instrument Correlation
   A set of two samples was run on both the Flemington and Burlington infra red spectrophotometer. Table 4

shows the results of this study. As can be seen from the data, the position on the chart where the peak is started has a great influence on the final result. Both instruments show good agreement when the methods which are presently used in the two laboratories for the determination of the bound acetate level are compared.

d. Change of Sample to Solvent Ratio

To overcome the nonlinearity of the instrument response, it was decided to alter the sample size and/or the solvent content of the sample to be analyzed. This was done to achieve the same absorbance for all bound acetate levels. Inaccurate results and nonreproducibility led to the dismissal of this step. In the future, a variable thickness cell may be tried to allow for change in absorbance.

4. Planned Correlation

Two copolymer samples of a 382 and a 315 type copolymer will be run on a round robin basis to find the correct level of bound acetate. These samples will serve as standards and will allow for an elimination of the blends.

LITERATURE

1. J. Haslam, H. A. Willis, Identification and Analysis of Plastics.

2. L. A. Weinberger, R. E. Kargarise, O.T.S. Bulletin No. PB 111438.

F. W. Kanzler

FWK/rjl

Attachment

TABLE 1

Bound Acetate Analysis

Sample ID	Resin Type	% Bound Acetate		Specification Range
		Flem.	Burl.	
609066	314	14.5	14.4	13.5-15.3
619150	315	15.0	14.8	13.5-15.3
639025	382	9.7	10.2	9.2-10.6
619155	315	15.8	15.1	13.5-15.3
719008	315-2	12.7	12.5	13.5-15.3
719017	315-2	14.2	14.0	13.5-15.3
659055 Pre.	385	14.8	14.4	13.1-14.9
659055 Lot	385	14.5	14.2	13.1-14.9
649040	384	14.0	13.8	13.1-14.9
659062	385	13.8	13.8	13.1-14.9
699019 Pre.	389	10.8	11.1	10.5-12.0

Analyst: J. E. Ravelli

TABLE 2

Bound Acetate Analysis

Correlation Date November, 1968

Sample ID	Resin Type	% Bound Acetate		Spec. Range
		Flem.	Burl.	
648845	384	13.0, 13.9	14.6, 14.5	13.1-14.9
658050	385	13.1, 13.6	14.5, 14.0	13.1-14.9
658055	385	12.9, 13.3	14.0, 13.6	13.1-14.9
698035	389	10.3	10.5, 10.0	10.5-12.0
698036	389	11.8	11.7, 11.7	10.5-12.0
698040	389	10.5	9.9	10.5-12.0
698041	389	9.9, 11.0	11,1, 10.3	10.5-12.0

Analyst: F. W. Kanzler

TABLE 3

Bound Acetate Analysis

Base line Comparison

Sample ID	Resin Type	% Bound Acetate			Spec. Range
		Flem.	Burl.	Burl. (Flem. Base line)	
719003	315-2	13.3	12.8	13.1	13.5-15.3
719004	315-2	13.2	12.4	12.7	13.5-15.3
719005	315-2	13.3	12.7	12.8	13.5-15.3
719006	315-2	13.5	12.6	12.9	13.5-15.3
719007	315-2	12.9	12.8	12.8	13.5-15.3
619160	315	14.5	14.2	14.5	13.5-15.3
659061	385	13.1	12.5	13.1	13.1-14.9
619170	315	14.9	15.4	15.7	13.5-15.3
639030	382	10.1	10.2	10.3	9.2-10.6

Analyst: J. E. Ravelli

TABLE 4

Bound Acetate Analysis

Base line and Peak Location Study*

Sample ID	Orig. Analysis Flem.	Burl.	Resin Type	Spec. Range	Flemington Infra Red Spectrophotometer Normal Flem. Analysis (Peak Start at 100% T) 1969 10/16	10/24	Peak Start at 75% T 10/24/69	Peak Start at 92% T 10/24/69	Burlington Infra Red Spectrophotometer Normal Burl. (Peak Start at 75% T) 1969 10/16	10/24	Flem. Base line Technique (Peak St. at 75% T 10/16	10/24	Peak Start at 90% T 10/24/69
659055	14.5	13.5	385	13.1-14.9	13.9	13.9	13.3	14.1	14.1, 13.9, 13.8	13.8	14.4, 14.4, 14.1	13.9	13.7
619170	14.9	15.2, 15.4	315	13.5-15.3	15.1	15.7	14.4	15.7	15.2	15.4	15.6	15.7	14.8, 14.9
619202 (Std.)	-	-	315	13.5-15.3	-	14.3	13.6	14.4	-	14.0	-	14.2	14.3

*The peak location study on the Burlington infra red spectrophotometer was only run on two types of peak start transmittance ranges. Since the 90% T peak start showed lower results, the Flemington type analysis at 100% T was not performed in Burlington.