I-184 (50M)

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INTER-OFFICE MEMO **TENNECO CHEMICALS, INC.**

TO Route List AT DATE October 19, 1970

FROM E. Farber AT Flemington COPY TO H. B. Carr
E. J. Hourihan
M. W. Williams

SUBJECT Vinyl Acetate Monomer

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LM
file

In addition to the tests now proceeding (e.g., LOP 853-1) to ascertain the usefulness of U.S.I.'s monomer, the attached notes from Leonard's article on VAM which appeared in High Polymers 24, (1), 263 (1970) and the Borden test procedures may also serve as guidelines for possible comparisons and evaluations of VAM.

E. Farber

EF:df
Att.

Borden Chemical

THE "BORDEN DILATOMETER TEST" FOR REACTIVITY OF VINYL ACETATE MONOMER

The use of dilatometry to study polymerization kinetics has been used in scientific researches for some time. This method has now been adapted by the Borden Chemical Company to give a very sensitive laboratory test for monomer purity. Its outstanding advantages are that it provides quantitative polymerization rates and induction periods in a very short time with a few milliliters of sample and a simple apparatus. This data, in addition to indicating whether the monomer polymerizes at a normal or abnormal rate, also provides specific information as to whether such abnormalities are caused by the presence of polymerization "inhibitors" and/or "retarders." Excellent correlation has been established between such test data and large scale polymerizations.

TEST METHOD

Apparatus:

1. Constant temperature bath (50°C ± 0.1°C test temperature). Bath liquid level should be high enough to cover top of dilatometer.

2. Dilatometer (See figure 1)

The Dilatometer stem is constructed of 2 mm. I.D. precision bore pyrex glass capillary tubing 230 mm. in length. The capillary stem is graduated in mms. with every 5th mm. mark being longer for ease of reading (precision bore capillary tubing may be purchased from Kontes Glass Co., Vineland, N.J.) and every 10th mark (1 cm.) being numbered. The numbering starts with zero at the top and increases downward. A graduated stem length of 200 mms. out of the 230 mm. total length has been found to be satisfactory. The spherical bulb at the bottom of the stem is about 10-12 ml. in volume. The vapor jacket surrounding the top of the dilatometer is made of 10 mm. I.D. pyrex glass tubing and is attached to the stem with a piece of rubber tubing. (Details of fabrication may be obtained from the Borden Chemical Co., Geismar, La.)

3. Hypodermic syringe equipped with 12 inch long metal needle of such diameter that it can be inserted into the 2 mm. I.D. stem. Alternatively, a piece of Teflon or other tubing may be used in place of the 12 inch metal needle.

4. Stoppered weigh flasks or Erlenmeyer flasks.

5. Time piece capable of being read in minute intervals.

Materials:

1. Benzoyl peroxide recrystallized. (See procedure at end of this article)

2. Vinyl acetate monomers.

Borden Chemical

GAS CHROMATOGRAPHY OF VINYL ACETATE MONOMER

The Borden Dilatometer Test for vinyl acetate monomer has already been presented as a means of measuring quantitatively the reactivity of a given monomer. The gas chromatograph provides a very sensitive instrument for characterizing the nature and amount of impurities present in a given monomer. A combination of the dilatometric and gas chromatographic data provides an excellent measure of the quality of a given monomer. The Borden Chemical Company uses both of these analytical techniques (in addition to other more standard analyses) for continuous routine quality control testing, in order to insure the highest product quality and uniformity.

Figure 3 shows a comparison between the gas chromatograph for Borden's commercial vinyl acetate and those of three other commercial producers. These chromatographs were run one immediately following the other with the identical instrument settings. Impurities numbered as 1, 2 and 3 have not been positively identified as yet. The outstanding purity of Borden's monomer is evident from the fewer number of peaks and by the much lower peak heights (and areas under these peaks).

Analysis Data

Instrument:	Beckman GC-2A (TC and HF detection in series)
Column Packing:	50:50 Pluronic P84 – Fatty acid ester, 35% on Chromosorb P Support
Column Length:	8 feet, 1/4 inch diameter aluminum
Column Temp.:	120°C, isothermal
Carrier Gas:	Helium 30 psi inlet
Sample Size:	5 microliter

Hydrogen Flame Detector

Hydrogen:	3.9 psi
Oxygen:	5.0 psi
Sensitivity:	5×10^3 attenuation
Recorder:	Fisher 1 M.V. full scale deflection
Chart Speed:	1 inch/Min.

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MONOMERS

oducers of vinyl acetate monomer ble 8). It is, of course, important id that monomer produced in the ve somewhat different properties.

8
for Vinyl Acetate

of Air Reduction Company, Inc. (52)

	Typical analysis
9.8% minimum	99.9%
.010% maximum	0.005%
.005% maximum	0.002%
.04% maximum	0.02%
Colorless to light yellow	Colorless
72.3–73.0°C	72.3–72.9°C
0.9335–0.9340	0.9336
14–17 ppm	15 ppm
275–325 ppm	300 ppm
130–165 min	140 min
none	none

a f America (46)

0.010 wt % maximum
99.9 wt % minimum
0.005 wt % maximum
0.04 wt % maximum
72.5–73.0°C
0.9335–0.9340
5 maximum
130–150 min

emical Company (43)

99.8% minimum
0.015% maximum
0.007% maximum
0.04% maximum
0.9335–0.9345
5 maximum
72.3–73.0

12–15[b]
None

130–165
0.20 minimum
220 maximum

TABLE 8 (*continued*)

D. Monsanto Chemical Company (48a)

Form	Clear liquid free from suspended matter
Color	5 maximum (APHA platinum–cobalt scale)
Assay	99.8% minimum
Aldehydes	0.013% maximum (calculated as acetaldehyde)
Acidity	0.007% maximum (calculated as acetic acid)
Water	0.04% maximum
Nonvolatile matter	0.015% maximum
Distillation range	72.3–73.0°C at 760 mm
Specific gravity @20/20°C	0.9335–0.9345
Inhibitor	14–17 ppm hydroquinone

[a] Shipments with longer activity time can be patterned to customer requirements.
[b] Available with 3–5 ppm hydroquinone on request.
[c] Borden reactivity test by dilatometer.

IV. ANALYSIS

Gas-liquid chromatography is an excellent tool for determining the nature and amount of impurities present in monomer samples. A technical data bulletin (43) of one of the manufacturers gives detailed information on the instrument involved, column packing, sample size, and sensitivity of the method.

The Borden Chemical Company (43) has introduced the "Borden Activity Test" as a means of specifying the reactivity of vinyl acetate in polymerization. This dilatometric method provides information on the nature of impurities which influence polymerization rate, differentiating between those which are polymerization inhibitors and those which are retarders. Figure 4 shows data obtained from polymerization of vinyl acetate at 50°C using 0.5% benzoyl peroxide as initiator. This information leads to determination of induction time (here 193 min) and initial rate of polymerization (here 0.24%/min). It has been stated that a high-purity commercial monomer inhibited at the 15 ppm hydroquinone level shows an initial polymerization rate of 0.20–0.24%/min and that, again at 15 ppm hydroquinone, induction times are normally 180–200 min. Lower rates than 0.20%/min indicate the presence of polymerization retarders. Higher induction times than 200 min indicate the presence of an inhibitory impurity.

Acetaldehyde as an impurity in vinyl acetate is determined by adding a sample of the monomer to excess 1*N* sodium bisulfite solution. The unreacted bisulfite is back-titrated with 0.1*N* iodine solution using starch as indicator.