

TENNECO CHEMICALS, INC.

TENNECO CHEMICALS, INC.

TO	J. C. Fisher	AT	Flemington	DATE	August 14, 1969
FROM	H. B. Carr	AT	Burlington	COPY TO	F. W. Kanzler
SUBJECT	B.A.C.M.'s				M. C. Spalding File

The following two B.A.C.M.'s are being issued by the Analytical Control Group:

B.A.C.M. #3 - Determination of Percent Active Oxygen and Assay of Lupersol 11 (t-Butyl Hydroperoxide)

This method provides the means for assaying the purity of this low temperature perester catalyst as an incoming raw material control test. Due to the critical storage requirement, a test frequency on stored catalyst will be established. A separate set of test conditions is outlined for t-butyl hydroperoxide since this impurity, which can be formed by hydrolysis of the perester, will inhibit polymerization.

B.A.C.M. #400 - Determination of Phenol in Recovered Vinyl Chloride Monomer

Phenol is added to recovered monomer to inhibit polymerization. Since this addition should be carefully controlled, this test method will be performed at a frequency necessary to assure that the proper level of inhibitor is maintained.

H. B. Carr

HBC/rjl

Attachment

TENNECO CHEMICALS, INC.

TENNECO PLASTICS DIV.

Burlington, New Jersey

B.A.C.M. #3

DATE ISSUED: August 7, 1969

Determination of Percent Active Oxygen and Assay of Lupersol 11
(t-Butyl Peroxypivalate)

APPLICATION:

The determination of the active oxygen content and assay of Lupersol 11 is important for the polymerization process since a poor initiator will help to delay the start of the reaction, resulting in an increase of the cycle time.

The initiator sample is dissolved in ethanol, hydrolyzed with sodium hydroxide in the presence of sodium arsenite. The solution is acidified and the excess sodium arsenite is titrated with ceric ammonium sulfate solution using osmium tetroxide as a catalyst and ferroin indicator. t-butyl hydroperoxide is determined and subtracted from the total active oxygen found to calculate the percent t-butyl peroxy-pivalate.

APPARATUS:

1. Vials, shell, short style, 12mm OD, 35 mm high (SGA #V-5320)
2. Beakers, volumetric, 400 ml
3. Magnetic stirrer and stirring bar
4. Pipette, 50 ml, 2 ml
5. Graduated cylinder 50 ml, 250 ml
6. Hot water bath heated to 88° - 95°C
7. Bottles, dropping, ground-in pipette, capacity 2 oz. (SGA #B-5840)
8. Burette, straight stopcock, Teflon plug, 50 ml, 0.1 ml division
9. Analytical Balance with readout to 0.1 mg
10. Iodine flask, 250 ml
11. Erlenmeyer flask, 250 ml

REAGENTS:

1. Ethyl alcohol, 3A reagent
2. Sodium arsenite solution (NaAsO_2), 0.1N (Dissolve 12.99 gm of NaAsO_2 in 300 ml of water, make up to 1000 ml, mix well)
3. Sodium hydroxide (NaOH), 1N (Dissolve 40 gm of NaOH in 1000 ml of water)
4. Sulfuric acid (H_2SO_4), 4N (Transfer carefully 120 ml of concentrated H_2SO_4 into 400 ml of water. Cool and make up to 1000 ml, mix well)
5. Osmium tetroxide, 0.01M solution in 0.1M H_2SO_4 (G. Fredrick Smith Chemical Co., Item #64)
6. Ferroin (1,10 - Phenanthroline ferrous sulfate 0.01M solution in water, G. Fredrick Smith Chemical Co., Item #166)
7. Ceric ammonium sulfate solution 0.1N in 1N H_2SO_4 (G. Fredrick Smith Chemical Co., Item #258)
8. Sodium iodide (NaI) 10% solution (Dissolve 39.54 gm in 500 ml of acetone. Filter through Whatman #1 paper)
9. Sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ or $\text{Na}_2\text{S}_2\text{O}_3$), 0.1N (Dissolve 24.82 gm of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ or 15.8 gm of $\text{Na}_2\text{S}_2\text{O}_3$ in 200 ml of water, make up to 1000 ml)
10. Iodine (I) 0.1N (Dissolve 12.69 gm of I in 300 ml of methanol, make up to 1000 ml, mix well)
11. Arsenious oxide (As_2O_3), Reagent grade
12. Sulfuric acid (H_2SO_4) 5N, (Transfer carefully 150 ml of concentrated H_2SO_4 into 400 ml of water. Cool and make up to 1000 ml)
13. Sodium hydroxide, Reagent grade
14. Hydrochloric acid, concentrated, Reagent Gr.
15. Starch solution, indicator (Dissolve 1 gm of starch in 200 ml of boiling water and cool)
16. Sodium bicarbonate, Technical Grade

STANDARDIZATION:A. Ceric Ammonium Sulfate Solution, 0.1N

1. Weigh out and record to the nearest 0.1 mg about 0.20 gm of previously dried and

cooled arsenious oxide and transfer into a 250 ml Erlenmeyer flask.

2. Add 25 ml of water in which 2 gm of sodium hydroxide have been dissolved.
3. Warm and swirl gently until all particles of arsenious oxide have been dissolved. (Undissolved particles have a tendency to "climb" the sides of the Erlenmeyer flask due to surface tension)
4. Add 75 ml of water and 25 ml of 5N sulfuric acid. 2 drops of 0.01M osmium tetroxide solution and 2 drops ferroin indicator solution.
5. Titrate the pink solution with the ceric ammonium sulfate solution to be standardized to a pale blue 30 second end-point (Caution: the end-point is extremely sharp and changes from a pale pink to a pale blue very fast). (Note 1)
6. Repeat steps 1. through 5. twice and average results.

Calculation:

$$\frac{\text{Wt. of the As}_2\text{O}_3}{\frac{49.45}{1000} \times \text{ml of ceric ammon. sulfate used}} = \text{N of ceric ammonium sulfate sol'n.}$$

B. Iodine Solution 0.1N (Secondary Standard)

1. Weigh and record to the nearest 0.1 mg about 0.20 gm of previously dried and cooled arsenious oxide and transfer to a 250 ml Erlenmeyer flask.
3. Swirl gently until all particles of arsenious oxide have been dissolved.
4. Dilute the solution to 100 ml with water. Cool under running water.
5. Add 2 ml of concentrated hydrochloric acid and 10 gm of sodium bicarbonate.
6. Add 2 ml of the starch solution and titrate with the iodine solution to be standardized to a lavender-blue 30 second end-point. (Note 1)

- Repeat steps 1. through 6. twice and average results.

Calculation:

$$\frac{\text{Wt. of the As}_2\text{O}_3}{\frac{49.45}{1000} \times \text{ml of Iodine used}} = \text{N of Iodine solution}$$

C. Sodium Thiosulfate Solution, 0.1N

- Pipette 50 ml of previously standardized Iodine solution into a 250 ml Iodine flask.
- Titrate while stirring with the sodium thiosulfate to be standardized to a colorless 30 second end-point. (Note 1)
- Repeat steps 1. and 2. twice and average results.

Calculation:

$$\frac{50 \times \text{N of Iodine sol'n.}}{\text{ml of Sod. Thiosulfate used}} = \text{N of Sodium Thiosulfate solution}$$

PROCEDURE:

A. Active Oxygen and Assay

- Transfer into a 400 ml beaker 50 ml of 3A ethyl alcohol. Place a magnetic stirring bar into the beaker.
- Weigh into a previously cooled vial 0.2 - 0.3 gm for a 75% Lupersol 11 solution, or 0.3 - 0.4 gm for a 45% Lupersol 11 solution. Record to the nearest 0.1 mg.
- Drop the vial and contents into the 400 ml beaker and mix with a magnetic stirrer.
- While stirring, pipette 50 ml sodium arsenite solution and 25 ml of 1N sodium hydroxide solution into the beaker.
- Place the beaker into the hot water bath (88° - 95°C) for about 30 minutes or until the volume in the beaker is 75 ml. (It is imperative that all the alcohol has been evaporated).

6. Remove the beaker from the hot water bath and let it cool to room temperature.
7. Add 40 ml of 4N sulfuric acid.
8. Add 2 drops of 0.01M osmium tetroxide and 2 drops of ferroin indicator solution.
9. Titrate with 0.1N ceric ammonium sulfate solution to a pale blue end-point. (Note 1)
10. Record the titre. (Note 2)

B. t-butyl Hydroperoxide

1. Transfer into a 250 Iodine flask 30 ml of 3A ethyl alcohol.
2. See step 2. above.
3. Drop the vial into the 250 ml Erlenmeyer flask and swirl to mix.
4. While swirling, pipette 20 ml of the 10% sodium iodide solution into the Erlenmeyer flask, stopper the flask and place in a dark cabinet for 25 minutes.
5. Remove from the cabinet and titrate with the 0.1N sodium thiosulfate solution to a colorless 30 second end-point. (Note 1)
6. Record the titre. (Note 2)

CALCULATIONS:

1. $\% \text{ Total active oxygen} = \frac{(B-S) \times N \times 0.008 \times 100}{\text{Sample Wt.}}$
2. $\% \text{ t-butyl peroxyvalate} = \frac{\% \text{ total act. O}_2 \text{ fr. 1.} - \% \text{ act. O}_2 \text{ fr. 3.} \times 100}{9.18}$
3. $\% \text{ active oxygen for t-butyl hydroperoxide} = \frac{(S-B) \times N \times 0.008 \times 100}{\text{Sample Wt.}}$
4. $\% \text{ t-butyl hydroperoxide} = \frac{(S-B) \times 0.04506 \times 100}{\text{Sample wt.}}$

B = Blank titre
S = Sample titre
N = Normality of titrant

Note 1: The first titration should be run as a trial to find the approximate volume of the titrant needed.

Note 2: Run a reagent blank along with the samples.

Written by: F. W. Kanzler

Issued by: H. B. Carr
Manager - Quality Control

TENNECO CHEMICALS, INC.

TENNECO PLASTICS DIV.

Burlington, New Jersey

B.A.C.M. #400

DATE ISSUED: August 8, 1969

Determination of Phenol in Recovered Vinyl Chloride Monomer

APPLICATION: Phenol is introduced in the vinyl chloride monomer recovery system prior to the compressor as an inhibitor. An accurate determination of the inhibitor is necessary so that in-process adjustments may be made.

The vinyl chloride monomer is evaporated in a beaker. The color is developed with Millon's reagent and the transmittance of the sample is compared with the transmittance of a standard on a spectrophotometer at a wavelength of 495 m μ . This method is for the determination of phenol to levels less than 100 parts per million.

APPARATUS:

1. Bausch and Lomb Spectronic 20 or equivalent.
2. Hot plate, Thermolyne, with adjustable temperature control.
3. 1000 ml Hoke sample bomb, fitted with valves on each end.
4. Triple beam balance with readout to 0.1 gm
5. Eye dropper
6. Analytical balance with a readout to 0.1 mg
7. Volumetric flask, 50 ml
8. Pipette 1 ml, 2 ml, 3 ml, 5 ml, 10 ml

REAGENTS:

1. Millon's reagent, (Dissolve 20 gm of mercury, reagent grade in 20 ml of cold fuming nitric acid, reagent grade. Dilute the resultant solution with 40 ml of water. Let stand for several hours and decant the clear solution).
2. Hydrochloric acid, reagent grade, diluted 1:1

PROCEDURE:A. Preparation of the Standard Solution and Standardization

1. Weigh accurately 0.0500 gm of phenol and transfer into a 50 ml volumetric flask. Dissolve the phenol in about 30 ml of water and make up to 50 ml. (Stock solution)
2. From the Stock solution pipette 1 ml, 2 ml, 3 ml, 5 ml, 10 ml aliquots into individual beakers. (These aliquots represent 10, 20, 30, 50 and 100 parts per million of phenol per 100 gm of MVC.)
3. Add three drops of 1:1 diluted hydrochloric acid and add water to bring the total liquid to 50 ml.
4. Place the beaker on a hot plate and heat the liquid to a gentle boil.
5. Add 10 drops of Millon's reagent and boil for one more minute.
6. Remove the beaker from the hot plate and let it cool to room temperature.
7. Run each standard on the Spectronic 20 at a wavelength of 495 m μ . Record the percent transmittance and prepare a graph plotting parts per million of phenol versus percent transmittance.

B. Preparation and Running of the Sample

1. Weigh 100.0 gm $\pm$ 0.1 gm of MVC into a previously tared beaker.
2. Let the MVC evaporate (do not let the beaker come to complete dryness).
3. Add three drops of 1:1 diluted hydrochloric acid and 50 ml of water.
4. Repeat steps 4. through 6. from procedure A.
5. Run each sample on the Spectronic 20 at a wavelength of 495 m μ and read the parts per million of phenol on the previously prepared graph. (If a pink color has not developed when the sample is viewed against a white background, record the phenol value as less than 2 parts per million.)

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8. Burette, straight stopcock, Teflon plug, 50 ml, 0.1 ml division
9. Analytical Balance with readout to 0.1 mg
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cooled arsenious oxide and transfer into a 250 ml Erlenmeyer flask.

2. Add 25 ml of water in which 2 gm of sodium hydroxide have been dissolved.
3. Warm and swirl gently until all particles of arsenious oxide have been dissolved. (Undissolved particles have a tendency to "climb" the sides of the Erlenmeyer flask due to surface tension)
4. Add 75 ml of water and 25 ml of 5N sulfuric acid. 2 drops of 0.01M osmium tetroxide solution and 2 drops ferroin indicator solution.
5. Titrate the pink solution with the ceric ammonium sulfate solution to be standardized to a pale blue 30 second end-point (Caution: the end-point is extremely sharp and changes from a pale pink to a pale blue very fast). (Note 1)
6. Repeat steps 1. through 5. twice and average results.

Calculation:

$$\frac{\text{Wt. of the As}_2\text{O}_3}{\frac{49.45}{1000} \times \text{ml of ceric ammon. sulfate used}} = N \text{ of ceric ammonium sulfate sol'n.}$$

B. Iodine Solution 0.1N (Secondary Standard)

1. Weigh and record to the nearest 0.1 mg about 0.20 gm of previously dried and cooled arsenious oxide and transfer to a 250 ml Erlenmeyer flask.
3. Swirl gently until all particles of arsenious oxide have been dissolved.
4. Dilute the solution to 100 ml with water. Cool under running water.
5. Add 2 ml of concentrated hydrochloric acid and 10 gm of sodium bicarbonate.
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Calculation:

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C. Sodium Thiosulfate Solution, 0.1N

1. Pipette 50 ml of previously standardized Iodine solution into a 250 ml Iodine flask.
2. Titrate while stirring with the sodium thiosulfate to be standardized to a colorless 30 second end-point. (Note 1)
3. Repeat steps 1. and 2. twice and average results.

Calculation:

$$\frac{50 \times \text{N of Iodine sol'n.}}{\text{ml of Sod. Thiosulfate used}} = \text{N of Sodium Thiosulfate solution}$$

PROCEDURE:

A. Active Oxygen and Assay

1. Transfer into a 400 ml beaker 50 ml of 3A ethyl alcohol. Place a magnetic stirring bar into the beaker.
2. Weigh into a previously cooled vial 0.2 - 0.3 gm for a 75% Lupersol 11 solution, or 0.3 - 0.4 gm for a 45% Lupersol 11 solution. Record to the nearest 0.1 mg.
3. Drop the vial and contents into the 400 ml beaker and mix with a magnetic stirrer.
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5. Place the beaker into the hot water bath (88° - 95°C) for about 30 minutes or until the volume in the beaker is 75 ml. (It is imperative that all the alcohol has been evaporated).

6. Remove the beaker from the hot water bath and let it cool to room temperature.
7. Add 40 ml of 4N sulfuric acid.
8. Add 2 drops of 0.01M osmium tetroxide and 2 drops of ferroin indicator solution.
9. Titrate with 0.1N ceric ammonium sulfate solution to a pale blue end-point. (Note 1)
10. Record the titre. (Note 2)

B. t-butyl Hydroperoxide

1. Transfer into a 250 Iodine flask 30 ml of 3A ethyl alcohol.
2. See step 2. above.
3. Drop the vial into the 250 ml Erlenmeyer flask and swirl to mix.
4. While swirling, pipette 20 ml of the 10% sodium iodide solution into the Erlenmeyer flask, stopper the flask and place in a dark cabinet for 25 minutes.
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CALCULATIONS:

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2. $\% \text{ t-butyl peroxyvalate} = \frac{\% \text{ total act. O}_2 \text{ fr. 1.} - \% \text{ act. O}_2 \text{ fr. 3.} \times 100}{9.18}$
3. $\% \text{ active oxygen for t-butyl hydroperoxide} = \frac{(S-B) \times N \times 0.008 \times 100}{\text{Sample Wt.}}$
4. $\% \text{ t-butyl hydroperoxide} = \frac{(S-B) \times 0.04506 \times 100}{\text{Sample wt.}}$

B = Blank titre
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N = Normality of titrant

Note 1: The first titration should be run as a trial to find the approximate volume of the titrant needed.

Note 2: Run a reagent blank along with the samples.

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