§ 63.1427 Process vent requirements for processes using extended cookout as an epoxide emission reduction technique.

(a) Applicability of extended cookout requirements. Owners or operators of affected sources that produce polyether polyols using epoxides, and that are using ECO as a control technique to reduce epoxide emissions in order to comply with percent emission reduction requirements in §63.1425(b)(1)(i) or (b)(2)(ii) shall comply with the provisions of this section. The owner or operator that is using ECO in order to comply with the emission factor requirements in §63.1425(b)(1)(iii) or §63.1425(b)(2)(iv) shall demonstrate that the specified emission factor is achieved by following the requirements in §63.1431. If additional control devices are used to further reduce the HAP emissions from a process vent already controlled by ECO, then the owner or operator shall also comply with the testing, monitoring, recordkeeping, and reporting requirements associated with the additional control device, as specified in §§63.1426, 63.1429, and 63.1430, respectively.

(1) For each product class, the owner or operator shall determine the batch cycle percent epoxide emission reduction for the most difficult to control product in the product class, where the most difficult to control product is the polyether polyol that is manufactured with the slowest pressure decay curve.

(2) The owner or operator may determine the batch cycle percent epoxide emission reduction by directly measuring the concentration of the unreacted epoxide, or by using process knowledge, reaction kinetics, and engineering knowledge, in accordance with paragraph (a)(2)(i) of this section.

(i) If the owner or operator elects to use any method other than direct measurement, the epoxide concentration shall be determined by direct measurement for one product from each product class and compared with the epoxide concentration determined using the selected estimation method, with the exception noted in paragraph (a)(2)(ii) of this section. If the difference between the directly determined epoxide concentration and the calculated epoxide concentration is less than 25 percent, then the selected estimation method will be considered to be an acceptable alternative to direct measurement for that class.

(ii) If uncontrolled epoxide emissions prior to the end of the ECO are less than 10 tons per year (9.1 megagrams per year), the owner or operator is not required to perform the direct measurement required in paragraph (a)(2)(i) of this section. Uncontrolled epoxide emissions prior to the end of the ECO shall be determined by the procedures in paragraph (d)(1) of this section.

(b) Define the end of epoxide feed. The owner or operator shall define the end of the epoxide feed in accordance with paragraph (b)(1) or (2) of this section.

(1) The owner or operator shall determine the concentration of epoxide in the reactor liquid at the point in time when all epoxide has been added to the reactor and prior to any venting. This concentration shall be determined in accordance with the procedures in paragraph (f)(1)(i) of this section.

(2) If the conditions in paragraphs (b)(2)(i), (ii), and (iii) of this section are met, the end of the epoxide feed may be defined by the reactor epoxide partial pressure at the point in time when all epoxide reactants have been added to the reactor. This reactor epoxide partial pressure shall be determined in accordance with the procedures in paragraph (g) of this section.

(i) No epoxide is emitted before the end of the ECO;

(ii) Extended cookout is the only control technique to reduce epoxide emissions; and
(iii) The owner or operator elects to determine the percent epoxide emission reduction for the ECO using reactor epoxide partial pressure in accordance with paragraph (e)(2) of this section.

(c) Define the onset of the ECO. The owner or operator shall calculate the uncontrolled emissions for the batch cycle by calculating the epoxide emissions, if any, prior to the onset of the ECO, plus the epoxide emissions at the onset of the ECO. The onset of the ECO is defined as the point in time when the combined unreacted epoxide concentration in the reactor liquid is equal to 25 percent of the concentration of epoxides at the end of the epoxide feed, which was determined in accordance with paragraph (b) of this section.

(1) The uncontrolled epoxide emissions for the batch cycle shall be determined using Equation 8.

\[ E_{c,u} = (C_{\text{liq},i})(V_{\text{liq},i})(D_{\text{liq},i}) + (C_{\text{vap},i})(V_{\text{vap},i})(D_{\text{vap},i}) + E_{\text{epox, bef}} \]  

[Equation 8]

Where:

- \( E_{c,u} \) = Uncontrolled epoxide emissions at the onset of the ECO, kilograms per (kg) batch.
- \( C_{\text{liq},i} \) = Concentration of epoxide in the reactor liquid at the onset of the ECO, which is equal to 25 percent of the concentration of epoxide at the end of the epoxide feed, determined in accordance with paragraph (b)(1) of this section, weight percent.
- \( V_{\text{liq},i} \) = Volume of reactor liquid at the onset of the ECO, liters.
- \( D_{\text{liq},i} \) = Density of reactor liquid, kg/liter.
- \( C_{\text{vap},i} \) = Concentration of epoxide in the reactor vapor space at the onset of the ECO, weight percent.
- \( V_{\text{vap},i} \) = Volume of reactor vapor space at the onset of the ECO, liters.
- \( D_{\text{vap},i} \) = Vapor density of reactor vapor space at the onset of the ECO, kg/liter.
- \( E_{\text{epox, bef}} \) = Epoxide emissions that occur prior to the onset of the ECO, determined in accordance with the provisions of §63.1426(d), kilograms.

(2) If the conditions in paragraphs (b)(2)(i), (ii), and (iii) of this section are met, the owner or operator may define the onset of the ECO as the point in time when the reactor epoxide partial pressure equals 25 percent of the reactor epoxide partial pressure at the end of the epoxide feed, and is not required to determine the uncontrolled epoxide emissions in accordance with paragraph (c)(1) of this section.

(d) Determine emissions at the end of the ECO. The owner or operator shall calculate the epoxide emissions at the end of the ECO, where the end of the ECO is defined as the point immediately before the time when the reactor contents are emptied and/or the reactor vapor space purged to the atmosphere or to a combustion, recovery, or recapture device.

(1) The epoxide emissions at the end of the ECO shall be determined using Equation 9.

\[ E_{\text{c,E}} = (C_{\text{liq},f})(V_{\text{liq},f})(D_{\text{liq},f}) + (C_{\text{vap},f})(V_{\text{vap},f})(D_{\text{vap},f}) \]  

[Equation 9]

Where:

- \( E_{\text{c,E}} \) = Epoxide emissions at the end of the ECO, kg.
- \( C_{\text{liq},f} \) = Concentration of epoxide in the reactor liquid at the end of the ECO, determined in accordance with paragraph (f)(1) of this section, weight percent.
- \( V_{\text{liq},f} \) = Volume of reactor liquid at the end of the ECO, liters.
- \( D_{\text{liq},f} \) = Density of reactor liquid, kg/liter.
- \( C_{\text{vap},f} \) = Concentration of epoxide in the reactor vapor space as it exits the reactor at the end of the ECO, determined in accordance with paragraph (f)(2) of this section, weight percent.
- \( V_{\text{vap},f} \) = Volume of reactor vapor space as it exits the reactor at the end of the ECO, liters.
- \( D_{\text{vap},f} \) = Vapor density of reactor vapor space at the end of the ECO, kg/liter.
(2) If the conditions in paragraphs (b)(2)(i), (ii), and (iii) of this section are met, the owner or operator may determine the reactor epoxide partial pressure at the end of the ECO instead of determining the uncontrolled epoxide emissions at the end of the ECO in accordance with paragraph (d)(1) of this section.

(e) Determine percent epoxide emission reduction. (1) The owner or operator shall determine the percent epoxide emission reduction for the batch cycle using Equation 10.

\[
R_{\text{batch cycle}} = \left( \frac{E_{c,u}}{E_{c,o}} \right) \left( 1 - \frac{R_{\text{addon},i}}{100} \right) \left( 1 - \frac{E_{c,o}}{E_{c,u}} \right) \right) * 100 \quad \text{[Equation 10]}
\]

Where:
- \( R_{\text{batch cycle}} \) = Epoxide emission reduction for the batch cycle, percent.
- \( E_{c,u} \) = Epoxide emissions at the end of the ECO determined in accordance with paragraph (d)(1) of this section, kilograms.
- \( E_{c,o} \) = Epoxide emissions that occur before the end of the ECO, determined in accordance with the provisions of §63.1426(d), kilograms.
- \( R_{\text{addon},i} \) = Control efficiency of combustion, recovery, or recapture device that is used to control epoxide emissions after the ECO, determined in accordance with the provisions of §63.1426(c), percent.
- \( R_{\text{addon},j} \) = Control efficiency of combustion, recovery, or recapture device that is used to control epoxide emissions that occur before the end of the ECO, determined in accordance with the provisions of §63.1426(c), percent.

(2) If the conditions in paragraphs (b)(2)(i), (ii), and (iii) of this section are met, the owner or operator may determine the percent epoxide emission reduction for the batch cycle using reactor epoxide partial pressure and Equation 11, instead of using the procedures in paragraph (e)(1) of this section.

\[
R_{\text{batch cycle}} = \left[ 1 - \frac{P_{\text{epox},f}}{P_{\text{epox},i}} \right] * 100 \quad \text{[Equation 11]}
\]

Where:
- \( R_{\text{batch cycle}} \) = Epoxide emission reduction for the batch cycle, percent.
- \( P_{\text{epox},i} \) = Reactor epoxide partial pressure at the onset of the ECO, determined in accordance with paragraph (c)(2) of this section, mm Hg.
- \( P_{\text{epox},f} \) = Reactor epoxide partial pressure at the end of the ECO, determined in accordance with paragraph (c)(2) of this section, mm Hg.

(f) Determination of epoxide concentrations. The owner or operator shall determine the epoxide concentrations in accordance with the procedures in this paragraph.

(1) The owner or operator shall determine the concentration of epoxide in the reactor liquid using either direct measurement in accordance with paragraph (f)(1)(i) of this section, or reaction kinetics in accordance with paragraph (f)(1)(ii) of this section. An owner or operator may also request to use an alternative methodology in accordance with paragraph (f)(1)(iii) of this section.

The owner or operator shall submit a standard operating procedure for obtaining the liquid sample, along with the test method used to determine the epoxide concentration. This information shall be submitted in the Precompliance Report.
(ii) Determine the epoxide concentration in the reactor liquid using Equation 12. \[ C_{liq,f} = C_{liq,i} e^{-kt} \] [Equation 12]

\( C_{liq,f} \) = Concentration of epoxide in the reactor liquid at the end of the time period, weight percent.

\( C_{liq,i} \) = Concentration of epoxide in the reactor liquid at the beginning of the time period, weight percent.

\( k \) = Reaction rate constant, 1/hr.

\( t \) = Time, hours.

**NOTE:** This equation assumes a first order reaction with respect to epoxide concentration. Where:

(iii) If the owner/operator deems that the methods listed in paragraphs (f)(1)(i) and (ii) of this section are not appropriate for the reaction system for a PMPU, then the owner/operator may submit a request for the use of an alternative method.

(2) The owner or operator shall determine the concentration of epoxide in the reactor vapor space using either direct measurement in accordance with paragraph (f)(2)(i) of this section, or by engineering estimation in accordance with paragraph (f)(2)(ii) of this section. An owner or operator may also request to use an alternative methodology in accordance with paragraph (f)(2)(iii) of this section.

(i) The owner or operator shall take two representative samples from a bleed valve off the reactor’s process vent. The owner or operator shall determine the total epoxide concentration using 40 CFR part 60, appendix A, Method 18.

(ii) Determine the epoxide concentration in the vapor space using Raoult’s Law or another appropriate phase equilibrium equation and the liquid epoxide concentration, determined in accordance with paragraph (f)(1) of this section.

(iii) If the owner/operator deems that the methods listed in paragraphs (f)(1)(i) and (ii) of this section are not appropriate for the reaction system for a PMPU, then the owner/operator may submit a request for the use of an alternative method.

(h) *Determination of pressure.* The owner or operator shall determine the total pressure of the system using standard pressure measurement devices calibrated according to the manufacturer’s specifications or other written procedures that provide adequate assurance that the equipment would reasonably be expected to monitor accurately.

(ii) *Determination if pressure decay curves are similar.* The owner or operator shall determine the pressure decay curve as defined in §63.1423. Products with similar pressure decay curves constitute a product class. To determine if two pressure decay curves are similar when the pressure decay curves for products have different starting and finishing pressures, the owner or operator shall determine the time when the pressure has fallen to half its total pressure by using Equation 13:

\[
\text{Time (P}_{\text{half 1}}) - \text{Time (P}_{\text{half 2}}) < 20\% \cdot T_{AVG} \] [Equation 13]

Where:

\( P_{\text{half 1}} \) = Half the total pressure of the epoxide for product 1.

\( \text{Time (P}_{\text{half 1}}) \) = Time when the pressure has fallen to half its total pressure for product 1.

\( P_{\text{half 2}} \) = Half the total pressure of the epoxide for product 2.

\( \text{Time (P}_{\text{half 2}}) \) = Time when the pressure has fallen to half its total pressure for product 2.

\( T_{AVG} \) = The average time to cookout to the point where the epoxide pressure is 25 percent of the epoxide pressure at the end of the feed step for products 1 and 2.

(i) *ECO monitoring requirements.* The owner or operator using ECO shall comply with the monitoring requirements of this paragraph to demonstrate continuous compliance with this subpart. Paragraphs (i)(1) through (3) of this section address monitoring of the extended cookout.

(1) To comply with the provisions of this section, the owner or operator shall monitor one of the parameters
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listed in paragraphs (i)(1)(i) through (iii) of this section, or may utilize the provision in paragraph (i)(1)(iv) of this section.

(i) Time from the end of the epoxide feed;

(ii) The epoxide partial pressure in the closed reactor;

(iii) Direct measurement of epoxide concentration in the reactor liquid at the end of the ECO, when the reactor liquid is still in the reactor, or after the reactor liquid has been transferred to another vessel; or

(iv) An owner or operator may submit a request to the Administrator to monitor a parameter other than the parameters listed in paragraphs (i)(1)(i) through (iii) of this section, as described in §63.1439(f).

(2) During the determination of the percent epoxide emission reduction in paragraphs (b) through (e) of this section, the owner or operator shall establish, as a level that shall be maintained during periods of operation, one of the parameters in paragraphs (i)(2)(i) through (iii) of this section, or may utilize the procedure in paragraph (i)(2)(iv) of this section, for each product class.

(i) The time from the end of the epoxide feed to the end of the ECO;

(ii) The reactor epoxide partial pressure at the end of the ECO;

(iii) The epoxide concentration in the reactor liquid at the end of the ECO, when the reactor liquid is still in the reactor, or after the reactor liquid has been transferred to another vessel; or

(iv) An owner or operator may submit a request to the Administrator to monitor a parameter other than the parameters listed in paragraphs (i)(2)(i) through (iii) of this section, as described in §63.1439(f).

(3) For each batch cycle where ECO is used to reduce epoxide emissions, the owner or operator shall record the value of the monitored parameter at the end of the ECO. This parameter is then compared with the level established in accordance with paragraph (i)(2) of this section to determine if an excursion has occurred. An ECO excursion is defined as one of the situations described in paragraphs (i)(3)(i) through (v) of this section.

(i) When the time from the end of the epoxide feed to the end of the ECO is less than the time established in paragraph (i)(2)(i) of this section;

(ii) When the reactor epoxide partial pressure at the end of the ECO is greater than the partial pressure established in paragraph (i)(2)(ii) of this section;

(iii) When the epoxide concentration in the reactor liquid at the end of the ECO is greater than the epoxide concentration established in paragraph (i)(2)(iii) of this section;

(iv) When the parameter is not measured and recorded at the end of the ECO; or

(v) When the alternative monitoring parameter is outside the range established under §63.1439(f) for proper operation of the ECO as a control technique.

(j) Recordkeeping requirements. (1) The owner or operator shall maintain the records specified in paragraphs (j)(1)(i) and (ii) of this section, for each product class. The owner or operator shall also maintain the records related to the initial determination of the percent epoxide emission reduction specified in paragraphs (j)(1)(i)(iii) through (x) of this section, as applicable, for each product class.

(i) Operating conditions of the product class, including:

(A) Pressure decay curve;

(B) Minimum reaction temperature;

(C) Number of reactive hydrogens in the raw material;

(D) Minimum catalyst concentration;

(E) Ratio of EO/PO at the end of the epoxide feed; and

(F) Reaction conditions, including the size of the reactor or batch.

(ii) A listing of all products in the product class, along with the information specified in paragraphs (j)(1)(i)(A) through (F) of this section, for each product.

(iii) The concentration of epoxide at the end of the epoxide feed, determined in accordance with paragraph (b)(1) of this section.

(iv) The concentration of epoxide at the onset of the ECO, determined in accordance with paragraph (c) of this section.

(v) The uncontrolled epoxide emissions at the onset of the ECO, determined in accordance with paragraph
(c)(1) of this section. The records shall also include all the background data, measurements, and assumptions used to calculate the uncontrolled epoxide emissions.

(vi) The epoxide emissions at the end of the ECO, determined in accordance with paragraph (d)(1) of this section. The records shall also include all the background data, measurements, and assumptions used to calculate the epoxide emissions.

(vii) The percent epoxide reduction for the batch cycle, determined in accordance with paragraph (e)(1) of this section. The records shall also include all the background data, measurements, and assumptions used to calculate the percent reduction.

(viii) The parameter level, established in accordance with paragraph (i)(3) of this section.

(ix) If epoxide emissions occur before the end of the ECO, the owner or operator shall maintain records of the time and duration of all such emission episodes.

(x) If the conditions in paragraphs (b)(2)(i), (ii), and (iii) of this section are met, the owner or operator is not required to maintain the records specified in paragraphs (j)(2)(i) through (iv) of this section, but shall maintain the records specified in paragraphs (j)(1)(x)(A), (B), and (C) of this section.

(B) The percent epoxide reduction for the batch cycle, determined in accordance with paragraph (e)(2) of this section. The records shall also include all the measurements and assumptions used to calculate the percent reduction.

(C) The reactor epoxide partial pressure at the end of the ECO.
(ii) The parameter for each product class, as determined in accordance with paragraph (i)(2) of this section.

(iii) If a combustion, recovery, or re-capture device is used in addition to ECO to reduce emissions, the information specified in §63.1430(g)(1).

(iv) If epoxide emissions occur before the end of the ECO, a listing of the time and duration of all such emission episodes that occur during the initial demonstration of batch cycle efficiency.

(3) The information specified in paragraphs (k)(3)(i) through (iii) of this section shall be provided in the Periodic Report, as specified in §63.1439(e)(6).

(i) Reports of each batch cycle for which an ECO excursion occurred, as defined in paragraph (i)(3) of this section.

(ii) Notification of each batch cycle when the time and duration of epoxide emissions before the end of the ECO, recorded in accordance with paragraph (j)(2)(iv) of this section, exceed the time and duration of the emission episodes during the initial epoxide emission percentage reduction determination, as recorded in paragraph (j)(1)(viii) of this section.

(iii) If a combustion, recovery, or re-capture device is used to reduce emissions, the information specified in §63.1430(h).

(l) New polyether polyol products. If an owner or operator wishes to utilize ECO as a control option for a polyether polyol not previously assigned to a product class and reported to the Agency in accordance with either paragraph (k)(2)(i)(B), (l)(1)(ii), or (l)(2)(iii) of this section, the owner or operator shall comply with the provisions of paragraphs (l)(1) or (2) of this section.

(l) If the operating conditions of the new polyether polyol are consistent with the operating conditions for an existing product class, the owner or operator shall comply with the requirements in paragraphs (l)(1)(i) and (ii) of this section.

(i) The owner or operator shall update the list of products for the product class required by paragraph (j)(1)(ii) of this section, and shall record the information in paragraphs (j)(1)(i)(A) through (F) of this section for the new product.

(ii) Within 180 days after the production of the new polyether polyol, the owner or operator shall submit a report updating the product list previously submitted for the product class. This information may be submitted along with the next Periodic Report.

(2) If the operating conditions of the new polyether polyol do not conform with the operating characteristics of an existing product class, the owner or operator shall establish a new product class and shall comply with provisions of paragraphs (l)(2)(i) through (iii) of this section.

(i) The owner or operator shall establish the batch cycle percent epoxide emission reduction in accordance with paragraphs (b) through (g) of this section for the product class.

(ii) The owner or operator shall establish the records specified in paragraph (j)(1) of this section for the product class.

(iii) Within 180 days of the production of the new polyether polyol, the owner or operator shall submit a report containing the information specified in paragraphs (k)(2)(i) and (ii) of this section.

(m) Polyether polyol product changes. If a change in operation, as defined in paragraph (m)(1) of this section, occurs for a polyether polyol that has been assigned to a product class and reported to the Agency in accordance with paragraph (k)(2)(i)(B), (l)(1)(ii), or (l)(2)(iii) of this section, the owner or operator shall comply with the provisions of paragraphs (m)(2) through (3) of this section.

(1) A change in operation for a polyether polyol is defined as a change in any one of the parameters listed in paragraphs (m)(1)(i) through (ix) of this section.

(i) A significant change in reaction kinetics;

(ii) Use of a different oxide reactant;

(iii) Use of a different EO/PO ratio;

(iv) A lower reaction temperature;

(v) A lower catalyst feed on a mole/mole fraction OH basis;

(vi) A shorter cookout;

(vii) A lower reactor pressure;

(viii) A different type of reaction, (e.g., a self-catalyzed vs. catalyzed reaction); or
(ix) A marked change in reaction conditions (e.g., a markedly different liquid level).

(2) If the operating conditions of the product after the change in operation remain within the operation conditions of the product class to which the product was assigned, the owner or operator shall update the records specified in paragraphs (j)(1)(i)(A) through (F) of this section for the product.

(3) If the operating conditions of the product after the change in operation are outside of the operating conditions of the product class to which the product was assigned, the owner or operator shall comply with the requirements in paragraph (m)(3)(i) or (ii) of this section, as appropriate.

(i) If the new operating conditions of the polyether polyol are consistent with the operating conditions for another existing product class, the owner or operator shall comply with the requirements in paragraphs (m)(3)(i)(A) and (B) of this section.

(A) The owner or operator shall update the list of products for the product class that the product is leaving, and for the product class that the product is entering, and shall record the new information in paragraphs (j)(1)(i)(A) through (F) of this section for the product.

(B) Within 180 days after the change in operating conditions for the polyether polyol product, the owner or operator shall submit a report updating the product lists previously submitted for the product class. This information may be submitted along with the next Periodic Report.

(ii) If the new operating conditions of the polyether polyol product do not conform with the operating characteristics of an existing product class, the owner or operator shall establish a new product class and shall comply with provisions of paragraphs (m)(3)(ii)(A) through (C) of this section.

(A) The owner or operator shall establish the batch cycle percent epoxide emission reduction in accordance with paragraphs (b) through (g) of this section for the product class.

(B) The owner or operator shall establish the records specified in paragraph (j)(1) of this section for the product class.

(C) Within 180 days of the change in operating conditions for the polyether polyol, the owner or operator shall submit a report containing the information specified in paragraphs (k)(2)(i) and (ii) of this section.

[64 FR 29439, June 1, 1999; 64 FR 31895, June 14, 1999, as amended at 65 FR 26500, May 8, 2000]

§ 63.1428 Process vent requirements for group determination of PMPUs using a nonepoxide organic HAP to make or modify the product.

(a) Process vents from batch unit operations. The owner or operator shall determine, for each PMPU located at an affected source, if the combination of all process vents from batch unit operations that are associated with the use of nonepoxide organic HAP to make or modify the product is a Group 1 combination of batch process vents, as defined in §63.1423. The annual uncontrolled nonepoxide organic HAP emissions, determined in accordance with paragraph (b) of this section, and annual average flow rate, determined in accordance with paragraph (c) of this section, shall be determined for all process vents from batch unit operations associated with the use of a nonepoxide organic HAP to make or modify the product, with the exception of those vents specified in paragraph (i) of this section, at the location after all applicable control techniques have been applied to reduce epoxide emissions in accordance with paragraph (a)(1) or (2) of this section.

(1) If the owner or operator is using a combustion, recovery, or recapture device to reduce epoxide emissions, this location shall be at the exit of the combustion, recovery, or recapture device.

(2) If the owner or operator is using ECO to reduce epoxide emissions, this location shall be at the exit from the batch unit operation. For the purpose of these determinations, the primary condenser operating as a reflux condenser on a reactor or distillation column shall be considered part of the unit operation.

(b) Determination of annual nonepoxide organic HAP emissions. The owner or operator shall determine, for each PMPU, the total annual nonepoxide organic HAP emissions from the combination