

DEPARTMENT OF ENVIRONMENTAL QUALITY
AIR QUALITY DIVISION
ACTIVITY REPORT: Scheduled Inspection

A404349641

FACILITY: Dow Silicones Corporation		SRN / ID: A4043
LOCATION: 3901 S Saginaw Rd, MIDLAND		DISTRICT: Saginaw Bay
CITY: MIDLAND		COUNTY: MIDLAND
CONTACT: Jennifer Kraut , Air Specialist		ACTIVITY DATE: 07/23/2019
STAFF: Gina McCann	COMPLIANCE STATUS: Compliance	SOURCE CLASS: MEGASITE
SUBJECT: EU502-01, EU502-07, EU325-01 and FG325-01		
RESOLVED COMPLAINTS:		

Inspection Date: 7/23/2019

Inspection Started: 8:30

Inspection Ended: 15:00

DOW Silicones/EGLE-AQD staff present during the inspection:

- Gina McCann (EGLE-AQD, Senior Environmental Quality Analyst)
- Jennifer Kraut (Air Specialist, DOW Silicones)
- Brandon Bishop (EHS Specialist, DOW MiOps)
- Maria Allen (502 Building Engineer, DOW Silicones)
- Alex Wright (502 Building Engineer, DOW Silicones)
- Scott Stachowiak (325 Building Engineer, DOW Silicones)

Records reviewed as part of the inspection were:

- ROP Annual report for 2018
- PTI 232-89 application and process flow diagram

EU502-01

Methyl vent system consisting of emissions from tanks T-100, T-102, T-150, T-151, T-208, T-20841, and T-25-100, emissions from maintenance procedures involving portable storage containing methyltrichlorosilane, methyldichlorosilane, dimethyldichlorosilane, dimethylchlorosilane, trimethylchlorosilane, phenyltrichlorosilane, and ethyltrichlorosilane, and the vent from the Cabot Mix Tank operation. This emission unit is subject to the requirements of 40 CFR Part 60, Subparts A and Kb and 40 CFR Part 61, Subparts A, J, and V.

The distillation vents flow to 304VENTRECOVERY and the FGTHROX/SITESCUBBERS or to FG325-01. This emission unit vents to the 337 Spray Scrubber System or to the dry vent tank of the THROX System. Emissions from loading stations 9G, 10G, DVST-28, and DVST 56 also have the option to vent directly to the Site Scrubber System via the "Bulk Move Vent" described in EU502-07. The most recent PTI for this emission unit is PTI No. 131-15.

- 337 Spray Scrubber (9950, 9960 – scrubbers typically alternate in operation but can operate in parallel and vent to SV337-001/002, respectively)
- THROX System comprised of thermal incinerator burner DV24422, quencher DV24424, HCl Absorber. This device is a CAM subject unit for VOCs.
- DV24425, IWS 1st Stage DV24427, IWS 2nd Stage DV 24428, vent SV2514-006
- Site Scrubber System comprised of two parallel spray tower scrubbers DV23709 and DV23710, vents SV2512-001/002

Special Condition (SC) VI.2. requires the plant to calculate the VOC emission rate from EU502-01 monthly, for the preceding 12-month rolling time period. VOC emissions are restricted to 2.5 ton per year (tpy) by

SC I.2. VOC emissions, for the 12-month rolling time period ending May 2019 were 0.26 tpy. SC I.1. restricts VOC emissions to 4.8 pounds per hour (pph) based on an annual time period. For the same time period ending May 2019, VOC emissions were 0.154 pph.

SC VI.3. and SC VII.4. requires the plant to comply with the applicable requirements of 40 CFR Part 60, Subpart Kb, Section 60.116b and Section 61.115b, respectively, for storage vessel nos. DV100, DV102, DV150, DV151, DV208, DV20841, and DV25-100. I requested records showing the dimension of the storage vessel and an analysis showing the capacity of the storage vessel, per 60.116b, for DV151. The plant appeared to be meeting the conditions of the NSPS Kb for storage vessel DV151.

SC IV.1. requires EU502-01 to exhaust to either the 337 spray scrubbers or the THROX system or the Site Scrubber System, which is a back-up for the THROX. Each system has a required control efficiency that it must meet to be considered operating in a satisfactory manner. SITESCRUBBERS and the 337SCRUBBERS do not have testing requirements associated with them. The control efficiencies listed seem to be from manufacturer specifications and the way to comply with the efficiencies is to meet the parametrics of flow and temperature, either specified in the emission unit table or a malfunction abatement plan (MAP). I reviewed the files and did not find a stack test performed on either unit to verify control efficiencies.

VII.1 through VII.3. require prompt reporting of deviations, semiannual and annual reporting of monitoring and deviations. The compliance reporting section of this report discusses deviations reported.

Compliance Reporting

No deviations were reported for the time period January 1, 2018 through December 31, 2018.

EU502-07

This emission unit consists of two sets of related equipment with different emission profiles and different vent control paths:

1. **Distillation Vents:** Trichlorosilane (TCS) distillation equipment for purifying crude TCS into various grades (electronic-, chemical-, and plant-grade) of TCS product as well as chemical-grade silicon tetrachloride.

Typically, the add-on control equipment for the Distillation Vents consists of the 304 Vent Recovery System followed by the dry vent tank at the THROX System. The dry vent tank is either sent to the THROX System burner or diverted to the Site Scrubber System. In the event both the THROX System and the Site Scrubber System are off-line, the Distillation Vents will be directed through the 337 Spray Scrubber System after 304 Vent Recovery. However, in the event 304 Vent Recovery System goes down, the Distillation Vents will be directed to the 325 Vent Recovery System. The 325 Vent Recovery System consists of two carbon bed banks (Nos. 1 and 2) and the 337 Venturi Scrubbers. Each one of the carbon beds (either No. 1 or No. 2) vent to one of the 337 Venturi Scrubbers (No. 1 or No. 2), or to the THROX System or the Site Scrubber System.

2. **Bulk Move Vents:** trichlorosilane (TCS), silicon tetrachloride (STC), and dichlorosilane (DCS) "bulk move" operations. These operations include the loading and unloading of storage tanks, railcars, and semi-trailers and occur primarily at 502 Building, supporting the distillation operations.

Typically, the add-on control equipment for the Bulk Move Vents is the Site Scrubber System. If the Site Scrubber System is down, the Bulk Move Vents have the capability to follow the vent path of the Distillation Vents as described above.

The 337 Spray Scrubber System discharges to the atmosphere through either SV337-001 or SV337-002. 337 Venturi Scrubber bank No. 1 discharges to the atmosphere through SV337-003. 337 Venturi Scrubber bank No. 2 discharges to the atmosphere through SV337-004. The THROX System discharges through SV2514-006. The Site Scrubber System discharge through either SV2512-001 or SV2512-002. The ROP lists this emission unit as being subject to the requirements of 40 CFR Part 60, Subparts A and Kb. However, this standard no longer applies, because the tanks now hold trichlorosilane instead of VOCs. This should be revised during the next ROP renewal. The most recent PTI for this emission unit is PTI No. 185-07B.

- 304 Vent Recovery System comprised of interchangers HX1 2040 and HX2 2040 and condensers HX1 2044 and HX2 2044
- THROX System comprised of thermal incinerator burner DV24422, quencher DV24424, HCl Absorber DV24425, IWS 1st Stage DV24427, and IWS 2nd Stage DV 24428, vent SV2514-006
- Site Scrubber System comprised of two parallel spray tower scrubbers DV23709 and DV23710, vents SV2512-001/002
- 337 Spray Scrubber (9950, 9960 – scrubbers typically alternate in operation but can operate in parallel and vent to SV337-001/002, respectively)
- Tanker trailer vapor equalization
- 325 Vent Recovery System consisting of carbon beds (Bank No.1 - 20587, 20588, 20589 and Bank No. 2 - 22200, 22205, 22210) and the 337 Venturi Scrubbers (Bank No. 1 - 9956, 9957, 9958 operate in series and Bank No. 2 - 22245-1, 22245-2, 22245-3 operate in series) used as a backup control device for the emission unit in the event 304 Vent Recovery goes down.

SC I.1. restricts trichlorosilane and tetrachlorosilane (combined) emissions to less than 6.0 tpy, based on a 12-month rolling time period as determined at the end of each calendar month. SC VI.2. is the associated monitoring and recordkeeping requirement requiring the plant, within 30 days following the end of each calendar month, to calculate and record emissions from the Distillation Vents for the previous calendar month to demonstrate compliance. Combined emissions of trichlorosilane and tetrachlorosilane were 0.26 tpy for the 12-month rolling time period ending May 2019.

SC II.1 restricts the amount of material per hour, based on a one-hour average, from the Bulk Move Vents to the Site Scrubber System to less than 1,000 pounds of material. I reviewed flow from July 1, 2018 through July 1, 2019. The maximum flow was 787.03 pounds per hour during this time period. At the time of the inspection the mass flow rate from the Bulk Move Vents to the Site Scrubber was 61.8 pph.

SC. II.2. restricts the amount of material per hour based on an annual average, from the Bulk Move Vents to the Site Scrubber System to less than 600 pounds of material. I reviewed flow from July 1, 2018 through July 1, 2019. The average flow was 216.95 pounds per hour.

SC IV.1. requires the plant to install, calibrate, maintain and operate in a satisfactory manner, a device to monitor and record the mass flow rate of the vapor flow rate the Bulk Move Vents to the Site Scrubber System on a continuous basis. During the inspection the production engineer disclosed the flow transmitter had not been calibrated. The plant thought it was a smart device that would recalibrate itself based off of instrumentation drift. I followed up the inspection with an email asking for more information on how the smart device works. On July 25th, 2019, Ms. Kraut sent the following response: "I've looked into your question, and it appears the flow meter is not a smart device and does not re-calibrate or correct itself. When I inquired as to calibration of the device, I was informed that calibration has never been checked and the instrument was installed in 2011. I will follow up with the building engineer to ensure this device is on a scheduled routine calibration check schedule. For your information, there are several alarms associated with this device to validate compliance with the bulk move material limits specified in

table EU502-07 of the ROP.” I have asked for follow up on when the flow meter is scheduled for calibration and the results of that calibration once it takes place. In a subsequent email, Ms. Kraut said the calibration check on the flow meter will be completed by mid-August and that she will email me with the results.

SC IV.2. restricts operation of the equipment in the table listed below, unless the vent streams from the equipment are exhausted to the emission control devices associated with them. Each system has a required control efficiency that it must meet to be considered operating in a satisfactory manner. SITSCRUBBERS and the 337SCRUBBERS do not have testing requirements associated with them. The control efficiencies listed seem to be from manufacturer specifications and the way to comply with the efficiencies is to meet the parametrics of flow and temperature listed under the control device templates or in a Malfunction Abatement Plan (MAP). I reviewed the files and did not find a stack test performed on either unit to verify control efficiencies.

Equipment	First Emission Control	Required Control Efficiency	Second Emission Control	Required Control Efficiency
a. Distillation Vents	i. 304 Vent Recovery System followed by	88%-99%*	1. THROX System or	99.9%
			2. Site Scrubber System or	99.4%
			3. 337 Spray Scrubbers	99.4%
	ii. Or 325 Vent recovery System followed by	99.9%	1. THROX System or	99.9%
			2. Site Scrubber System or	99.4%
			3. 337 Venturi Scrubbers	99.4%

SC VI.3. requires the plant to comply with the applicable requirements of 40 CFR Part 60, Subpart Kb. This standard no longer applies, because the tanks listed now hold trichlorosilane instead of VOCs. This should be revised during the next ROP renewal.

VII.1 through VII.3. require prompt reporting of deviations, semiannual and annual reporting of monitoring and deviations. The compliance reporting section of this report discusses deviations reported.

Compliance Reporting

No deviations were reported for the time period January 1, 2018 through December 31, 2018.

VII.4. requires the plant to comply with the applicable requirements of 40 CFR Part 60, Subpart Kb. This standard no longer applies, because the tanks listed now hold trichlorosilane instead of VOCs. This should be revised during the next ROP renewal.

EU325-01

TCS (trichlorosilane) vent recovery system. EU325-01 receives vents from different processes to recover TCS. EU325-01 is located in 317 building. This emission unit typically vents to the carbon bed and venturi scrubber system described in FG325-01; however, the emission unit may vent to the 337 wet scrubber in the event the venturi scrubber system is down. The most recent PTI for this emission unit is PTI No. 44-06B.

- Carbon bed bank No. 1 (regenerative) comprised of carbon beds 20587, 20588, and 20589
- Carbon bed bank No. 2 (regenerative) comprised of carbon beds 22200, 22205, and 22210
- Venturi scrubber bank No. 1 comprised of venturi scrubbers 9956, 9957, and 9958 (operate in series)
- Venturi scrubber bank No. 2 comprised of venturi scrubbers 22245-1, 22245-2, and 22245-3 (operate in series)
- 337 wet scrubber (9950, 9960 – scrubbers typically alternate in operation but can operate in parallel and vent to SV337-001/002, respectively). NOTE – 337 scrubber acts as backup to venturi scrubber bank Nos. 1 and 2
- FGTHROX
- FGSITESCRUBBERS

The plant is limited 14.6 pph of hydrogen chlorine during maintenance and/or upset conditions for a maximum of 200 hours per rolling 12-month time period, per SC I.2. and IV.1., respectively. Mr. Stachowiak said the plant doesn't utilize this option. The plant will turn flow off and divert between the two carbon bed banks instead. Records are maintained per SC VI.1.

SC.I.1. restricts hydrogen chloride to 1.9 pph, which is determined by having either carbon bed bank No. 1 (carbon beds 20587, 20588, and 20589) or carbon bed bank No. 2 (carbon beds 22200, 22205, and 22210) is installed, maintained, and operated in a satisfactory manner (SC III.1.). Operating conditions for the carbon bed banks are defined under FG325-01 and is how compliance with the pph limit is maintained. See FG325-01 section of this report for further discussion on compliance of this condition.

VII.1 through VII.3. require prompt reporting of deviations, semiannual and annual reporting of monitoring and deviations. The compliance reporting section of this report discusses deviations reported.

Compliance Reporting

No deviations were reported for the time period January 1, 2018 through December 31, 2018.

FG325-01

Carbon bed and venturi scrubber system used to control emissions from EU325-01, EU502-01, and EU502-07. The 337 scrubber acts as a backup to the venturi scrubber system. The most recent PTI for this emission unit is PTI No. 44-06B.

- Carbon bed bank No. 1 (regenerative) comprised of carbon beds 20587, 20588, and 20589. Carbon bed bank No. 1 vents to either venturi scrubber bank No. 1, venturi scrubber bank No. 2, or the 337 scrubber. The typical mode of operation for carbon bed bank No. 1 is: one bed receives process exhaust, one bed is regenerating, and one bed is on standby with an alternating schedule every 6 hours.
- Carbon bed bank No. 2 (regenerative) comprised of carbon beds 22200, 22205, and 22210. Carbon bed bank No. 2 vents to either venturi scrubber bank No. 1, venturi scrubber bank No. 2, or the 337 scrubber. The typical mode of operation for carbon bed bank No. 2 is: one bed receives process

exhaust, one bed is regenerating, and one bed is on standby with an alternating schedule every 6 hours.

- Venturi scrubber bank No. 1 comprised of venturi scrubbers 9956, 9957, and 9958 (operate in series). Venturi scrubber bank No. 1 vents to vent No. SV337-003.
- Venturi scrubber bank No. 2 comprised of venturi scrubbers 22245-1, 22245-2, and 22245-3 (operate in series). Venturi scrubber bank No. 2 vents to vent No. SV337-004.
- 337 wet scrubber (9950, 9960 – scrubbers typically alternate in operation but can operate in parallel and vent to SV337-001/002, respectively). NOTE: 337 scrubber acts as a backup to venturi scrubber bank Nos. 1 and 2.

SC III.1. requires the plant to implement corrective action if the concentration of chlorosilanes from carbon bed bank No. 1 and 2 exceeds 100 ppm by volume. SC VI.1. and VI.2. are the associated recordkeeping requirements to monitor and record, on a continuous basis, the concentration of chlorosilanes from carbon bed bank No.1 and carbon bed bank No. 2. During the inspection, emissions were diverted to carbon bed bank 1 and the concentration of chlorosilanes was 0.5 ppmv. I reviewed records for the time period July 1, 2018 through July 1, 2019. Chlorosilanes were below the limits for this time period except for a period of time on December 30, 2019. See discussion under compliance reporting for deviation.

SC III.2. requires the plant to implement corrective action if while venting to venturi scrubber bank No.1, if the combined liquid flow rate of venturi scrubber Nos. 9956, 9957 and 9958 is less than 30 gallons per minute, or the individual liquid flow rate of No. 9958 is less than 10 gallons per minute. SC VI.3. is the associated recordkeeping requirement to monitor and record, on a continuous basis, the liquid flow rate for venturi scrubber Nos. 9956, 9957 and 9958, when venting to venturi scrubber bank No. 1. During the inspection the combined flow rate of venturi scrubber Nos. 9956, 9957 and 9958 was 508.3 gallons per minute (gpm). A low alarm was set at 50 gpm and a low low alarm was set at 10 gpm.

I reviewed liquid flow rates for venturi scrubber bank No. 1 from July 1, 2018 through July 1, 2019. The combined flow rate of venturi scrubber Nos. 9956, 9957 and 9958 maintained 30 gallons per minute or more, and the individual liquid flow rate of No. 9958 was more than 10 gallons per minute during times of normal operation. A few apparent exceedances were noted during this time period; however, these were instantaneous values and the 15-minute average was within appropriate values.

SC III.3. requires the plant to implement corrective action if while venting to venturi scrubber bank No.2, if the combined liquid flow rate of venturi scrubber Nos. 22245-1, 22245 2 and 22245-3 is less than 30 gallons per minute, or the individual liquid flow rate of No. 22245-3 is less than 10 gallons per minute. SC VI.4. is the associated recordkeeping requirement to monitor and record, on a continuous basis, the liquid flow rate for venturi scrubber Nos. 22245-1, 22245 2 and 22245-3, when venting to venturi scrubber bank No. 2. During the inspection the combined flow rate of venturi scrubber Nos. 22245-1, 22245 2 and 22245-3 was 61.8 gpm and the individual flow rate of venturi scrubber 22245-3 was 16.3 gpm. A low alarm was set at 10 gpm and the low low alarm was set at 10 gpm.

I reviewed liquid flow rates for venturi scrubber bank No. 1 from July 1, 2018 through July 1, 2019. The combined flow rate of venturi scrubber Nos. 22245-1, 22245 2 and 22245-3 maintained 30 gallons per minute or more, and the individual liquid flow rate of No. 22245-3 9958 was more than 10 gallons per minute during times of normal operation. A few apparent exceedances were noted during this time period; however, these were instantaneous values and the 15-minute average was within appropriate values.

SC III.4. restricts the concentration of HCl in the outlet water from venturi scrubber Nos. 9958 and 22245-3 to less than 10 percent by weight, respectively. SC VI.3. and VI.4. are the recordkeeping requirements associated with the process/operational restrictions. I reviewed data from July 1, 2018 through July 1,

2019. There were three apparent spikes above 10 percent by weight of HCl. These were instantaneous readings and the 15-minute average was less than 10 percent by weight for all three areas noted. At the time of the inspection the plant appeared to be meeting this requirement.

SC III.5. requires emissions from the process (after the carbon bed system) to be controlled by the 337 main scrubber in the event of a malfunction of venturi scrubber bank Nos. 1 and 2. The HCl emission rate from the process before entering the 337 main scrubber shall not exceed 1,490 pounds per hour. The plant shall not operate the process in this mode for more than 48 hours per calendar month, nor 144 hours per 12-month rolling time period as determined at the end of each calendar month. Mr. Stachowiak said the plant alternates between venturi bank No. 1 and 2 and if both were to malfunction then the plant shuts down. This permit flexibility is not utilized. I reviewed data from July 1, 2018 through July 1, 2019. Operation hours were zero during times of malfunction.

SC IV.1. requires the plant to equip and maintain the carbon bed system (carbon bed bank Nos. 1 and 2) with a monitor capable of detecting carbon breakthrough. The monitor shall be calibrated according to the manufacturer's specifications. Mr. Stachowiak provided the last two calibration checks on the carbon bed system. The system is calibrated annually.

SC IV.2. requires the plant to equip and maintain each venturi scrubber (venturi scrubber Nos. 9956, 9957, 9958, 22245-1, 22245-2 and 22245-3) with a liquid flow indicator. Mr. Stachowiak provided the last two calibration checks on each of the venturi scrubbers. The system is calibrated annually.

VII.1 through VII.3. require prompt reporting of deviations, semiannual and annual reporting of monitoring and deviations. The compliance reporting section of this report discusses deviations reported.

Compliance Reporting

12/9/18-12/18/18 FG325-01 SC IV.1. (PTI 44-06B)

IR analyzer used to measure the chlorosilane concentration at the outlet failed. New IR and spare parts were ordered. THROX controlled emissions. No exceedances.

NAME



DATE

8/5/19

SUPERVISOR

