



west virginia department of environmental protection

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ENGINEERING EVALUATION / FACT SHEET

BACKGROUND INFORMATION

Application No.: R13-1953H
Plant ID No.: 107-00001
Applicant: E.I. duPont de Nemours and Company
Facility Name: Washington Works
Location: Washington, Wood County
NAICS Code: 325211, 325120, and 325222
Application Type: Modification
Received Date: April 30, 2012
Engineer Assigned: Laura M. Jennings
Fee Amount: \$1,000.00
Date Received: May 7, 2012
Complete Date: May 31, 2012
Due Date: August 30, 2012
Applicant Ad Date: April 26, 2012
Newspaper: *The Parkersburg News and Sentinel*
UTM's: Easting: 442.3767 km Northing: 4346.8331 km Zone: 17
Description: A new compound will be used in the C2 process area as a replacement for APFO. Update of permit to reflect equipment shutdowns on Line #2, restart of Line #2 sparge system and revised calculations and emissions to reflect Line #2 finishing diversion to Line #3 and new operating scenario using the new compound including addition of VOCs to some emission points. Updated insignificant and emergency vent lists.

DESCRIPTION OF PROCESS

The C2 area manufactures fluoropolymer resins by reacting fluromonomers in the presence of APFO, catalyst and demineralized water. Unreacted fluromonomers are vented to recycling facilities at the end of the reaction. For most product types, the fluoropolymer and water slurry is pumped to agglomerators that mechanically separate the fluoropolymer from the water. Alternatively, the reactor output may be sent to facilities which concentrate the dispersion to higher solids and package the dispersion for sale.

A new compound will be used in the C2 process area as a replacement for APFO in some of the current dispersion product lines. The new compound is a Dimer Acid/Salt (CAS #13252-13-6 and CAS #62037-80-3). A permit determination related to this change for dispersion production in the C2 area and the associated VOC emissions was submitted to WVDAQ on July 31, 2009 and subsequent approval was received on August 27, 2009 (PD09-047).

This modification application covers the use of the new compound in the solid polymer portion of the process. Because this change will be phased in over several years, the current limits associated with the APFO process must remain in effect in addition to the new limits needed for VOC emissions related to the new compound.

The changes submitted in this application include:

1. Inclusion of the new Dimer Acid/Salt compound that will be used in the C2 process area as a phased in replacement for APFO. The new compound may also be referred to as FRD 903/902.
2. Revised calculations to reflect new or increased VOC emissions related to the new compound and its degradation product E1.
3. Addition of acetonitrile emissions as an impurity in the new compound from emission points C2EJE and C2EFE.
4. Increase in emissions from C2EQ to reflect additional screen pack changes.
5. Revised emission calculations reflect operating scenarios using 100% APFO or 100% new compound. The use of both compounds will occur over a multi-year phase in period. Therefore, permit limits will be established to cover both scenarios.
6. Addition of VOC emissions from emission point C2DTE due to E1.
7. Change in service for C2DJ from backup to C2DK to water only service receiving decant waters from C2EG. No regulated pollutants will be emitted from C2DJ in this service; therefore, control device C2DJC and emission point C2DJE are being requested to be removed.
8. Updates to insignificant equipment and emergency vent lists.
9. Removal of equipment ID's C2DI, C2KI, C2KL, C2DM, C2KN, C2EB, C2DBC, C2KT, C2DO, and C2KJ and associated emission points previously removed from service in 2007.
10. Restart of Line #2 Sparge Bin C2DH to take extruded polymer from Line #3. This unit will not operate if both C2DK and C2ET are operating.
11. Update C2ENC equipment form to reflect current air flow rates and pollutant inlet/outlet information.

Equipment List:

The following changes have either occurred since permit R13-1953G was issued June 28, 2007 or are being requested in this modification.

Table 1: Changes to the equipment table

Emission Unit ID	Date of Change	Type of Change	Emission Unit ID	Date of Change	Type of Change
C2DA	Sept 09	Modification	C2DI	June 07	Removal

C2DE	Sept 09	Modification	C2DJ	July 12	Removal
C2DG	Sept 09	Modification	C2DM	June 07	Removal
C2DH	July 12	Modification	C2DO	June 07	Removal
C2DK	July 12	Modification	C2EB	June 07	Removal
C2DW	July 12	Modification	C2KI	June 07	Removal
C2EC	Sept 09	Modification	C2KJ	June 07	Removal
C2EF	July 12	Modification	C2KL	June 07	Removal
C2EG	July 12	Modification	C2KN	June 07	Removal
C2EH	July 12	Modification	C2DBC	June 07	Removal
C2EN	July 12	Modification	C2DJC	July 12	Removal
C2EQ	July 12	Modification	C2DMC	June 07	Removal
C2ER	July 12	Modification	C2EUC	June 07	Removal
C2ES	July 12	Modification	C2KMC4	June 07	Removal
C2ET	July 12	Modification	C2KMC3	June 07	Removal
C2KD	July 12	Modification	C2KP	July 12	Modification
C2KO	July 12	Modification	C2KW	Sept 09	Modification

The installation and modification plan is:

- Equipment ID's C2DI, C2KI, C2KL, C2DM, C2KN, C2EB, C2DBC, C2KT, C2DO, and C2KJ were removed from service with notice to WVDAQ dated August 10, 2007.
- Use of the new Dimer acid/salt compound for commercial production in the finishing area is estimated to being in the 3Q2012.
- Restart of Line #2 sparge bin C2DH in 3Q2012.

SITE INSPECTION

The DuPont Washington Works site is well known to WV DAQ. The next inspection of the facility has been assigned to be completed by September, 2012. The last full on site inspection was conducted in September, 2009 and they were found to be in compliance.

The writer conducted a site visit on May 23, 2012 and met with John Mentink and Okey Tucker for the purpose of reviewing the process and RACT analysis associated with this permit application.

ESTIMATE OF EMISSIONS BY REVIEWING ENGINEER

Overview:

Emissions were calculated based on the Ideal Gas Law for ideal gases. To determine annual emissions, the number of batches or the number of yearly cleaning or outages were used. For non-ideal situations, an equation of state was used to determine mole fractions. Air measurements determine pounds per event. Polymer rates may have a surrogate such as motor amps, screw speed, etc. for hourly emissions or number of batches for annual emissions. Emissions per pound of polymer are either engineering estimates, determined by off gas analysis, scaling up from a pilot plant, or simple stack measurements.

The values presented in the detailed calculations were derived from a combination of engineering calculation software (TK Solver) based on the Ideal Gas Law and analytical measurements.

All calculations and variables were reviewed by the writer and verified based on the available information.

Reactors:

Polymerization takes place at high temperature and pressure in an aqueous medium. After polymerization is complete, unreacted materials are recycled to the monomer production area for re-use. After the initial vent to recycle or to the thermal converter, the reactors contain residual unreacted gas that is vented to atmosphere prior to processing the next batch.

The vent to atmosphere is accomplished by applying vacuum to the reactor head space to reach a nominal pressure of 5.2 psia (-9.5 psig vacuum). Next, the atmospheric vent is closed and N₂ is added to reach ambient pressure. Then the aqueous batch is dropped into a decanter. N₂ is left on during this transfer process, so the net result is that the residual gas in the reactor head space is drawn into the next vessel downstream of the reactor and emitted from this vessel.

For emission determination and allocation, the total amount that is emitted from both the reactor and the next vessel downstream is calculated based on the total amount of gas in the reactor after recycle to monomers (or to thermal converter), and then this total is allocated to reactor vent and decanter (or stabilization tank) vent based on the vacuum pressure setting.

Emissions from the reactor and associated vessel (decanter or stabilization tank) depend upon the amount and composition of the gas remaining in the reactor head space after venting to the monomers area (or thermal converter), and the head space temperature and pressure.

There are several combinations of cases that must be evaluated in order to determine the maximum potential emissions from these vessels. There are four basic types of polymers made in the reactors; one using only TFE, two others with small amounts of co-monomers, and a copolymer (PFA). Each product within the four basic types was evaluated with respect to aqueous phase volume, and the worst case (highest reactor head space volume) product was used as the basis for emission calculations. Each of the four product types were evaluated for both a pure monomer case and a maximum impurity case. Pure

monomer is the worst case for potential VOC emissions, and maximum impurities is the worst case for ODCs and HAPs. Only certain product recipes utilize the FRD903/902 compounds.

A small fraction of batches must be aborted after the initial pressure up phase. Because the aqueous phase is smaller for an aborted batch than for a normal batch, this case becomes the worst case for maximum hourly potential emissions. However, because batches are aborted infrequently, the effect on annual potential emissions is minimal. Pure monomer is the worst case for an aborted batch because the total amount of impurities introduced into the reactor is less for an aborted batch than a batch which is reacted to completion.

Summary:

Because of the number of changes to emissions associated with this modification, Emissions Table 2 provides comprehensive emissions for all emission points regardless of whether or not there was a change. The change in emissions covered by this permit modification are provided in Table 3.

Table 2 - Emissions Table

Emission Point ID	Emission Unit ID	Control Device	Regulated Pollutant	Maximum Potential Uncontrolled Emissions		Maximum Potential Controlled Emissions	
				lb/hr	tpy	lb/hr	tpy
Area	C2EE	None	VOC	0.01	0.01	0.01	0.01
C2EJE	C2EJ C2DG	None	VOC	107.19	3.60	107.19	3.60
			HCl	0.003	0.001	0.003	0.001
			Toluene	0.003	0.002	0.003	0.002
			Acetonitrile	0.002	0.002	0.002	0.002
			ODC	0.28	0.01	0.28	0.01
			Non-regulated	0.79	0.01	0.79	0.01
C2EFE	C2EJ C2EF	None	VOC	75.10	7.51	75.10	7.51
			HCl	0.003	0.001	0.003	0.001
			Toluene	0.003	0.003	0.003	0.003
			Acetonitrile	0.003	0.004	0.003	0.004
			ODC	0.28	0.01	0.28	0.01
			Non-regulated	0.79	0.01	0.79	0.01
C2DKE	C2DK	C2DKC	VOC	6.30	5.51	6.30	5.51
			PM10	5.20	4.55	0.01	0.01

C2EGE	C2EG	C2EGC	VOC	9.40	11.60	9.40	11.60
			PM10	7.70	8.43	0.01	0.01
C2DAE	C2DA C2DE C2EC C2KW C2KX	None	VOC	11.90	2.10	11.90	2.10
			Non-regulated	1.50	2.15	1.50	2.15
C2DTE	C2DW C2EH	C2DWT1/ C2DWC2, C2EHC1 /C2EHC2, C2DTC3 C2DTC3	APFO	15.08	32.75	0.46	0.99
			PM10	290.57	633.8 3	0.48	1.03
			VOC	1.10	2.75	1.10	2.75
C2DSE	C2DS	C2DSC	PM10	800	8.63	0.08	0.01
C2ENE	C2EN	C2ENC	PM10	4000	11000	0.40	1.10
C2KPE	C2KP	C2KPC	PM10	1000	11000	0.10	0.11
C2KUE	C2KU	None	Flourides	0.151	0.003	0.151	0.003
T7ME	C2ES	T7ME	HF	0.28	0.77	See R13-1823	
			CrF3	0.016	0.05		
			PM10	10.16	27.94		
			Flourides	7.60	20.91		
			Non-regulated	75.44	207.8		
C2ERE	C2ER	None	VOC	4.00	10.50	4.00	10.50
			HF	0.036	0.125	0.036	0.125
			PM10	1.00	2.73	1.00	2.73
			Non-regulated	0.50	1.67	0.50	1.67
C2KDE	C2KD	None	VOC	0.18	0.56	0.18	0.56
			HF	0.06	0.18	0.06	0.18
C2EUE	C2EU	C2EUC	PM10	4.00	11.0	0.01	0.01
C2DHE	C2DH	None	VOC	3.25	0.13	3.25	0.13
			HF	0.016	0.01	0.016	0.01
C2ETE	C2ET	None	VOC	3.25	11.16	3.25	11.16
			HF	0.016	0.060	0.016	0.060
C2EVE	C2EV	None	VOC	67.69	0.33	67.69	0.33
			Butanone	52.674	0.253	52.674	0.253

			Di-sec-octyl-phthalate	0.299	0.002	0.299	0.002
			Methanol	0.467	0.003	0.467	0.003
			Chromium III Compounds	0.299	0.01	0.299	0.01
C2KOE1	C2KO	C2KOC1	VOC	0.05	0.04	0.05	0.04
			HF	0.013	0.012	0.013	0.012
C2KOE2	C2KO	C2KOC2	PM	0.01	0.01	0.01	0.01
C2EQE	C2EQ	C2EQC	VOC	0.60	0.18	0.60	0.18
			HF	0.021	0.005	0.001	0.001
			PM10	0.04	0.05	0.01	0.01
			CO	0.01	0.01	0.01	0.01
Area	C2KQ	None	VOC	5.50	1.51	5.50	1.51

Table 3: Net Emission Changes

Regulated Pollutant	Emission Limit R13-1953G		Emission Limit R13-1953H		Emissions Change	
	lb/hr	tpy	lb/hr	tpy	lb/hr	tpy
PM10	3.6	5.51	2.10	5.02	-1.50	-0.49
VOC	293.4	55.73	295.51	57.48	2.11	1.75
Hydrogen Flouride (HF)	1.85	1.52	1.32	0.42	-0.53	-1.10
Total HAPs	n/a	0.03	n/a	0.03	0	0

REGULATORY APPLICABILITY

STATE REGULATIONS

45CSR7 TO PREVENT AND CONTROL PARTICULATE MATTER AIR POLLUTION FROM MANUFACTURING PROCESSES AND ASSOCIATED OPERATIONS

There is no change to the applicability as a result of this permit modification. The permittee continues to be subject to 45CSR7. References to equipment that have been removed from service have been deleted from the permit requirements.

45CSR13 PERMITS FOR CONSTRUCTION, MODIFICATION, RELOCATION AND OPERATION OF STATIONARY SOURCES OF AIR POLLUTANTS,

NOTIFICATION REQUIREMENTS, ADMINISTRATIVE UPDATES, TEMPORARY PERMITS, GENERAL PERMITS, PERMISSION TO COMMENCE CONSTRUCTION, AND PROCEDURES FOR EVALUATION

This application meets the definition of a modification permit according to the definition in section 2.17. The changes result in an increase in VOC emissions of 6.5 pph and 11.83 tpy when compared to equipment in service in the previous 12 months. This emissions increase does not take into consideration emissions decreases from equipment that was shut down in 2007.

The process area is also covered by permit R13-2617 (site wide 45CSR21 and 45CSR27 requirements and the thermal converter [T7ME] is covered by the current revision of permit R13-1823.

The applicant has demonstrated compliance with 45CSR13 by submitting a complete permit application for the modification, submitting the application fee, and placed a Class I legal advertisement in a newspaper of general circulation in the area where the source is located.

45CSR14 PERMITS FOR CONSTRUCTION AND MAJOR MODIFICATION OF MAJOR STATIONARY SOURCES OF AIR POLLUTION FOR THE PREVENTION OF SIGNIFICANT DETERIORATION

As of January 2, 2011, pursuant to actions taken by the USEPA, Greenhouse Gases (GHGs) became a regulated pollutant under the major NSR program. As such, an evaluation must be done for any increase in GHG emissions resulting from construction or modification to determine PSD applicability per 40 CFR 52.21. There are no new emissions of components listed in table A-1 of 40 CFR 98.2; therefore, PSD for GHG does not apply.

45CSR21 REGULATION TO PREVENT AND CONTROL AIR POLLUTION FROM THE EMISSION OF VOLATILE ORGANIC COMPOUNDS

DuPont is located in Wood County, WV and is subject to 45CSR21 for VOC emissions.

45CSR21-40.3c requires RACT analysis on a case by case basis for those VOC emissions greater than 6 pph which are constructed, modified, or begin operation after the date 45CSR21 becomes effective. Two emission points [C2DKE and C2EGE] in this application have increases that will cause them to now exceed 6 pph. This is due to the formation of E1 (a degradation product) from the use of the new compound (Dimer Acid/salt "FRD 903/902").

RACT analysis was conducted on two alternatives for VOC control from

C2DKE and C2EGE. Because the E1 is not water soluble, carbon absorption and destruction in the existing thermal converter were the considered alternatives. The estimated total annual cost for controls are \$36,333/ton VOC for carbon absorption and \$35,404/ton VOC for thermal destruction at maximum production rates.

Several units will have new or increased VOC emissions. The proposed changes will result in a net increase in VOC emissions of 6.5 pph and 11.83 tpy when compared to equipment in service in the previous 12 months. No emissions credit was taken for equipment that was shut down in 2007. Scrubber C2DTC will now emit VOC's with this change and there is no scrubber control efficiency for VOCs due to its insolubility.

45CSR30 REQUIREMENTS FOR OPERATING PERMITS

The process area associated with this permit application operates under Title V permit R30-10700001-2010, Part 2 of 14. The applicant submitted a joint application that includes a minor modification to their Title V permit.

FEDERAL REGULATIONS

There are no new federal regulations as a result of this permit application.

TOXICITY OF NON-CRITERIA REGULATED POLLUTANTS

There is one new hazardous air pollutant associated with this modification.

Acetonitrile:

Acetonitrile has many uses, including as a solvent, for spinning fibers, and in lithium batteries. It is primarily found in air from automobile exhaust and manufacturing facilities. Acute (short-term) inhalation exposure results in irritation of mucous membranes. Chronic (long-term) exposure results in central nervous system effects, such as headaches, numbness, and tremors. No data are available on its carcinogenic effects in humans; EPA has classified it as a Group D, not classifiable as to human carcinogenicity.

AIR QUALITY IMPACT ANALYSIS

The proposed project does not meet the definition of a major modification according to the definitions in 45CSR14 and 45CSR19; therefore, modeling is not required for this permit application.

MONITORING OF OPERATIONS

The attachments in Appendix A have been updated to reflect recordkeeping changes as a result of this modification.

CHANGES TO PERMIT R13-1953G

- Miscellaneous updates were made to the title page, headers, etc. to reflect current administration and current permit revision.
- Section 1.0 - (1) removal of emission units as identified in the process description section; (2) removal of the following equipment that is on the Insignificant List: C2DQ, C2ED, C2EE, C2EZ, C2KT, C2KY, C2KZ; and (3) updated emission point id from n/a to C2DAE for C2KW and C2KX.
- Section 3.1.3 - updated template reference from 45CSR15 to 45CSR34.
- Section 4.1.1, 4.1.2, 4.1.3, and 4.1.4 - (1) removed equipment that is no longer in service as identified in the process description section; (2) updated significant figures to DAQ rounding policy; (3) updated emissions to reflect emissions in Table 2; (4) updated 4.1.4 to “total HAPs” for all emission points and identified in footnote.
- Section 4.1.10 - changed reference from permit R13-1823E to “the current revision of permit R13-1823”.
- Sections 4.1.11, 4.1.13, 4.1.14, 4.2.1, 4.2.2, 4.2.3, and 4.2.4 - removed references to equipment that is no longer in service as identified in the process description section.
- Section 4.1.22 - removed compliance date for MON MACT because the compliance date is in the past.
- Section 4.2.1 - corrected reference from 4.1.1 to 4.1.11.
- Appendix A, Attachment A - (1) changed parameter language from “C2EJE” to “system #1” and “C2EFE” to “system #2”; (2) Deleted parameters for C2DI and C2EB that were removed from service; (3) Added monitoring as indicated in Table 4.

Table 4: Additions to Monthly Record Keeping, Attachment A

Equipment ID	Value	Monthly Monitoring Parameter
Facility		# of completed GenX batches
C2DA		# of GenX dispersion batches
C2DW		Max pph held for one hour during the month
C2EH		Max pph held for one hour during the month
C2DT, C2DW, C2EH		Max pph rate of all TDD for one hour during the month

- Appendix A, Attachment B - deleted emission points C2DAE, C2DJE, C2DME, C2EBE1, C2EBE2, C2KAE, C2KIE, and C2KNE that have been removed from service.
- Appendix A, Attachment C - (1) deleted emission points C2DBE, C2DME, C2EBE1/C2EBE2, C2KAE, C2KIE from VOC Emissions and added C2DTE; (2) deleted emission points C2DBE, C2DJE, C2DME, C2EBE1/C2EBE2, and C2KIE from PM10 emissions; (3) deleted C2DBE, C2DME, C2EBE1/C2EBE2, C2KAE, C2KIE, and C2KNE from HF emissions; (4) and combined Toluene & Total HAP emissions section

- into "total HAPs".
- Appendix A, Attachment D - deleted scrubber C2DBC.

RECOMMENDATION TO DIRECTOR

The writer recommends that the Modification Permit R13-1953H be granted to DuPont, Washington Works facility located in Wood County, WV. Based on the information provided in the permit application, the applicant meets all applicable federal and state air regulations pertaining to the requested change.

Laura M. Jennings
Permit Engineer

Date