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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION IX
75 Hawthorne Street
San Francisco, CA 94105

September 30, 2002

Teresa K. Makarewicz
Manager-Environmental Affairs
Shell Oil Products US
Martinez Refinery
P.O. Box 711
Martinez, CA 94553-0071

RE: United States v. Equilon Enterprises, LLC

Dear Ms. Makarewicz:

This letter is in response to your June 17, 2002, request for approval of alternative monitoring plans for the marine vapor recovery loading facility ("MVRLF") owned by Shell Oil Products US ("Shell") at its petroleum refinery in Martinez, California. The United States Environmental Protection Agency ("USEPA"), Region 9, approves the proposed alternative monitoring plans as modified. See Enclosure. The enclosed alternative monitoring requirements do not alter any of the other requirements of New Source Performance Standards, Subparts A and J that may apply to the MVRLF.

If you have any questions regarding this response, please contact John Kim, Air Enforcement Office, at (415) 972-3984.

Sincerely,

Jack P. Broadbent
Director, Air Division

Enclosure

cc: Ellen Garvey, BAAQMD

Alternative Monitoring Provisions for MVRLF

Shell shall comply with the requirements of 40 C.F.R. Part 60, Subparts J and A, except as explicitly listed below. The following alternate monitoring requirements shall only apply to the marine vapor recovery loading facility at the Shell Martinez refinery.

1.0 Monitoring methods and Frequency

(a) Gasoline and Finished Gasoline Component Vapors with Sulfur Specifications- Shell shall take a one-time detector tube sample using a Gastec #4LL H_2S tube on the gas inlet to the thermal oxidizer. If the gas stream composition changes, or if the gas stream will no longer be required to meet product specifications, then the gas stream must be resubmitted for approval under the alternative monitoring plan.

(b) Non-Gasoline/Non-Finished Gasoline Component Vapors Mixed with Natural Gas

i. Products with Sulfur Specifications- Shell shall take a one-time detector tube sample and submit an alternative monitoring plan similar to the plan for the gasoline and finished gasoline component vapors each time the new product is loaded.

ii. Products without Sulfur Specifications- Shell shall sample the gas stream at least every 2 hours while the marine vessel recovery system is processing the vessel vapors to assure that the gas stream complies with the less than 162 ppm 3-hour rolling H_2S average requirement. For each product, Shell may propose a less frequent sampling schedule if the measured H_2S concentration is insignificant.

2.0 Recordkeeping Requirements

(a) Shell shall keep a record of each gas sampling performed pursuant to Section 1.0. Each record shall identify the date and location of sampling.

(b) Shell shall maintain records for a period of five (5) years after the generation of such documentation, except this alternative monitoring plan, which shall be kept permanently, or until it has been replaced with a different alternative monitoring plan or the MVRLF is permanently taken out of service.

3.0 Reporting Requirements

When loading the products without product sulfur specifications, Shell shall submit a written report to USEPA within 5 days of exceeding the Subpart J requirement for H_2S concentration. The report shall include, but not limited to the date and location of sampling and the duration of the exceedance.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
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San Francisco, CA 94105

DEC 04 2002

Ms. Teresa K. Makarewicz
Manager-Environmental Affairs
Shell Oil Products US
Shell Martinez Refinery
P.O. Box 711
Martinez, CA 94553-0071

RE: Alternate Monitoring Plans ("AMPs") for CR-2 Oxidizer Vent to F-14011 or F-13425, Lubricants Hydrotreater #1 Vacuum Flash Dryer Vent to F-34, Lubricants Hydrotreater #2 Vacuum Flash Dryer Vent to F-13000, and Sulfonation Unit SO_2 Absorber Vent to F-69.

Dear Ms. Makarewicz:

This letter is in response to your letters of September 26, 2001, October 24, 2001, and November 29, 2001, requesting approval of AMPs for four refinery fuel gas streams at the Shell Martinez refinery. Equilon Enterprises, LLC d.b.a. Shell Oil Products US ("Shell") provided additional information on November 6, 2002, through an E-mail. As part of the September 26, 2001 letter, Shell also requested approval of an alternate test method for measuring SO_2 emissions at the Catalytic Cracking Unit. This request has been forwarded to the Office of Air Quality Planning and Standards ("OAQPS"), which is responsible for reviewing alternate test methods. As for the above four AMPs, the United States Environmental Protection Agency ("USEPA"), Region 9, has made the final determination as follows:

Regulatory Background

The New Source Performance Standards for Petroleum Refineries (Petroleum Refinery NSPS), 40 C.F.R. §§ 60.100 through 60.109, include emission standards and monitoring requirements for fuel gas combustion devices ("FGCDs"). 40 C.F.R. § 60.104(a)(1) requires the owner or operator of a FGCD at a petroleum refinery to burn no refinery fuel gas that contains hydrogen sulfide (H_2S) in excess of 230 milligrams per dry standard cubic meter (0.10 grain per dry standard cubic foot; 162 parts per million by Volume, dry basis). Pursuant to 40 C.F.R. § 60.105(a)(3), the owner or operator of a FGCD subject to 40 C.F.R. § 60.104(a)(1) is required to install, calibrate, maintain, and operate a continuous monitoring system ("CMS") to monitor and record the concentration by volume of sulfur dioxide emitted into the atmosphere. The specifications for the CMS are codified in 40 C.F.R. § 60.105(a)(3)(i-iv).

40 C.F.R. § 60.13(i) also sets forth: "After receipt and consideration of written application, the Administrator may approve alternative procedures to any monitoring procedures or requirements of [Part 60]...."

Shell's Request

On September 26, 2001, Shell requested approval of AMPs for Caustic Regenerator #2 Oxidizer Combined Vent to F-14011 or F-13425, Lubricants Hydrotreater Unit #1 Vacuum Flash Dryer Vent to F-34, Lubricants Hydrotreater Unit #2 Vacuum Flash Dryer Vent to F-13000, and Sulfonation Unit SO_2 Absorber Vent to F-69. Shell also submitted additional information for the Lubriants Hydrotreater Unit #1 on October 24, 2001, and for the Sulfonation Unit on November 29, 2001. Under the provisions of a Consent Decree (Civil Case Number H-01-0978, United States v. Equilon Enterprices, LLC), Shell is required to implement the approved AMPs for these refinery fuel gas streams by December 31, 2002.

As part of the review process, USEPA has summarized the proposed AMPs in the enclosure to this letter.

Approval of Shell's Request

USEPA has determined that the requests contain all of the information specified in the policy "Conditions for Approval of [An] Alternative Monitoring Plan for Miscellaneous Refinery Fuel Gas Stream" and the proposed AMPs for these fuel gas streams are appropriate. Therefore, the Administrator of USEPA, by authority duly-delegated to the undersigned, approves the proposed AMPs.

The approval of the proposed AMPs does not alter any of the other requirements of New Source Performance Standards, Subparts A and J that may apply to the Shell Martinez refinery. In addition, USEPA doesn't consider complying with the values of the proposed representative process parameters is equivalent to complying with the NSPS emission standards. As stated in the proposed AMPs, a representative process parameter functions as an indicator of a stable and low H_2S concentration for the stream. If the measured value of the process parameter is less than the proposed value, Shell shall immediately conduct draeger tube sampling at the proposed location and initiate any corrective actions.

If you have any questions regarding this response, please contact John Kim, Air Enforcement Office, at (415)972-3984.

Sincerely,

Jack P. Broadbent

Jack P. Broadbent
Director, Air Division

Enclosure

cc: Mr. Peter Hess, BAAQMD

Summary of Proposed AMPs

1. AMP for Caustic Regenerator #2 Oxidizer Combined Vent to F-14011 or F-13425.

Process Unit:	Delayed Coking Department/ Caustic Regenerator #2 ("CR-2").
Fuel Gas Stream:	CR-2 Oxidizer Combined Vent to F-14011 or F13425.
Proposed Sampling Location:	Unit Pressure Control Valve. 49 PV-137A
Pollutant Monitored:	H_2S
Proposed Process Parameter:	CR-2 Caustic Strength
Proposed Value of the Process Parameter:	2 % by weight NaOH

Shell states that CR-2, which consists of an oxidation tower and two stages of separation, regenerates spent caustic. The mixing of air in the oxidation column regenerates the caustic and produces a vent gas, which is routed to Heater F-14011 in the Heavy Gasoline Hydrotreater Unit or Heater F-13425 in the Delayed Coker Unit.

The C3/C4 treaters upstream of CR-2 have H_2S removal capacity via amine contracting followed by caustic treating. The amine treating in combination with the caustic treating allows very little opportunity for H_2S to enter CR-2. In addition, H_2S readily reacts with caustic to form sodium sulfide, which reacts with the oxygen in the oxidizer column to create sodium thiosulfate and sodium hydroxide. These components stay in the aqueous phase, and H_2S is not re-created.

To show the actual concentration H_2S in the vent gas, Shell tested fourteen samples for the frequently operated gas streams and seven samples for the infrequently operated gas streams between April 15 and 28, 2001. These samples showed 0 ppmv of H_2S.

Shell identified a minimum CR-2 caustic strength of 2 % wt NaOH as a representative process parameter that can function as an indicator of a stable and low H_2S concentration for the stream. The vent gas is expected to have 0 ppmv H_2S since H_2S readily reacts with caustic to form sodium sulfide as long as free sodium hydroxide is available. The minimum CR-2 caustic strength of 2 % weight NaOH will indicate that free NaOH is available to react with any potential H_2S in the stream.

Shell proposes the following H_2S monitoring schedule:

a. Twice per week for a period of six months (52 samples);
b. Once per quarter for a period of six quarters (6 samples);
Twice per year; and
d. Whenever the concentration of NaOH falls below 2 %.

Sampling and analyses a-c will be done randomly, and the CR-2 caustic strength will be tested and reviewed once per day by the CR-2 operator.

2. AMP for Lubricants Hydrotreater Unit #1 Vacuum Flash Dryer Vent to Heater F-34

Process Unit:	Lubricants Hydrotreater Unit #1 ("LHU-1")
Fuel Gas Stream:	Vacuum Flash Dryer Vent to Heater F-34.
Proposed Sampling Location:	3/4" Bleeder Upstream of the Flame Arrestor.
Pollutant Monitored:	H_2S
Proposed Process Parameter:	Product Stripper Column Steam Flow, 74FC133.
Proposed Value of the Process Parameter:	750 lbs per hour.

The Lubricants Hydrotreater Unit #1 produces lubricant base oils and feed stocks for downstream processing units. The process of hydrotreating reduces the level of organic sulfur, organic nitrogen, and aromaticity of the hydrocarbon feedstocks. Byproducts of the hydrotreating process include H_2S, ammonia (NH_3), light hydrocarbon liquid, and light hydrocarbon gasses. The majority of these byproducts are removed when the hydrotreated oil enters a flash vessel where the system pressure is reduced. The reduction in pressure causes hydrocarbon liquid with low boiling points to vaporize and separate from the remaining hydrocarbon liquid. The trace amounts of remaining H_2S, NH_3, excess H_2, and light hydrocarbon gases are stripped by high pressure steam in the product stripper. The desirable heavy hydrocarbon liquid from the product stripper is fed to the vacuum flash dryer ("VFD"). The water vapor and any other gasses in the VFD are educted out of the VFD to Heater F-34 to maintain the low operating pressure of the VFD.

To show the actual concentration H_2S in the vent gas to Heater F-34, Shell tested fourteen samples between Oct 8 and 21, 2001. These samples showed 0 ppmv of H_2S. Due to the flash vessel and the product stripping process described above, the H_2S sampling results are typical of what would be expected from this fuel gas stream.

Shell identified a minimum steam flow rate of 750 pounds per hour in the product stripper column as the representative process parameter. The minimum steam flow rate of 750 pounds per hour should ensure enough upward vapor traffic in the product stripper column to adequately drive any H_2S in the hydrotreated product overhead. Therefore, there should not be much, if any, H_2S remaining in the hydrotreated product when it is routed to the VFD.

Shell proposes the following H_2S monitoring schedule:

a. Twice per week for a period of six months (52 samples);
b. Once per quarter for a period of six quarters (6 samples);
c. Twice per year; and
d. Whenever the steam flow rate falls below 750 lbs per hour.

Sampling and analyses a-c will be done randomly, and the steam flow rate in the product stripper column will be continuously recorded and monitored several times each shift by operating personnel.

3. Alternative Monitoring Plan for Lubricants Hydrotreater #2 Vacuum Flash Dryer Vent to Heater F-13000

Process Unit:	Lubricants Hydrotreater Unit #2 ("LHU-2")
Stream:	Vacuum Flash Dryer Vent to Heater F-13000.
Proposed Sampling Location:	3/4" Bleeder Upstream of the Flame Arrestor.
Pollutant Monitored:	H_2S
Proposed Process Parameter:	Product Stripper Column Steam Flow, 78FC26.
Proposed Value of the Process Parameter:	2,000 lbs per hour.

The Lubricants Hydrotreater Unit #2 produces lubricant base oils and feed stocks for downstream processing units. The process of hydrotreating contacts hydrocarbon liquid with hydrogen at high pressure and high temperature over specially formulated catalyst. Hydrotreating reduces the level of organic sulfur, organic nitrogen, and aromaticity of the hydrocarbon feedstocks. Byproducts of the hydrotreating process include H_2S, NH_3, light hydrocarbon liquid, and light hydrocarbon gasses. The majority of these byproducts are removed when the hydrotreated oil enters a flash vessel where the system pressure is reduced. The reduction in pressure causes hydrocarbon liquid with low boiling points to vaporize and separate from the remaining hydrocarbon liquid. The trace amounts of remaining H_2S, NH_3, excess H_2, and light hydrocarbon gases are stripped by high pressure steam in the product stripper. The desirable heavy hydrocarbon liquid from the product stripper is fed to the VFD. The water vapor and any other gasses in the VFD are educted out of the VFD to Heater F-13000 to maintain the low operating pressure of the VFD.

To show the actual concentration H_2S in the vent gas to Heater F-13000, Shell tested fourteen samples between October 10 and 23, 2001. These samples showed 0 ppmv of H_2S in the vent gas. Due to the flash vessel and product stripping process described above, the H_2S Sampling results are typical of what would be expected from this fuel gas stream.

Shell identified a minimum steam flow rate of 2,000 pounds per hour in the product stripper column as the representative process parameter. Shell believes that the minimum steam flow rate of 2,000 pounds per hour should ensure enough upward vapor traffic in the product stripper column to adequately drive any H_2S in the hydrotreated product overhead. Therefore, there should not be much, if any, H_2S remaining in the hydrotreated product when it is routed to the VFD.

Shell proposes the following H_2S monitoring schedule:

a. Twice per week for a period of six months (52 samples);
b. Once per quarter for a period of six quarters (6 samples);
c. Twice per year; and
d. Whenever the steam flow rate falls below 2,000 lbs per hour.

Sampling and analyses a-c will be done randomly, and the steam flow rate in the product stripper column will be continuously recorded and monitored several times each shift by operating personnel.

4. Alternate Monitoring Plan for Sulfonation SO_2 Absorber Vent to F-69

Process Unit	Sulfonation Unit/Asphalt Plant
Stream:	SO_2 Absorber Vent to Heater F-69
Proposed Sampling Location:	3/4" Bleeder Downstream of Vent Outlet
Pollutant Monitored:	H_2S
Proposed Process Parameter:	SO_2 Absorber Make-up Caustic Flow, 764FC2646
Proposed Value of the Process Parameter:	0.5 gallon per minute

Shell states that the Sulfonation Unit produces lubricant base oils and specialty industrial products. The process of sulfonation contacts hydrocarbon liquid with fuming sulfuric acid (equivalent strength of 105 % H_2SO_4). A byproduct of the sulfonation process is Lubes Spent Acid ("LSA") which is a mixture of high molecular weight sulfonates, sulfuric acid, and trace amounts of tolusol. LSA is stored temporarily on-site prior to offsite processing at a local acid reclaimer. While in storage, vapor consisting of SO_2, nitrogen, and trace amounts of solvent is generated. The vapor is directed to the SO_2 absorber vessel, C-70, where the vapor stream is contacted with a dilute caustic solution. The dilute caustic solution absorbs and reacts with the SO_2 vapor to form sodium sulfite which is dissolved in the water. The remaining gas is directed to Heater F-69.

The vent gas is expected to have no H_2S since the original hydrocarbon feed to the SU has been hydrotreated, steam stripped, and flash dried in the VFD. However, if there happened to be some H_2S in the vapor stream, it would be treated by the C-70 dilute caustic stream prior to routing to F-69.

Shell tested 14 samples from the vent stream to F-69 for H_2S concentration between November 16 and 29, 2001. These samples showed 0 ppmv H_2S as expected. Due to the hydrotreating, steam stripping, and flash drying processes described above, the H_2S sampling results are typical of what would be expected from this fuel gas stream.

Shell identified a minimum SO_2 Absorber make-up caustic flow of 0.5 gallons per minute as the representative process parameter. Any H_2S in the vent stream should react with the caustic to form sodium sulfide. The proposed flow rate of caustic ensures that there will be free caustic available for this reaction.

Shell proposes the following H_2S monitoring schedule:

a. Twice per week for a period of six months (52 samples);
b. Once per quarter for a period of six quarters (6 samples);
c. Twice per year; and
d. Whenever the caustic flow falls below 0.5 gallons per minute.

Sampling and analyses a-c will be done randomly, and the SO_2 Absorber make-up caustic flow will be continuously recorded and monitored several times each shift by operating personnel.