April 7, 1999

Dr. Henry Lau
USEPA
Office of Pollution Prevention and Toxics
(7406)
401 M St. SW
Washington, D.C. 20460

Re: HPV Questions about Spent Sulfuric Acid

Dear Dr. Lau;

Thank you for listening to my concerns about our spent sulfuric acid and willingness to evaluate whether it should be part of the HPV Challenge program. Hopefully the explanation that follows will be sufficient for you to judge. If not please contact me and we will try to make the description more complete.

One of our unit processes at a refinery is the alkylation plant. It takes light gases in the C3 to C4 range and joins them together into higher carbon chain materials that become a high-octane blend stock for normal gasoline. It involves joining isobutane with butylenes or propylenes to produce the gasoline range hydrocarbon.

This reaction is done in the liquid phase in a high purity sulfuric acid. The quality of the alkylate is dependant on the following in order of priority:

1. Isobutane/olefin ratio
2. Reaction temperature
3. Degree of mixing
4. Acid strength(purity)
5. Feed composition

After the alkylation is completed the acid and hydrocarbon are separated by fractionation. The acid is recycled and the hydrocarbon mixture is separated. The isobutane is recycled, the gasoline range products are captured and stored, and the propane and butane gases are sent to the fuel gas system for fuel. Unfortunately, the alkylation process does produce a small portion of hydrocarbons that are in the C12-C16 range. These are outside of the gasoline range of hydrocarbons. These "oils" are soluble in the acid and are called "acid soluble oils", ASO's. If the concentration of these ASO's reaches about 20%, the reaction could "run away" producing mostly ASO's. For this reason and for reasons of corrosion control and quality of alkylate, the normal operating purity of the acid is about

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801-524-2700

93%. This is usually maintained by removing a slipstream of contaminated acid and feeding in an equivalent slipstream of fresh acid.

This slipstream of sulfuric acid that has accumulated the alkyl esters of C12-C16 hydrocarbons is what we call "spent acid". This material is collected and sent to a third party sulfuric acid plant. The sulfuric acid plant regenerates the spent acid by removing the hydrocarbon and returns the fresh, 99% purity, acid to the refinery for reuse.

Sinclair Oil has reported this spent acid as CAS No. 68611-55-2. We have listed it because we considered it to be "otherwise used" in the process. We do not manufacture sulfuric acid. We do not sell it as a product. We send the spent acid to be regenerated or recycled. When we receive the sulfuric acid, it is pure and considered inorganic. During its use as a catalyst it becomes contaminated with hydrocarbon. The spent acid does fit the CAS No. that is shown, but is not a product manufactured for sale.

Sinclair Oil Corporation has two questions then.

1. Should we be reporting this spent acid in our TSCA reports done every four years?
2. Should this spent acid be considered for the HPV Challenge program?

Thank you for your consideration of these questions. Sinclair Oil Corporation will likely join the Petroleum Consortium for the HPV Challenge program. We will have to seek out other consortiums for materials not covered by the Petroleum Consortium. Thus I am trying to determine if the spent acid will be part of the program and if I need to seek this additional partnership. If you need additional information please give me a call at 801-524-2745.

Sincerely yours,

Klaue F Forsgren, VP
Sinclair Oil Corporation

Cc: Kevin Brown

April 26, 1999

Dr. Henry Lau
USEPA
Office of Pollution Prevention and Toxics
(7406)
401 M St. SW
Washington, D.C. 20460

Re: HPV Questions about Spent Sulfuric Acid

Dear Dr. Lau;

Thank you for continuing to listen to my concerns about our spent sulfuric acid and willingness to evaluate whether it should be part of the HPV Challenge program. I have contacted Koch Sulfur who has a sulfuric acid plant in Riverton, Wyoming. They are the ones who receive our spent sulfuric acid and regenerate it. They have provided the enclosed process description of their recycling process. Hopefully their process explanation will be sufficient for you to determine what category we fit in. If not please contact me and we will try to make the description more complete.

A couple of explanations will be helpful to you now. You asked if the spent sulfuric acid is used as a fuel. The answer is yes and no. A typical analysis of the spent acid is 90% sulfuric acid, 7% water, and 3% hydrocarbon. When the spent sulfuric acid is atomized into the decomposition furnace, which is direct fired with natural gas, the acid decomposes as shown but the hydrocarbon burns into CO_2 and H_2O. If the hydrocarbon were not present, it would take more natural gas to maintain the temperature in the burner. The 3% hydrocarbon contributes some small BTU input, probably reducing the natural gas input by 1-2%.

The second question you asked was "did the production of the new sulfuric acid involve a chemical reaction?" Acid is ionic. The decomposition in the furnace is to SO_2, CO_2, H_2O, and O_2. The SO_2 is converted to SO_3 with a vanadium pentoxide catalyst. The SO_3 is then absorbed into 98% concentration H_2SO_4 where it combines with the 2% water that is left to produce the 99.5% H_2SO_4 we use at the refinery. When water and SO_3 mix, they go to sulfuric acid. You will have to decide if the joining of ionic materials to provide other ionic materials involves a chemical reaction or not.

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It is important to note that the contamination of the sulfuric acid with hydrocarbon does not involve a chemical reaction. It is contaminated by not being able to remove the 3% hydrocarbon from the sulfuric acid as we normally do in the alkylation unit.

The spent acid is sulfuric acid that has been contaminated by the hydrocarbon. The spent acid is shipped to Koch who burns the hydrocarbon during the acid decomposition process and converts the acid to its basic components. These are then reunited in the normal process of the manufacture of sulfuric acid and sold back to Sinclair. I do believe this fits the classical definition of recycle

Sinclair has a contract to purchase sulfuric acid from Koch. The contract calls for a price per ton that is based on the current market for acid. The contract requires that we send to them all of our spent acid for recycle. The spent acid is not considered to be a feed stock that we sell to them. The cost of fresh acid with no spent acid for recycling is less than the cost of fresh acid with recycling of spent acid. Again, this fits the classical definition of recycle.

Thank you for your consideration of these questions. Sinclair Oil Corporation will join the Petroleum Consortium for the HPV Challenge program. We will have to seek out other consortiums for materials not covered by the Petroleum Consortium. Thus I am trying to determine if the spent acid will be part of the program and if I need to seek this additional partnership. If you need additional information please give me a call at 801-524-2745.

Sincerely yours,

Klane F Forsgren, VP
Sinclair Oil Corporation

Cc: Kevin Brown, w/o attachments

[redacted] [redacted]

Process Description

The process for regeneration of alkylation spent sulfuric acid can be divided into two areas; decomposition and gas cleaning, and contact section - conversion of cleaned SO_2 to concentrated sulfuric acid.

Decomposition and Gas Cleaning

Spent acid is fed to the decomposition furnace from the 2000 ton spent acid storage tank [redacted] to produce 100 STPD of product acid. The spent acid is atomized into the furnace by two 25 TPD and one 50 TPD air atomized spray burners. [redacted] In the furnace the spent acid is decomposed at 1800°F to sulfur dioxide, carbon dioxide, oxygen, and water. Undecomposed sulfuric acid is minimized by efficient spent acid atomization, and furnace operation at 1800°F with low exit oxygen (2%). The decomposition reaction is highly endothermic, requiring a considerable amount of heat. Heat is provided by [redacted] natural gas/propane. To minimize fuel requirements and reduce the gas cleaning system size and cost, combustion air is preheated to 700°F using excess heat available from the converter system. Air preheating reduces natural gas requirements by about 35%-40%. [redacted]

Furnace exit gas, at 1800°F, is cooled in the existing fire tube waste heat boiler to 600°F, producing 275 psig saturated steam. The partially cooled gas is quench cooled to its adiabatic saturation temperature (165°F-170°F) by direct contact with a 20%-30% sulfuric acid circulating solution in a venturi contactor. The venturi quench system removes some of the undecomposed sulfuric acid and furnace ash. A small purge stream is withdrawn from the venturi circulating system and filtered in a sand filter to remove ash. The filtered weak acid purge is used for product acid dilution. If the spent acid feed composition changes to the point dissolved impurities in the purge could contaminate product acid, the filtered purge can be recycled to the furnace and decomposed. Ash collected on the sand filter at the rate of 100-250 pounds per day is backwashed to the water cooling tower, and eventually to the pond in the cooling tower blowdown.

The cooled gas leaves the venturi cyclonic separator and enters the graphite shell and tube gas cooler where sufficient water is condensed from the gas to permit production of product acid at the concentrations desired. The gas travels down through the

ACID [redacted]

tubes of the vertical heat exchanger and is cooled to 105°F by 75°F cooling water flowing on the shell side of the exchanger. Gas cooler condensate is used for make-up water in the venturi quench system; is sprayed into the inlet gas to the gas cooler to flush the top tubesheet to prevent solids build-up, and the excess is air stripped of dissolved SO_2 and routed to the water cooling tower. The gas cooler is designed to accept 50 psig steam on the shell side to permit sulfur removal should the furnace operate deficient of oxygen.

The final cleaning step is removal of residual sulfuric acid mist and solids from the gas in a lead tube electrostatic mist precipitator. Weak acid and solids collected in the precipitator drain to the venturi quench system.

Contact System

In the contact section of the plant the cleaned SO_2 gas is dried by direct contact with 98% sulfuric acid, diluted with dry air from the air drying tower to a concentration of 10.6% SO_2, heated to 790°F using a portion of the heat from the SO_2 oxidation reaction, converted to SO_3 in four beds of vanadium pentoxide catalyst, and absorbed in water contained in 98% sulfuric acid to produce sulfuric acid.

Gas System - The cleaned SO_2 gas is dried to -40°F dew point by direct contact with a circulating 98% sulfuric acid stream in the packed SO_2 drying tower. The dry SO_2 gas passes through an entrainment separator before leaving the tower and entering the main gas blower. Air from the air fan (existing main blower) is dried in the existing drying tower by direct contact with 98% sulfuric acid, and used as quench air in the converter and to dilute the SO_2 gas entering the main blower to a concentration of 10.6% SO_2.

The main blower (relocated Jeffrey City blower with new motor drive and inlet guide vane control) receives the diluted SO_2 gas at 20" H_2O pressure and increases the gas pressure to 70" H_2O to force it through the remainder of the plant.

Cold SO_2 gas from the blower is heated to converter inlet temperature of 790°F in gas to gas heat exchangers using a portion of the heat of the SO_2 to SO_3 oxidation reaction. The gas is first heated to 465°F in the shell side of the No. 4B (cold) heat exchanger using a portion of the heat in the gas leaving the fourth catalyst bed. Final heating is accomplished in the Hot (No. 1) heat exchanger that cools the gas between the first and second catalyst beds.

ACID [redacted]

The catalyst in the converter (18,000 liters of new ring type catalyst) is arranged in four layers or passes, with cooling between each layer to maintain optimum conversion of SO_2 to SO_3. The gas enters the first converter catalyst bed at 790°F, where 64% of the SO_2 is converted to SO_3. Heat of reaction increases the gas temperature to 1123°F. The gas is cooled to 820°F in the tube side of the hot heat exchanger and enters the second catalyst pass where conversion increases to 87% and the temperature increases to 939°F. The gas is cooled to 820°F by the addition of quench air from the air drying tower and enters the third bed. In the third catalyst bed conversion is increased to 96% and the temperature to 866°F. The gas is again cooled by air quench to 800°F and enters the fourth catalyst bed where final conversion of SO_2 occurs increasing conversion to 98%.

Gas leaves the converter at 812°F and is cooled in the tube side of the air preheat exchanger (No. 4A) to 569°F, while preheating furnace combustion air to 700°F. The gas is further cooled to 347°F in the tube side of the cold (No. 4B) heat exchanger before entering the oleum and absorption tower.

In the absorption tower, SO_3 contained in the gas is absorbed into a circulating stream of 98% sulfuric acid. The gas, containing less than 2000 ppm of SO_2, passes through a mist eliminator before exiting to atmosphere via the stack.

Acid System - A portion (100 gpm) of the 98% acid at 160°F flowing to the existing air drying tower is diverted to the SO_2 drying tower, where it dries the wet SO_2 gas from the gas cleaning system. The acid leaves the tower and is pumped to the inlet of the air drying tower where it combines with the remainder (200 gpm) of the air drying tower acid and enters the tower at 170°F.

The combined fresh and SO_2 drying tower acid dries the dilution and quench air in the existing air drying tower. Acid leaves the tower at 173°F and flows to the existing acid pump tank.

In the existing absorption tower, 300 gpm of 98% acid at 180°F contacts the gas from the converter-heat exchange system and absorbs SO_3 from the gas. The acid leaves the tower at 230°F and flows to the existing pump tank. Acid from the drying tower and absorption tower are combined with dilution water, from filtered quench tower purge or fresh make-up water, to control concentration. Pump tank acid at 98% concentration and 203°F is pumped (existing pump) through the existing cast iron drying and absorber acid coolers for recirculation to the towers.

Product acid at 99.5% strength is withdrawn from the acid stream leaving the absorption tower and pumped via the existing product

ACID [redacted]

pump through the product cooler (existing) to storage. The existing product system is used for 93.19%, 98.5% product acid and oleum.

Utility Systems

The existing water cooling tower system is upgraded to provide 75°F water at the required heat removal duty. Cold cooling water is routed to the gas cooler, oleum cooler and product cooler. Cooling water return from the gas cooler is then used for the drying and absorber coolers. Water collected from the acid cooler sump at 120°F is returned to the tower by the hot well pump. Cooling tower make-up water includes about 5 gpm of gas cooler condensate and purge filter backflush and about 15 gpm of fresh water. Cooling tower blowdown at the rate of about 7 gpm containing up to 0.25% furnace ash is routed to the existing evaporation pond.

Saturated steam at 275 psig at a rate varying from 7900 to 4700 pounds per hour, depending on the quantity of spent acid and sulfur burned in the furnace, is used in the air fan turbine driver (existing main blower) exhausting at 50 psig. The exhaust 50 psig steam , as well as excess 275 psig steam are used for sulfur, building, and storage tank heating.

Electric power will be brought to the No. 2 plant control building by the utility company at 4160 volts and 480 volts where the motor control center for the new equipment is located.

The existing instrument air system is utilized to provide air for new instruments and atomization air for the spent acid burners.

To: Bill Frick
From: Alice Crowe
Subject: EPA's Reinterpretation of NSPS Subpart J Relative to Proposed Sulfur Gasoline Standards

This message is a followup to the conversation we had in your office about NSPS Subpart J "Regulation-by Enforcement" issues, particularly Region V's new interpretation that the addition of a new sulfur recovery unit (SRU) subjects all existing SRU's fed by the same gas stream to NSPS and the impact this reinterpretation will have in light of EPA's proposed Tier II sulfur requirements for gasoline.

If gasoline sulfur rules due out from EPA in the year 2000 require refiners to reduce sulfur to a 30 ppm level as is presently required by the California Air Resources Board (CARB) from the typical non-California level of 300-500 ppm, refiners will have to hydrotreat fluid catalytic cracker (FCCU) feed or gasoline blending component streams. New hydrotreaters for this requirement could easily cost 10 to 20 million dollars. However, the cost of compliance with the proposed sulfur gasoline rules does not stop there. The removal of sulfur from gasoline pursuant to Tier II requirements will create a ripple effect throughout the refinery.

The removal of sulfur from gasoline by hydrotreating creates hydrogen sulfide (H2S). The additional H2S must be absorbed and concentrated by the amine treating unit (ATU). Some refiners will have spare capacity in their ATU's which is capable of absorbing the additional H2S. However, in the absence of spare ATU capacity, additional millions of capital dollars will be required to expand ATU capability.

Concentrated H2S from the ATU will be sent to the sulfur recovery unit (SRU). The ripple effect continues. If there is not spare capacity in the existing SRU, the refiner will have to add a new SRU at a cost of 10 to 20 million dollars. Even if a new SRU is not required, EPA's reinterpretation of NSPS would subject existing SRU's to Subpart J solely because of an emissions increase ignoring the clearly stated exemptions in the rule. For the addition of a new SRU, EPA's reinterpretation of NSPS would subject all existing SRU's in the refinery to Subpart J based on their erroneous argument of common feed source.

As a final potential ripple effect, in order to meet the NSPS Subpart J standards for SO2, a refiner might have to install a wet scrubber following the tail gas incinerator on the SRU. This is yet another 10 to 20 million dollar capital expense.

Thus, EPA's reinterpretation of NSPS Subpart J coupled with the significant lowering of gasoline sulfur levels could result in significant multiple capital expenditures in the tens of millions of dollars each for new or expanded hydrotreaters, ATU's, SRU's, and even tail gas scrubbers.

EPA Region V's reinterpretation of Subpart J is that the addition of a single SRU (the "affected facility" subject to NSPS) triggers NSPS requirements for the new unit and for existing grandfathered units, regardless of number or age or regulatory status, that are supplied with the same feed gas stream, even if the existing units are not themselves altered. This is in direct contradiction to EPA regulations which provide that the addition of a new affected facility to a stationary source does not by itself subject any other facility in the source to NSPS.

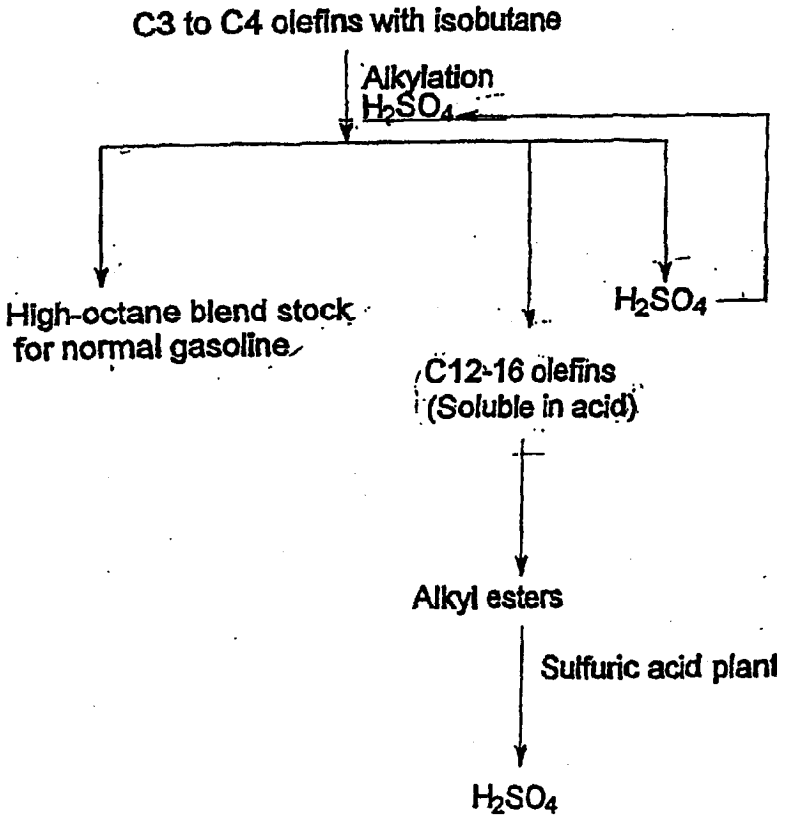
The NSPS standard for SRU's with an oxidation control system (ie. an incinerator) is 250 ppm SO2. The standard for SRU's without an incinerator is 300 ppm of total reduced sulfur (TRS) and 10 ppm H2S. By subjecting SRU's to this standard, EPA is currently effectively requiring a 95 to 98 % reduction in the amount of SO2 that would be emitted to the atmosphere in the absence of SRU's. The additional requirement for reducing sulfur in gasoline by approximately 90% (from 300 to 30 ppm), will add only 1% or so to the total sulfur already being removed from crude oil by refineries and converted into elemental sulfur by SRU's. In other words, EPA's gasoline sulfur regulations are an excellent example of the law of diminishing returns. The last small amount of sulfur is proposed to be removed from refinery product streams such as gasoline at tremendous cost versus the large amount of sulfur already being removed at much more modest cost.

HPV Questions about Spent Sulfuric Acid

Questions:

1. In the Sinclair letter of April 7, 1999, the alkylation process does produce a small portion of hydrocarbons that are in the C12-C16 range. These are outside of gasoline range of hydrocarbons. These "oils" are soluble in the acid and are called "acid soluble oils" (ASO). If the concentration of these ASO's reaches about 20% the reaction could "run away" producing mostly ASO's. For this reason and for reasons of corrosion control and qulaity of alkylate, the normal operating purity of the acid is about 93%. This is usually maintained by removing a slipstream of contaminated acid and feeding in an equivalent slipstream of fresh acid. The slipstream of sulfuric acid that has accumulated the alkyl esters of C12-16 hydrocarobns is what industry call "spent acid". This material is collected and sent to a third party sulfuric acid plant. The sulfuric acid plant regenrates the spent acid by removing the hydrocarbon and returns the fresh, 99% pruity, acid to the refinery for reuse. Sinclair Oil has reported this spent acid as CASRN 68611-55-2.

2. We are not sure that the CASRN 68611-55-2, represents "Sulfuric acid, mono-C10-16-alkyl esters" is an appropriate CASRN for the chemical substance in question, "alkyl esters of C12-16 hydrocarbons" (spent acid).—
3. The "spent acid" is a byproduct in the manufacture of high-octane blend stock for normal gasoline. The byproduct is not reportable if it has commerical value only to municipal or private organizations who (i) burn it as a fuel, (ii) dispose of it as a waste, including in a landfill or for enriching soil, or (iii) extract component chemical substances which have commercial value.
4.


C3 to C4 olefins with isobutane
Alkylation
H_2SO_4
High-octane blend stock for normal gasoline
H_2SO_4
C12-16 olefins (Soluble in acid)
Alkyl esters
Sulfuric acid plant
H_2SO_4