United States Patent [19]

Brooks

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[45] **Feb. 17, 1981**

[54] **METHOD FOR TREATING EFFLUENT GAS FROM SULFONATION PROCESS**

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[51] **Int. Cl.**[3] **C07C 143/24**; C07C 143/02

[52] **U.S. Cl.** .... **260/505 R**; 260/513 T; 260/504 R

[58] **Field of Search** .... 260/513 T, 505 R, 504 R

[56] **References Cited**

U.S. PATENT DOCUMENTS

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Kirk-Othmer "Encyclopedia of Chem. Tech." (1969) pp. 465–473.

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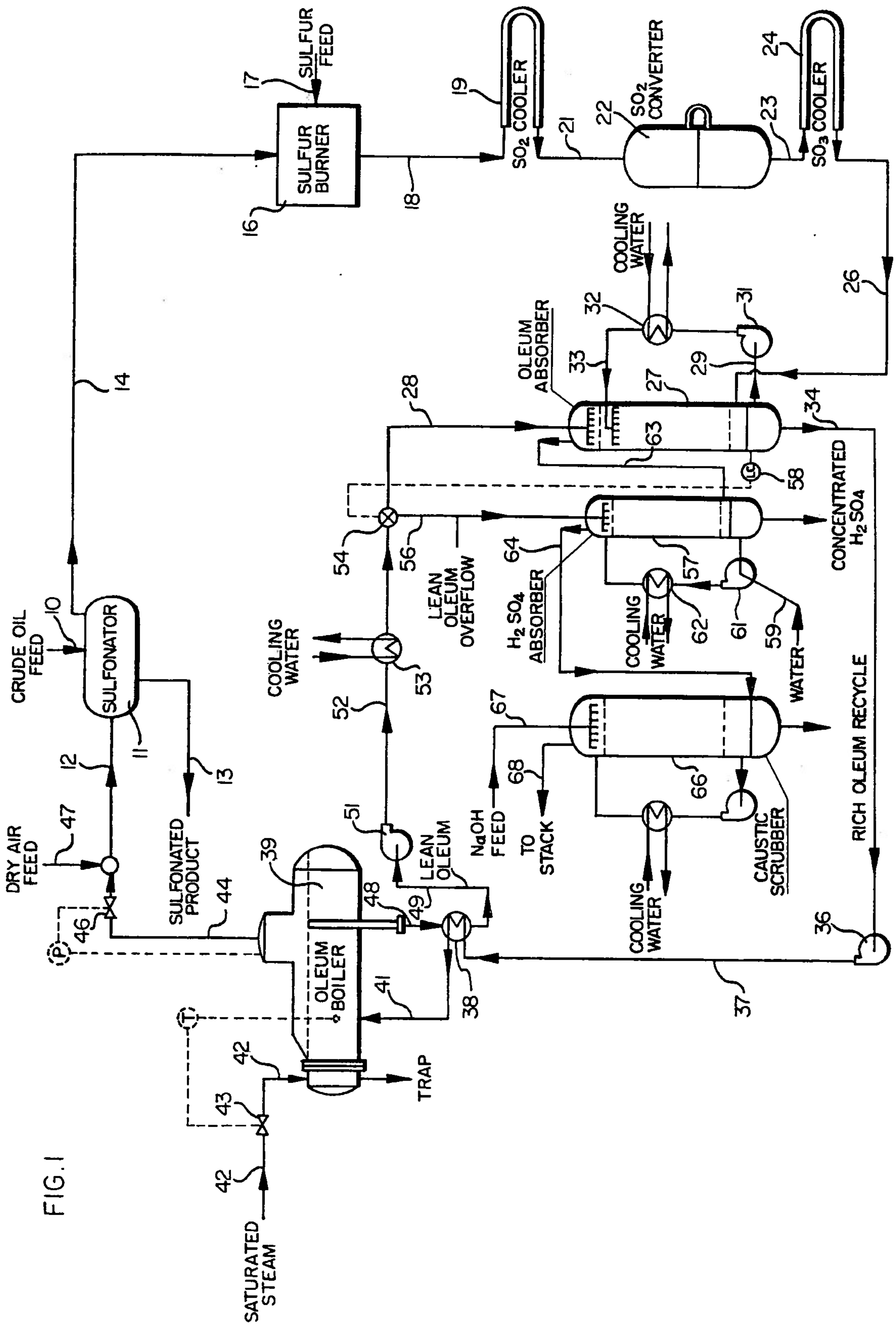
[57] **ABSTRACT**

A relatively large amount of SO_2 effluent gas from a sulfonation process is converted to SO_3 and recycled back to the sulfonation process as part of the SO_3 sulfonating agent. The rest of the SO_3 used as the sulfonating agent is derived from a sulfur burner located downstream of the sulfonation operation and in the recycle path of the SO_2 in the effluent gas. Hydrocarbons in the effluent gas are converted to CO_2 and H_2O in the sulfur burner. The H_2O and SO_3 are removed from the gas stream at an SO_3 absorber which forms rich oleum from which the SO_3 is subsequently removed for use in the sulfonation operation, leaving lean oleum which is used at the SO_3 absorber to remove H_2O and SO_3 from the gas stream. Gases leaving the SO_3 absorber include some SO_3 and are passed through an H_2SO_4 absorber along with water and lean oleum to produce concentrated H_2SO_4.

15 Claims, 2 Drawing Figures



SULFUR FEED
SULFUR BURNER
SO_2 COOLER
SO_2 CONVERTER
SO_3 COOLER
COOLING WATER
OLEUM ABSORBER
CONCENTRATED H_2SO_4
LEAN OLEUM OVERFLOW
H_2SO_4 ABSORBER
WATER
RICH OLEUM RECYCLE
CRUDE OIL FEED
SULFONATOR
DRY AIR FEED
SULFONATED PRODUCT
LEAN OLEUM
NaOH FEED
TO STACK
CAUSTIC SCRUBBER
OLEUM BOILER
TRAP
SATURATED STEAM

FIG. 1

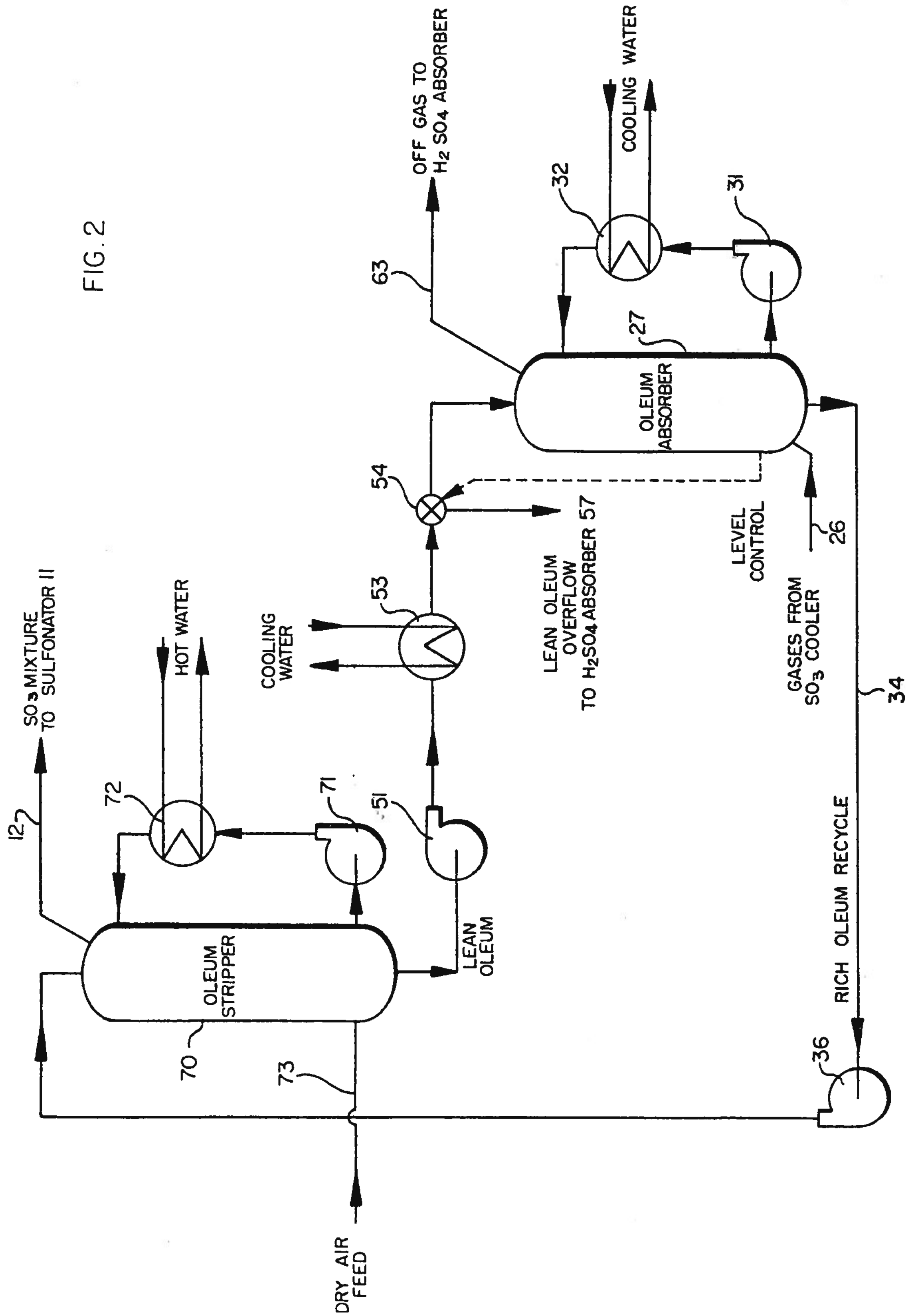

OFF GAS TO
H_2 SO_4 ABSORBER
COOLING WATER
32
31
63
27
OLEUM
ABSORBER
54
LEAN OLEUM
OVERFLOW
TO H_2SO_4 ABSORBER 57
LEVEL
CONTROL
26
GASES FROM
SO_3 COOLER
34
53
COOLING
WATER
SO_3 MIXTURE
TO SULFONATOR 11
HOT WATER
12
72
71
51
LEAN
OLEUM
OLEUM
STRIPPER
70
73
RICH OLEUM RECYCLE
36
DRY AIR
FEED

FIG. 2

METHOD FOR TREATING EFFLUENT GAS FROM SULFONATION PROCESS

BACKGROUND OF THE INVENTION

This invention relates to a process for sulfonating liquid organic feed stocks and more particularly it relates to a sulfonation process, using sulfur trioxide (SO_3) as the sulfonating agent, in which provision is made for treating the effluent gases from the sulfonation process to recover for reuse any SO_3 or SO_2 therein and to eliminate therefrom noxious fumes before discharging the gases to the atmosphere.

Sulfonation of a wide variety of organic liquid feedstocks, and particularly relatively highly refined hydrocarbons, such as "detergent alkylate", benzene, toluene and the like, has been practiced conventionally for many years. Although several different sulfonating agents, such as concentrated sulfuric acid, oleums of various strengths, and SO_3 have been used, treatment with SO_3 is usually the process of choice, since the reaction is essentially instantaneous and proceeds to completion, thus minimizing equipment requirements for a given rate of production.

In a common process for sulfonation with SO_3, the SO_3 in vapor form is mixed with dry air and brought into contact with the liquid feed stock to produce a sulfonic acid which is then neutralized to form sulfonate. Although the desired sulfonated product is quickly and simply obtained, the effluent gases from the sulfonation step present a disposal problem, since they contain, in addition to excess SO_3 not consumed in the sulfonation step, vapors of the liquid feed stock, as well as SO_2 formed during the sulfonation step and perhaps some residual SO_2 introduced into the sulfonation process with the SO_3. Generally, the amount of SO_2 in the effluent gases is sufficiently small that it can be removed from the effluent gases by scrubbing, without economic disadvantage. For example, with some relatively highly refined hydrocarbons, the SO_2 content of the effluent gas is only 2–3 wt. % of the SO_3 introduced at the sulfonation step.

In the case of sulfonating crude oil or gas oil, however, the SO_2 content of the effluent gas can be in the range 5–15 wt. % of the SO_3 introduced at the sulfonation step. "Gas oil" is a term conventionally used in the petroleum industry to describe a hydrocarbon friction near the bottom "cut" in the atmospheric distillation of petroleum, or its equivalent.

Therefore, in the sulfonation of crude oil or gas oil, or in the sulfonation of relatively highly refined hydrocarbon at very large rates of sulfonation (e.g., 50 to 100 million pounds of sulfonate per year), the amount of SO_2 (and SO_3) in the effluent gases from the sulfonation step can be quite large, and this amount represents an excessive economic loss unless the SO_2 (and SO_3) in the effluent gases is recovered for re-use in the sulfonation step.

Recent proposals for tertiary recovery of petroleum involve the use of sulfonated petroleum fractions which are injected into wells to increase the recovery of petroleum trapped within the rock or sand formation. For such use, large quantities of sulfonated petroleum fractions, typically having a molecular weight of 300–1000, are necessary. These large quantities are produced by SO_3 sulfonation at very large rates, and, in doing so, substantial quantities of SO_2 are formed.

Moreover, in view of the increasingly rigorous standards relating to atmospheric pollution, a sulfonation effluent gas stream containing substantial concentrations of SO_2 and SO_3 cannot be discharged directly to the atmosphere, and, particularly in the case of a plant treating large volumes of feed stocks, disposal of the effluent gases from the sulfonation step presents a serious problem.

SUMMARY OF THE INVENYION

The effluent gas from the sulfonation step contains SO_2, SO_3, residual air and hydrocarbon mist and vapor. In accordance with the present invention, the SO_2 and SO_3 is recovered for further use by feeding the effluent gas to a sulfur burner along with make-up sulfur. The sulfur burns to SO_2 and is catalytically oxidized to SO_3, along with the residual SO_2. The hydrocarbon materials burn to carbon dioxide and water.

The resulting SO_3 can be recycled back to the sulfonation step, but the water should not be recycled as it would react with the SO_3 to form H_2SO_4, and the SO_3 would not be available to enter into the sulfonation step, which is undesirable. The water is removed before the sulfonation step with an SO_3 absorption step performed on the gases downstream of the sulfur burner (said gases comprising SO_3 and H_2O plus CO_2 and residual O_2 and N_2).

In the SO_3 absorption step, the catalytically oxidized gases from the sulfur burner are contacted with lean oleum. Some of the SO_3 is absorbed by the lean oleum to form rich oleum. The water reacts with some of the SO_3 to form sulfuric acid which in turn reacts with additional SO_3 to form oleum. The carbon dioxide, along with oxygen and nitrogen from the residual air, are unaffected by the oleum absorption step and can be discharged to the atmosphere without creating pollution problems.

The rich oleum is then desorbed to produce SO_3 for the sulfonation process and lean oleum, and the lean oleum from the desorption process is recycled to the SO_3 absorption step. Some sulfuric acid is formed as a byproduct and is removed from the system, and some of the water formed by burning the hydrocarbon mist may enter into this sulfuric acid. Because the sulfur dioxide is reoxidized and recycled, the use of expensive alkaline agents to remove substantial amounts of SO_2 by scrubbing is avoided.

The catalytic oxidizing step used to oxidize the SO_2 to SO_3, and the immediately preceding sulfur burning step are both performed downstream of the sulfonating step and constitute the steps from which is derived all the SO_3 with which the liquid organic feed stock is sulfonated.

Other features and advantages are inherent in the method claimed and disclosed or will become apparent to those skilled in the art from the following detailed description in conjunction with the accompanying diagramatic drawings.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow sheet of a continuous process embodying the method of the invention; and

FIG. 2 is a flow sheet of an alternative step in the process of FIG. 1, demonstrating a different method of desorbing or stripping dissolved SO_3 from the SO_3-rich oleum employed therein.

DETAILED DESCRIPTION

As shown in FIG. 1, a stream of crude oil or other feed is introduced through line 10 to sulfonator 11, to which is introduced through line 12 a mixture of SO_3 and dry air, typically containing about 3–15% by volume of SO_3, e.g., 8–10%. In sulfonator 11, sulfonation proceeds in conventional fashion, yielding a desired liquid sulfonation product (e.g., sulfonic acid) which is recovered through line 13 for eventual neutralization to produce a sulfonate, for example.

The effluent gases from sulfonator 11, optionally after passage through a liquid deentrainment device such as a cyclone separator (not shown), pass through line 14 to a conventional sulfur burner 16, to which makeup sulfur is supplied as necessary through line 17. The gas stream entering sulfur burner 16 contains essentially all of the oxygen and nitrogen present in the dry air fed to sulfonator 11 and, in addition, unreacted SO_3, typically up to about 1.5% by volume, SO_2 formed during the sulfonation step, typically in a concentration of about 0.5–2% by volume, and untreated vapors of the liquid feed stock introduced into sulfonator 11 through line 10. Some of these vapors may be removed by a mesh filter or electrostatic precipitator (not shown) located upstream of sulfur burner 16.

In sulfur burner 16, typically operated at a temperature of about 1,100°–1,500° F. (593°–815° C.) in conventional fashion, the sulfur feed 17 burns to form SO_2, and the entrained hydrocarbon liquid entering through gas line 14 burns to form CO_2 and water vapor, while the SO_2 and SO_3 entering through gas line 14 remain essentially unchanged.

The gases produced in sulfur burner 16, leaving through line 18, pass through SO_2 cooler 19, wherein the temperature of the gas stream is lowered to about 850°–1,100° F. (454°–593° C.) in conventional fashion, and enter SO_2 converter 22 via line 21. In SO_2 converter 22, SO_2 in the gas stream reacts with oxygen (from the air originally supplied upstream at sulfonator 11) in the presence of a suitable catalyst such as vanadium oxide, to form SO_3, in conventional fashion. The efficiency of conversion is conventionally such that about 98% of the SO_2 entering is converted to SO_3.

The gases leaving SO_2 converter 22 comprise SO_3, some residual SO_2, CO_2, H_2O and residual O_2 and N_2. These gases pass, via line 23, to SO_3 cooler 24, in which the temperature of the stream is reduced to a temperature above the dew point of H_2SO_4 (e.g., 550° F. (288° C.)) to prevent condensation of sulfuric acid in the stream. Leaving SO_3 cooler 24, the cooled gases pass through line 26 to the base of SO_3 absorber tower 27, through which the gases pass upwardly against a downwardly-flowing stream of lean oleum entering the top of the tower through line 28. A recycle sidestream is drawn from the base of tower 27 through line 29, pump 31 and heat exchanger 32 wherein it is cooled, and delivered to the top of tower 27 through line 33. The rate of recycle and the temperature of the cooling water used in heat exchanger 32 are coordinated to maintain a temperature at the base of tower 27 within the range of about 100°–150° F. (38°–66° C.) e.g., 140° F. (60° C.), to facilitate absorption of SO_3 into the stream of lean oleum 28 entering the top of SO_3 absorber tower 27.

The process conditions in SO_3 absorber 27 are adjusted such that lean oleum 28, which has typically an SO_3 content of about 18–25% by weight when it enters the top of tower 27, absorbs sufficient SO_3 to reach about 20–30% SO_3 by weight as it leaves the bottom of SO_3 absorber tower 27 via line 34. The SO_3-rich oleum is conveyed via pump 36 and line 37 through heat exchanger 38, wherein it is heated, and enters oleum boiler 39 through line 41. The oleum in boiler 39 is heated by appropriate means such as saturated steam entering through line 42, the quantity of steam being regulated by temperature-controlled valve 43 to maintain an appropriate temperature within the boiler. The heated oleum within boiler 39 evolves SO_3 vapors which leave the boiler through line 44, the rate being regulated by pressure-controlled valve 46. After addition of an appropriate amount of dry air through line 47, the mixture of air and SO_3 is passed to sulfonator 11 through line 12, as previously described.

The liquid phase within oleum boiler 39, which has been depleted of some of its SO_3 to a level below that in the rich oleum stream (e.g., to 18–25% SO_3 by weight in the depleted oleum), leaves via line 48, and, after heat exchange with entering SO_3-rich oleum in exchanger 38, passes through line 49, pump 51, line 52 and heat exchanger 53 (wherein it is cooled) to proportioning valve 54, wherein a split in the stream is made. A first portion of the depleted or lean oleum passes through line 28 to the top of SO_3 absorber 27. A second portion or sidestream of lean oleum (lean oleum overflow) flows via line 56 to the top of H_2SO_4 absorber tower 57. The relative proportions of the two oleum streams (i.e., line 28 to SO_3 absorber 27 and line 56 to H_2SO_4 absorber 57) are controlled by level control 58 to maintain a desired level at the base of tower 27.

In H_2SO_4 absorber 57, the lean oleum entering through line 56 is diluted by the addition of water through line 59 to form concentrated sulfuric acid into which is absorbed SO_3 from the upwardly flowing stream of gases entering the bottom of H_2SO_4 absorber 57 through line 63. A portion of this concentrated H_2SO_4 is recycled by pump 61 through heat exchanger 62, wherein it is cooled, to the top of H_2SO_4 absorber 57 wherein it descends against the upwardly-flowing stream of gases from SO_3 absorber 27. The strength of the concentrated H_2SO_4 at the bottom of H_2SO_4 absorber 57 is approximately 96–98%. Treatment of the gases from SO_3 absorber 27 in this manner at absorber 57 is effective in removing substantially all of the residual SO_3 content from gas stream 63.

In some circumstances, it may be acceptable to discharge the gas stream leaving H_2SO_4 absorber 57 via line 64 directly to the atmosphere. Gas stream 64 does, however, contain a small concentration of SO_2 which can, if necessary or desirable, be scrubbed in caustic scrubber 66 with an aqueous solution of NaOH, entering through line 67, in conventional fashion. The offgases leaving caustic scrubber 66 via line 68, now containing essentially no noxious components, can be discharged to the atmosphere without creating any pollution problems.

An alternative method of removing the last traces of SO_2 is to reheat gas stream 63 to 850° F. (454° C.) and pass it through an additional catalytic converter stage, much like converter 22, where 98% of the residual SO_2 is converted to SO_3. The gases leaving the converter are then cooled and fed to H_2SO_4 absorber 57, forming H_2SO_4. The gas leaving absorber 57 through line 64 has such a low SO_2 content that it can be discharged directly to the atmosphere.

As previously noted, during the operation of SO_3 absorber 27, the SO_3 content of rich oleum stream 34 leaving the absorber is generally within the range 20–30% by weight. 30% is a practical maximum for the SO_3 content in oleum. In general, it will usually be found desirable, in the interests of economy, to maintain the concentration of SO_3 in rich oleum stream **34** at as low a level as feasible within that range, since a relatively high SO_3 concentration in rich oleum stream **34** will be accompanied by the production of a relatively large amount of concentrated H_2SO_4 at absorber **57**.

More specifically, assume a given amount of SO_3 introduced into absorber **27** through line **26**. In order to produce a relatively high SO_3 concentration in the oleum in line **34** there must be a relatively smaller proportion of lean oleum introduced into absorber **27** through line **28** than would be introduced to make a relatively low SO_3 concentration in the oleum in line **34**. The lower the proportion of lean oleum directed into line **28** at valve **54**, the higher the proportion of lean oleum directed into line **56** leading to H_2SO_4 absorber **57**; and, the higher the proportion of lean oleum entering H_2SO_4 absorber **57**, the larger the amount of concentrated byproduct H_2SO_4 formed at H_2SO_4 absorber **57**.

Normally, H_2SO_4 is not as desirable a product, from a practical or economical standpoint as is oleum. Therefore, to minimize H_2SO_4 production and maximize oleum production, oleum would be produced at SO_3 absorber **27** at a concentration somewhat less than 30%, although still within the range 20–30%. However, if the by-product H_2SO_4 made at absorber **57** can be used in an economical manner there will be no penalty in maintaining a high concentration of SO_3 (e.g., 30%) in rich oleum stream **34**, because the accompanying production of large amounts of concentrated H_2SO_4 can be accommodated.

In the operation of oleum boiler **39** it will usually be desirable to avoid excessively depleting the SO_3 content of lean oleum stream **48**, since the boiling point of the oleum in boiler **39** increases as the SO_3 content is reduced, thereby requiring the use of greater amounts of stream or other heat supply to the boiler. In addition, the corrosivity of the oleum increases as the SO_3 content drops, a factor which may cause excessive corrosion of equipment. In general, therefore, it will usually be found desirable to maintain the SO_3 content of the lean oleum in boiler **39** within the range of about 18–25% by weight.

In summary, the SO_3 content in rich oleum stream **34** is somewhere in the range 20–30%, while the SO_3 content in lean oleum stream **48** is less than that of the rich oleum stream but is at least about 18% by weight of dissolved SO_3. Thus, for example, if the SO_3 content of the rich oleum stream is 30%, the SO_3 content of the lean oleum stream typically would be 25%, but, conceivably, it could be as high as 29%.

In FIG. **2** there is depicted an alternative embodiment of the invention in which SO_3 is stripped from rich oleum by contact with dry air in oleum stripper **70**, rather than by boiling the SO_3-rich oleum in a boiler as shown in FIG. **1**. In FIG. **2**, except for oleum stripper **70**, and its associated equipment (recycle pump **71** and heat exchanger **22**) all of the other equipment duplicates that in FIG. **1**. Dry air fed by line **73** to the base of oleum stripper **70** strips SO_3 from the heated oleum to produce a mixture of SO_3 and air which is passed by line **74** to sulfonator **11** (FIG. **1**), as previously described.

The foregoing detailed description has been given for clearness of understanding only, and no unnecessary limitations should be understood therefrom as modifications will be obvious to those skilled in the art.

What is claimed is:

1. In the method which comprises sulfonating a liquid organic feed stock by contacting said liquid feed stock with a gas mixture containing air and SO_3 derived from a sulfur burning step and separating the resulting liquid sulfonated product from a gas phase containing residual air, unreacted SO_3, vapors from said feed stock and SO_2, the steps of:

(1) burning sulfur in the presence of said separated gas phase to produce additional SO_2;

(2) catalytically treating the gas phase produced in step (1) to convert SO_2 contained therein to SO_3, said sulfur burning and catalytic treating steps being performed downstream of said sulfonating step and constituting said sulfur burning step from which is derived said SO_3 with which said liquid organic feed stock is sulfonated;

(3) treating the gas from step (2) with lean oleum to absorb in said oleum a substantial proportion of the SO_3 contained therein, producing SO_3-rich oleum;

(4) desorbing SO_3 from said SO_3-rich oleum to produce SO_3 vapor and lean oleum;

(5) mixing the SO_3 vapor produced in step 4 with air;

(6) contacting said liquid organic feed stock with the mixture of air and SO_3 produced in step (5);

(7) using at least a portion of the lean oleum produced in step (4) for absorbing SO_3 in step (3);

(8) removing SO_3 remaining in the gas after step (3) and then discharging said gas to the atmosphere.

2. In the method of claim **1** wherein:

said vapors from said feed stock are converted to CO_2 and H_2O vapor at said sulfur burning step (1),

and said method comprises removing said H_2O vapor from the process, before step (6), by reacting the H_2O with some of said SO_3 from step (2) to produce oleum, at step (3);

said CO_2 being discharged to the atmosphere after step (3).

3. In the method of claim **1** wherein said SO_3 vapor is produced in said desorbing step (4) by heating said SO_3-rich oleum.

4. In the method of claim **1** wherein said steps of desorbing and mixing with air (4) and (5) are performed simultaneously by stripping SO_3 vapor from said SO_3-rich oleum with a stream of air.

5. In the method of claim **1** wherein said SO_3-rich oleum contains about 20–30% by weight of dissolved SO_3.

6. In the method of claim **1** wherein said lean oleum contains less dissolved SO_3 than said rich oleum and at least about 18% by weight of dissolved SO_3.

7. In the method of claim **1** wherein said feedstock is a petroleum fraction.

8. In the method of claim **1** wherein:

the SO_2 content of said separated gas phase is greater than about 5% by weight of the SO_3 contacting said liquid feed stock.

9. In the method of claim **1** wherein:

said liquid feed stock is selected from the group consisting of crude oils and gas oils.

10. A method as recited in claim **1** and comprising:

dividing said lean oleum into first and second portions;

using said first portion of the lean oleum for absorbing SO_3 in said gas-treating step (3);

adding water to said second portion of lean oleum to produce concentrated sulfuric acid and using said concentrated sulfuric acid at said SO_3-removing step (8) to absorb any SO_3 remaining in the gas treating step (3);

and discharging to the atmosphere the gas remaining after said water-adding step.

11. In the method of claim **10** where the gas remaining after said water-adding step is washed with caustic to remove acidic components prior to being discharged to the atmosphere.

12. In the method of claim **10** wherein a portion of the concentrated sulfuric acid produced in said water-adding step is recycled at that step to absorb said SO_3.

13. In the method of claim **1** wherein:

said vapors from said feed stock are converted to CO_2 and H_2O vapor at said sulfur burning step (1), said CO_2 and said H_2O vapor being part of the gas from step (2);

and said method comprises separating said H_2O vapor and said CO_2 from said SO_3 in said gas from step (2), so that the SO_3 produced at step (4) is substantially free of H_2O vapor and CO_2 at the time of said contacting step (6).

14. A method as recited in claim **1** and comprising: removing residual SO_2 from said gas, after said SO_2 removing step (8) and before discharging said gas to the atmosphere.

15. A method as recited in claim **1** and comprising: removing H_2O vapor from the gas from step (2) at the same time as said SO_3 is absorbed from said gas.

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UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 4,251,456

DATED : February 17, 1981

INVENTOR(S) : Burton Brooks

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 5, line 41, "stream" should be --stream--.

Column 6, line 35, "step (1)," should be --step (1);--.

Column 8, line 11, "after said SO_2" should be --after said SO_3--.

Signed and Sealed this

Twelfth **Day of** *May 1981*

[SEAL]

Attest:

RENE D. TEGTMEYER

Attesting Officer — *Acting Commissioner of Patents and Trademarks*