

⑫ **EUROPEAN PATENT APPLICATION**

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**Bulletin 80/25**

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⑤④ **Desulphurization of oil.**

⑤⑦ Sulphur present in petroleum oils represents a very undesirable pollutant when the oils are burnt.

A process of treating oil containing sulphur is provided wherein the oil is contacted with hydrogen fluoride. The hydrogen fluoride converts the sulphur to a sulphur fluoride which may be removed from the oil.

The sulphur fluoride may then be converted to other forms of sulphur thus allowing for regeneration of the hydrogen fluoride for reuse in the process.

**EP 0 020 053 A1**

This invention relates to a method of desulphurizing oil, particularly crude oil.

As is well known in the petroleum art, many crude oils have very high sulphur contents and thus are unsuitable for a number of uses, if not being totally unsuitable. This is because on combustion of the oil the sulphur forms pollutants in the form of noxious gases and acids.

Desulphurization of oil has been a major problem which has not been satisfactorily overcome on an economic basis by  
10 the existing prior art methods.

It is the object of this invention to provide a method of desulphurizing oil.

In its broadest form the invention provides a process of treating petroleum oil to reduce the sulphur content thereof, comprising treating said oil with hydrogen fluoride at an effective concentration level such that available sulphur in the oil is converted to a sulphur fluoride compound, and separating the oil from the sulphur fluoride produced by the reaction.

Preferably the oil is substantially dehydrated before  
20 treatment with the hydrogen fluoride. Furthermore, prior to reaction with the HF some oils may be advantageously treated with an oxidizing agent, such as sulphur trioxide gas, to oxidize certain forms of sulphur present to a form more readily reactable with HF.

The hydrogen fluoride may be utilized in liquid or gas state. The gas state is preferred as the conversion of the sulphur to a gas is not hindered by water present as in a liquid HF reaction. Water tends to cause any sulphur fluorides formed to precipitate and thus complicate its separation from the oil.

30 By using HF as a gas the sulphur forms mainly sulphur

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tetrafluoride in gaseous form and is readily separated from the liquid oil along with excess HF.

It is preferable from the economic point of view that the sulphur fluoride and the excess hydrogen fluoride emanating from the hydrogen fluoride contact with oil be reclaimed, particularly to reuse the fluoride. To this end the hydrogen fluoride and sulphur fluorides removed from one gas-liquid reaction are passed to a gas separation tower wherein due to their significantly different specific gravities, they  
10 may be easily separated. The hydrogen fluoride being the lighter gas separating out of the top of the gas separation tower and being recycled to the hydrogen fluoride gas storage, the sulphur fluorides being the heavier of the gases being removed from the bottom of the gas separation tower from where they can be passed to a hydrolyzation unit to convert the sulphur gas to sulphur crystals and the fluorides to hydrogen fluoride. The hydrogen fluoride emanating from the gas-water contact unit can then also be fed back to the hydrogen fluoride storage.

20           The invention will now be described by way of example only with reference to the accompanying drawing wherein there is shown a process flow sheet of the preferred form of this invention.

Oil, usually crude oil which has been extracted from the ground, generally contains a certain percentage of water. As it is preferable for the primary reaction of this invention to have a minimum amount of water in the oil for contact with the hydrogen fluoride gas, it is necessary to substantially dehydrate the oil before reacting the oil with the hydrogen  
30 fluoride gas. Thus oil 18 is fed to a dehydration unit 10.

To dehydrate the oil, temperature drying at 240°F or temperatures thereabove is suitable. Alternatively, a selective oil-water separator may be used to dehydrate the oil.

The dehydrated oil is then fed 20 to an oxidizing chamber 11 such as a counter-current flow gas-liquid contact unit. In the oxidizing chamber an oxidizing agent such as gaseous SO<sub>3</sub> is contacted with the oil by, say, being bubbled 21 through the oil. This oxidizes some of the free and bound sulphurs to an oxide form thus making it more available for reaction with the HF.

The liquid oil is then fed 22 to the main reactor 12. The reactor is preferably a counter-current flow gas-liquid contacting unit. This unit may be a distillation tower, packed column, spray tower or other suitable unit. The oil descends down the tower whilst hydrogen fluoride gas 23 is fed from storage unit 15 into the unit 12 from the bottom of the tower and passes up the tower. The hydrogen fluoride gas contacts the descending oil and converts the sulphur that will react which may be in a free form or in compound with other substances in the oil to sulphur fluorides, generally sulphur tetrafluoride. The sulphur fluorides which are gaseous along with the remaining hydrogen fluoride gas leave the top of the gas-liquid contact unit and are preferably then passed 24 to a gas separation tower 13 wherein as above described, the lighter hydrogen fluoride is removed 25 at the top, whilst the heavier sulphur fluorides are removed from the bottom 26. The gas separation tower 13 is not essential, but very desirable. The sulphur fluorides are then heated to from 220°F to 240°F and compressed to from 60 to 100 psig before being passed to a

gas-water contact unit 14 at similar temperatures and pressures, where on contact with water sprays 27 sulphur precipitates out and may be removed 35 for further use. The fluoride from the sulphur fluorides is converted to hydrogen fluoride gas, removed 28 from the unit 14 and this is combined with the hydrogen fluoride gas leaving the gas separation tower to be passed back to the hydrogen fluoride gas storage 15.

Oil leaving the main reactor 12 has thus had its sulphur content reduced to from 0.1 to 0.05% providing the  
10 reaction in the reactor 12 has been carried out with sufficient residence time, concentrations and at a reasonable temperature, about 50°C.

The oil 34 leaving the reactor 12 contains a small amount of entrained HF which can be removed by treating the oil with an ammonia solution 33 to form salts with the fluoride compounds in the aqueous phase.

The oil phase 31 may then be extracted from the aqueous phase 32 by say phase separation apparatus 30.

Thus, it can be appreciated that due to the high rate  
20 of reclamation of hydrogen fluoride gas, the process is very efficient. The oil leaving the gas-liquid contact unit is substantially desulphurized and of course the degree of desulphurization is dependant upon the efficiency of the gas-liquid contacting unit and the residence time therein. Obviously, to increase the level of desulphurization further contacting may be desirable. The temperature of the HF gas passing into the gas-liquid contact unit is preferably around 80°F, although this temperature may be varied according to the conditions desirable with particular oils. The desulphurized  
30 oil leaving the gas-liquid contact unit may then be passed for

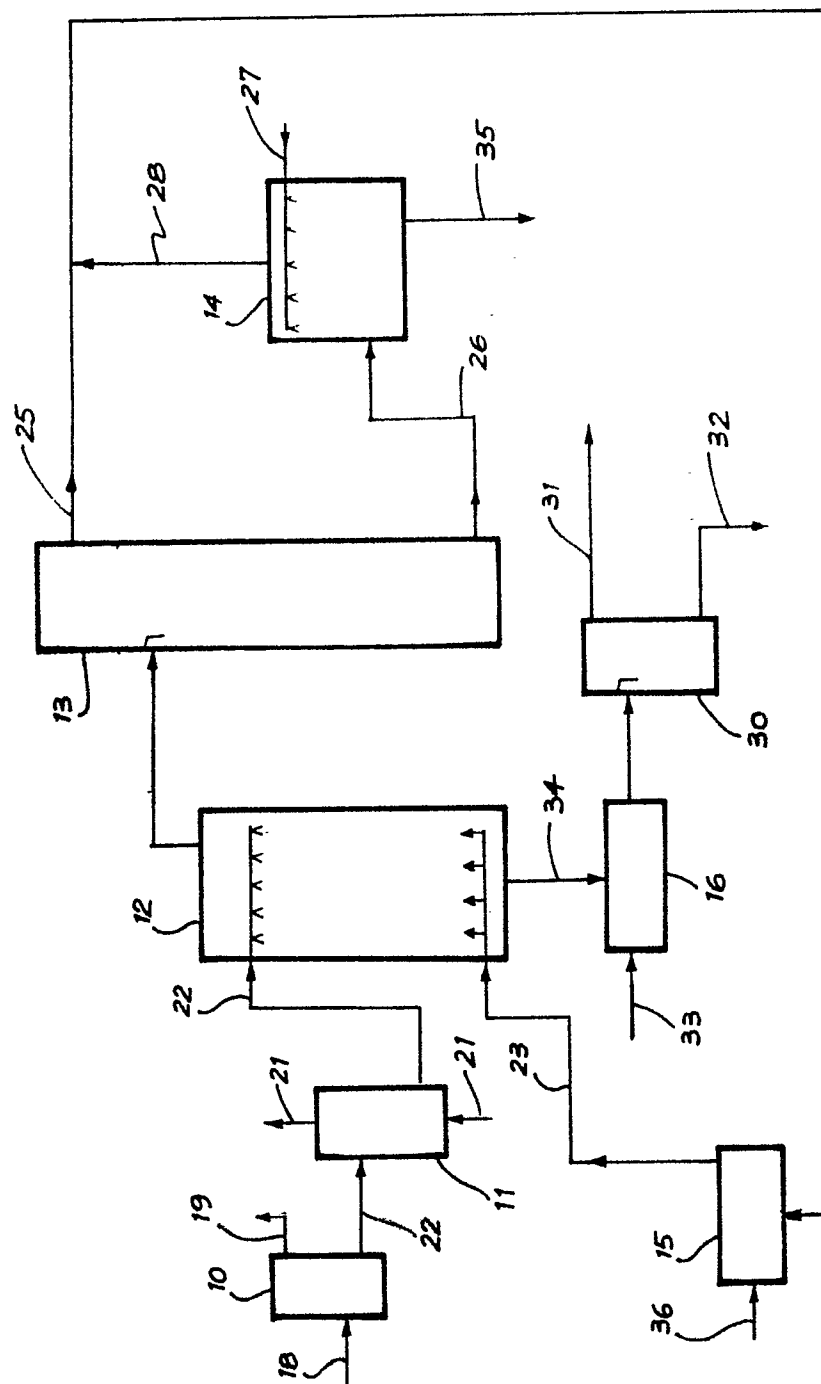
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further processing in normal refinery practice.

Where the hydrogen fluoride used in the main reaction unit 12 is in the form of a liquid instead of a gas, the reaction with sulphur will still take place, however there may be some precipitation of sulphur components due to contact with water present in the mixture. Thus, the separation of the oil from the resulting reaction mixture would comprise a solids separation stage as well as a liquid phase separation stage, thus allowing the oil to be extracted and passed to, 10 say, an ammonia treatment stage 30 for stripping the oil of non-hydrocarbon components.

## WHAT WE CLAIM IS:

1. A process of treating petroleum oil to reduce the sulphur content thereof, comprising treating said oil with hydrogen fluoride at an effective concentration level such that available sulphur in the oil is converted to a sulphur fluoride compound, and separating the oil from the sulphur fluoride produced by the reaction.
2. ~~The~~ process of claim 1 wherein the oil is substantially dehydrated before the reaction with hydrogen fluoride.
3. The process of claim 1 or 2 wherein the oil is treated by an oxidizing agent prior to reaction with the hydrogen fluoride.
4. The process of claim 1 wherein the hydrogen fluoride is fed to the reaction oil in a gaseous state.
5. The process of claim 4 wherein the gaseous products of the reaction with oil are removed and treated to recover the hydrogen fluoride.
6. The process of claim 5 wherein the recovery of hydrogen fluoride is recovered by firstly separating the gas stream into an HF and sulphur fluoride gas stream, and wherein the sulphur fluoride gas stream is contacted with water to precipitate out sulphur compounds.
7. The process of claim 1 wherein the oil removed from the reaction with hydrogen fluoride is treated with ammonia solution to remove entrained fluorides from the oil.

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European Patent  
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# EUROPEAN SEARCH REPORT

Application number

EP 80 30 1580

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. <sup>3</sup> )
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	<p><u>US - A - 2 343 841</u> (R.E. BURK)</p> <p>* Page 1, right-hand column, lines 13-22; page 2, right-hand column, lines 11-38; page 2, left-hand column, lines 1-17; claims 1-12 *</p> <p>--</p> <p>CHEMICAL ABSTRACTS, vol. 68, nr. 12, March 11, 1968, ref. 51529r page 5006, column 1 COLUMBUS OHIO (US) D.F. VARFOLOMEEV et al.: "Refining of highly unsaturated sulfurous distillates of thermal origin"</p> <p>* The whole document *</p> <p>--</p> <p><u>GB - A - 732 068</u> (STANDARD OIL)</p> <p>* Page 1, lines 23-51; claims 1-9 *</p> <p>--</p> <p><u>FR - A - 1 138 769</u> (DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ)</p> <p>* Abstracts 1<sup>0</sup>-12<sup>0</sup>; page 1, right-hand column, paragraphs 1 and 2, left-hand column, paragraph 2; page 2, right-hand column, paragraphs 2,3, and 4; left-hand column, paragraphs 1,5 and 6; page 3, right-hand column; paragraph 1 *</p> <p>--</p> <p><u>GB - A - 1 547 664</u> (EXXON)</p> <p>* Page 1, lines 12-14, lines 65-96; page 2, lines 1-13; lines 45-63; page 3, lines 80-91; page 5, lines 3-74; claims 1-9 *</p> <p>--</p> <p>../..</p>	<p>1, 5</p> <p>1</p> <p>1</p> <p>1, 2, 3</p> <p>1, 2, 4, 5, 6</p>	<p>C 10 G 17/07</p> <p>TECHNICAL FIELDS SEARCHED (Int.Cl. <sup>3</sup>)</p> <p>C 10 G 17/07</p> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons</p> <p>&amp;: member of the same patent family, corresponding document</p>
<p><input checked="" type="checkbox"/> The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search	Examiner	
The Hague	04.09.1980	LO CONTE	

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# EUROPEAN SEARCH REPORT

Application number  
EP 80 30 1586  
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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. <sup>3</sup> )
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	<p><u>US - A - 2 971 905</u> (H. BIEBER)</p> <p>* Column 2, lines 48-72; column 3, lines 1-9; column 4, lines 10-38; claim 1 *</p> <p>---</p>	1,7	
	<p><u>US - A - 2 643 971</u> (A.P. LIEN)</p> <p>* Column 1, lines 11-19; lines 34-53; column 2, lines 14-29; lines 46-55; column 3, lines 1-8; column 5, lines 10-17; claims 1-6 *</p> <p>---</p>	1,5	
	<p><u>US - A - 2 581 064</u> (F.M. ARCHIBALD)</p> <p>-----</p>		
			TECHNICAL FIELDS SEARCHED (Int. Cl. <sup>3</sup> )