(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 341 802 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **89300137.0**

(51) Int. Cl.[4]: **C10M 175/00**

(22) Date of filing: **09.01.89**

The title of the invention has been amended (Guidelines for Examination in the EPO, A-III, 7.3).

(30) Priority: **15.03.88 ZA 881823**

(43) Date of publication of application:
15.11.89 Bulletin 89/46

(84) Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

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(54) Removal of metal contaminants from oil.

(57) Oil containing undesirable metal values, such as contaminated vacuum residue oil, or used lubricating oil is treated at elevated temperature, with an aqueous solution of an anion capable of reacting with the metal values to form water-soluble salts, such as chlorides or nitrates, and then separating the aqueous phase from the oil.

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REMOVAL OF METAL VALUES FROM OIL

FIELD OF THE INVENTION

This invention relates to the removal of metal values from oil. In one aspect, the invention relates to the removal of contaminants from vacuum residue which is the final residue oil produced by the Kellog or Synthol process. In another aspect, the invention relates to the removal of metal values that may still be present in a lubricating or other oil.

BACKGROUND OF THE INVENTION

In the manufacture of synthetic fuel oil from coal in the Kellogg or Synthol process, a final residue oil is produced which is commonly referred to as vacuum residue. This oil generally contains a significant amount of incombustible material called ash, and this is primarily the iron catalyst used in the process, together with some inorganic salts and other incombustible materials. Similarly, used lubricating oils contain additives and ingressed metals.

It is an object of the present invention to remove these contaminants from the vacuum residue or other oils in order to render it useful as a fuel for firing of furnaces, or in internal combustion engines, or for other purposes where reduced contaminants is required.

In the process described in the Applicants's RSA Patent 85/5142 the vacuum residue was heated to a temperature of about 100 °C and then blended with water and the aqueous phase and the aqueous/ash phases were separated by centrifuge and the oil phase recovered. The ash content could be reduced from 2500ppm to about 600ppm which was satisfactory for certain purposes but for others required further treatment.

It is a further object of the present invention to provide a method of post-treating the oil to reduce its ash content to the order of about 10ppm.

THE INVENTION

According to the invention an oil containing an ash content is treated with an aqueous solution of an anion capable of reacting with the metal values present to form water-soluble salts, and separating the aqueous phase from the oil phase.

The separation is preferably carried out by centrifugation.

The preferred an ions for use in the present invention are halides, and particularly chlorides, or nitrates. Thus, in one form of the invention the oil is treated with a solution of ammonium chloride. In another form of the invention a solution containing nitric acid and sodium chloride is used. In both cases the solutions may be saturated with respect to chloride ions. The nitric acid may be about 6 percent.

The reaction between the anion solution and the contaminated oil is preferably conducted at an elevated temperature, preferably at or just below the boiling point of water. The solution may be heated to about 80 °C prior to addition. The ratio of solution to oil is about 1:9.

The principal metal values in vacuum residue are sodium, calcium and iron and these are easily removed according to the present invention as chlorides or nitrates.

If highly emulsified oil is required to be treated it should be demulsified or have the water removed from it by one or another method.

This oil should then have the particulate material removed from it, by heating it to 90 °C, passing it through a coarse filter and subjecting it to a high gravitational separation process such as the Alfa Laval AX 213 super centrifuge, but preferably at a G-force above 15 000 G's.

Filtration should then be carried out using a post-centrifuge 5 micron filter to remove particulate matter with a specific gravity such as that it will float in the oil.

The feedstocks which can be used include used lubricating oil, lube oil sludge collected from lube oil circulation centrifuges, oil sludge ex tank bottoms and the residues therefrom, miscellaneous washing processes, for example, tanker cleanings and oil drum cleaning plants.

This oil, after pre-cleaning, will typically have an ash content of between 1 and 2%, where ash is defined as the residue obtained in the ASTM D482 method ash determination.

DETAILS OF THE INVENTION

Pre-treated oil (as above) is heated to a temperature of 90 - 95 °C, preferably using a shell and tube steam-heated heat exchanger.

The oil is held in a suitably designed tank, fitted with a circulation/agitation system. In this tank a 4% by volume, heated (also at a temperature of 90 °C) nitric acid solution is added. This nitric acid solution comprises a 28% HNO_3 in water (w/w).

This aqueous acid/oil mixture is agitated for a period until complete contact between oil/contaminants and the acid solution occurs. This normally takes one to two hours. The temperature of the mixing vessel is maintained at 90 °C by internal or external heating coils.

A further 25% water is added at a temperature of 90C, and mixing is continued vigorously for a period ranging from five to thirty minutes.

This mixture is fed through an adapted high speed, three phase centrifuge which separates the oil from the contaminants. The water is passed to an effluent treatment plant.

A further 25% of water is added to the oil obtained from step 3.5 in a tank fitted with a circulating/agitating system, maintaining the temperature at 90 °C, using internal or external heating coils.

This mixture is fed to a high speed, three phase centrifuge. It is optional to dose the theoretical amount of caustic soda to neutralise the remaining acid component of the oil if a fully neutralised oil is required.

A final optional step would be to pass this oil through a high speed super-centrifuge to remove the last traces of acid.

EXAMPLE 1

Waste oil comprising of a mixture of fuel oil, lube oil sludge ex the lube purifier, lube oil additives and diesel oil

		BEFORE	AFTER
Water	%	1,0	0,2
Ash	%	1,7	0,13
Elemental Analysis of Contaminants			
Fe	ppm	4 000	109
Ca	ppm	4 000	18
Al	ppm	100	0
Si	ppm	1 000	20
Na	ppm	2 000	34
Va	ppm	5	0
S	ppm	1 600	1 300

EXAMPLE 2

A used lubricating oil was processed as above. The results are as follows:

		BEFORE	AFTER
Ash	%	1,25	0,03
Water	%	5	0,10
Fe	ppm	246	4
Ni	ppm	1	0
Al	ppm	25	0
P	ppm	443	5
Si	ppm	63	10
Na	ppm	134	8
Ca	ppm	1 417	11
V	ppm	1	0
Cr	ppm	9	0
S	ppm	11 483	8 521

EXAMPLE 3

A product, waxy oil 20, which is the residual oil from the synthol oil-from-coal plant was processed as above. Results are follows:

		BEFORE	AFTER
Fe	ppm	560	67
P	ppm	264	102
Na	ppm	90	31
Si	ppm	7	0
Ca	ppm	219	5
S	ppm	27	15
Ash	%	0,20	0,04

Claims

1. A method of removing metal values from an oil containing undesirable metal values including the step of treating the oil with an aqueous solution of an anion capable of reacting with such metal values to form water-soluble salts, and separating the aqueous phase from the oil phase.

2. The method according to claim 1 in which the anion is chosen from chloride and nitrate.

3. The method according to claim 1 in which aqueous ammonium chloride is used as the treatment aqueous solution.

4. The method according to claim 1 in which a solution of nitric acid and sodium chloride is used as the treatment aqueous solution.

5. The method according to claim 3 or claim 4 in which the solution is saturated with respect to chloride ions.

6. The method according to any of the above claims in which the ratio of treatment aqueous solution to oil is about 1:9.

7. The method according to any of the above claims in which the treatment is carried out at a temperature at or just below the boiling point of water.

8. The method according to any of the above claims substantially as described in any of the examples.

9. The method according to any of claims 1 - 7 substantially as described in the "Details of the Invention".

10. The product of the method as claimed in any of the above claims.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 30 0137

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	US-A-4 204 946 (C.B. JOHNSON) * Abstract; figure 1; column 1, line 7 - column 3, line 48; claims 1,3 *	1,6,7, 10	C 10 M 175/00
Y		3	
X	US-A-3 607 731 (G.L. GULLIK) * Abstract; column 2, line 72 - column 3, line 8; claims 1,2,10 *	1,2,10	
Y		7	
D,Y	PATENT JOURNAL, February 1986, page 179, left-column, no. 85/5142; & ZA-A-85 5142 (FUEL FIRING SYSTEMS (PTY) LTD) * Title; abstract *	7	
X	FR-A-2 530 656 (G. SUDER) * Abstract; page 1, line 1 - page 2, line 16; page 3, lines 4-11; claims 1,2 *	1,2,7	
Y		3	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
X	DE-A-3 514 970 (E. BAER VERFAHRENSTECHNIK GmbH) * Abstract; claim 1; page 2, line 4 - page 5, line 6 *	1,10	C 10 M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10-04-1989	FISCHER W.H.F.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P0401)