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(54) **Oil improvement process**

(57) Waste or other oil is treated in a process in which water is added to the oil prior to the addition of an acidic material, thereby reducing or entirely avoiding tar formation. As shown, an oil feedstock is passed through heat exchanger (1), centrifuge (4) and filter (7), and then injected with water at point (10), preferably forming an emulsion, prior to the addition of 98% sulphuric acid (13). After standing in vessel (14) (or residing in a connecting pipeline) a de-ashing and de-emulsifying chemical (16) is added. Following de-emulsification, the mixture is centrifuged to provide clean oil (22) and water (20) for recycling (and effluent). Optionally a flash vessel (25) is used to remove more water/light ends from oil (22). The product is passed through the heat exchanger (1) prior to storage 2. The aqueous effluent and/or the purified oil phase (22) may be treated with caustic to remove any residual acidity.

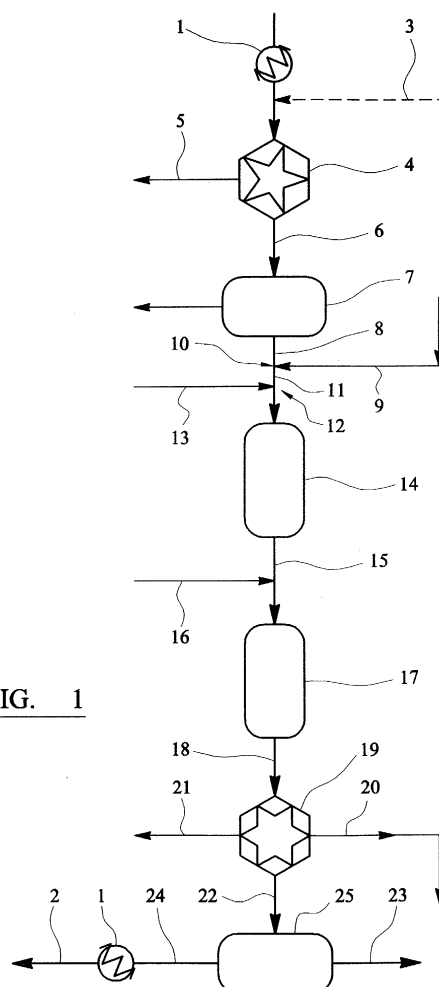


FIG. 1

Description

[0001] The present invention relates to a process and apparatus for the treatment of oils.

[0002] The invention was developed in response to a need to purify waste oils to make them suitable for further use. Accordingly it has a particular relevance thereto, and will be more particularly described in that context. However, the treatment of other oils is not excluded from the compass of the invention.

[0003] It is known to collect used oils from sites such as garages, workshops and other industrial premises, and to process them so that they can be used in another application, most commonly as a low grade fuel for use in power stations, particularly during the starting and stopping of coal fired plant, for stabilising the combustion process, and/or for providing a temporary power boost; and in quarries, particularly for the heating of rotary kilns where crushed rock is heated and dried before being coated with bitumen, the resulting coated product being used as roadstone. The alternative fuels to use in these applications are virgin heavy fuel oil and gas oil respectively.

[0004] The recycling of used oils as fuels is environmentally desirable in that it avoids the problem of disposal thereof, and reduces the amount of oil that would otherwise need to be extracted from a natural source, or to be formed synthetically using non-waste materials such as a natural gas feedstock.

[0005] By their nature, waste oils contain impurities and/or degradation products. Common impurities include particulate contamination, water, and original or degraded additives many of which contain metal atoms. Not only do these affect the combustion properties of the waste oil, but it is highly undesirable from the environmental point of view that oils with such levels of contamination should be burned. Accordingly, it is necessary to treat the waste oil to remove (or reduce) contaminants prior to their use as a fuel.

[0006] Furthermore, the very act of treating waste oils can itself produce environmentally undesirable contamination, for example in the form of vapours of volatile organic compounds or VOCs, and in the form of metal containing by-products which are difficult to treat further (see below). Accordingly, any acceptable waste oil treatment must be arranged with these factors in mind.

[0007] It is known to remove particulate contamination from waste oils by filtration and/or centrifugal separation. The latter process can also serve to remove some of the water contamination where the water is already physically separate.

[0008] It is also known to chemically treat waste oils to remove the metal of metal containing contaminants (and/or the metal contaminants themselves), and one known process is to treat the oils with an acidic material to solubilise the metals which can then be removed in an aqueous phase.

[0009] Water is commonly removed by treatment of

the oils with a demulsifying agent (emulsion breaker), followed by separation as in a centrifuge for example.

[0010] Of the above processes, perhaps the most difficult is the treatment of the oils with an acidic material. This often leads to the formation of tarry residues, which are highly acidic, difficult to handle and still need to be disposed of in bulk.

[0011] The present invention provides a method of oil treatment comprising the steps of treating the oil with water followed by treating the oil with an acidic material. Preferably the water is added in a manner such as to form a dispersion, and more preferably an emulsion, for example by injecting it ahead of a mixing device or pump such as a centrifugal pump.

[0012] Preferably the water is added at a rate of at least 5% m/m (mass/mass), more preferably at least 10% and most preferably at least 13% m/m. Preferably it is added at a rate of no more than 20% m/m and more preferably no more than 17% m/m.

[0013] Preferably the acidic material is subsequently injected so as to be dispersed in the oil, for example just ahead of a second mixing device or pump such as a second centrifugal pump. A preferred acidic material is inhibited concentrated sulphuric acid, e.g. 98% sulphuric acid.

[0014] Preferably the acidic material is added at a rate of 500-10,000 ppm (parts per million m/m), more preferably 1,000 to 8,000 ppm and most preferably 2,000 to 7,000 ppm.

[0015] It has been found that the method according to the invention substantially avoids tar formation, or at least leads to a highly significant reduction in tar formation, thus providing a cleaner and more efficient oil treatment process.

[0016] After the acidic material has been added, the mixture is preferably left for some time preferably at least 20 minutes, more preferably at least 40 minutes, and most preferably at least one hour, for reaction to occur, and preferably the mixture is stored in a holding tank for this period. Alternatively, in a continuous process, a pipeline receiving the oil/water/acid mixture may be dimensioned according to the flow rate to permit the requisite residence time therein.

[0017] Subsequent to reaction with the acidic material a de-emulsifying and/or de-ashing chemical may be added, and the resulting phases separated, one of the separated phases being a purified oil phase. The latter may be further purified by being subjected to flash evaporation to provide a purified oil product in which relatively volatile VOCs and any remaining water are further reduced, but in many circumstances this is not expected to be necessary.

[0018] Advantageously the purified oil phase is treated with alkali, e.g. a caustic solution, to neutralise any residual acidity, which otherwise may prove unacceptably aggressive towards metal (for example during subsequent storage). Treatment of the separated aqueous phase with alkali such as a caustic solution is preferred

to ensure that effluent from the process is not acidic.

[0019] As particularly described the oil is pretreated by heating and/or by phase separation before the water is added. Heating can serve to promote phase separation e.g. of an aqueous phase.

[0020] The invention extends to apparatus arranged to perform the method.

[0021] Further features and advantages of the invention will become clearer upon a perusal of the appended claims, to which the reader is referred, and upon a reading of the following more detailed description of an exemplary embodiment of the invention, made with reference to the accompanying drawing, in which:

Figure 1 illustrates in diagrammatic form a process for the conversion of waste oils to a product useful as a fuel oil.

[0022] Much or all of the process is carried out at temperatures somewhat above ambient, commonly in the region of 70-95° C, more preferably around 75-85° C (around 80° C is presently being used) and accordingly waste oil from a reservoir tank is initially passed through a heat exchanger 1 where it is warmed by heat exchange with the product 2 (exchanger 1 is shown at both ends of the process), and then subject to further heat input 3 if necessary.

[0023] The heating process has the effect of de-watering the oil to a considerable extent, and accordingly the oil is then passed through a decanting centrifuge, where the separated oil and also some semi-solid waste products are removed as a stream 5. The treated oil 6 from centrifuge 4 is then filtered in an filter 7 to remove the bulk of the remaining solid or semi-solid contaminants. Preferably, the filter 7 is enclosed to retain any VOC vapours. The centrifuge 4 would conventionally be enclosed so that vapour release is no problem there.

[0024] The oil feed 8 output from filter 7 is then injected with water at a point 10 in a pipeline just prior to a first centrifugal pump (not shown), so that the water produces an emulsion 11. Subsequently, at a point 12 in the pipeline, 98% sulphuric acid 13 is injected just ahead of a second centrifugal pump (not shown), and the mixture of materials is then allowed to stand in a first reaction vessel 14 for about one hour to allow reactions to proceed (alternatively in a continuous process a sufficiently large pipeline is used in lieu of vessel 14 to provide a residence time between its ends of about an hour).

[0025] The reaction product 15 in a pipeline from vessel 14 is then treated by injection with a de-ashing and de-emulsifying chemical 16 and then stored in a second reaction vessel 17 for around one hour to enable de-emulsification and other processes to proceed.

[0026] The material 18 leaving the vessel 17 comprises a treated oil phase together with an aqueous phase and semisolid waste material. It is passed into a three-phase high speed centrifuge 19, which separates the

aqueous phase 20 for purification and recycling to the water injection point 11, the semisolid waste 21 for disposal, and the treated oil phase 22.

[0027] At this point the treated oil phase 22 is amply clean enough for use as a fuel oil. Nevertheless, it may contain some residual acidity, and in a preferred arrangement the phase 22 is treated (not shown) with a caustic solution to neutralise this acidity. Furthermore, whether or not there is any preceding caustic treatment, the fuel oil phase 22 will commonly still contain some water and some relatively volatile VOCs, and at least in some circumstances this is undesirable. Therefore, as shown, as an optional additional stage, the treated oil phase 22 is passed into a flash vessel 25 where water and other relatively volatile materials 23 are removed for disposal, the purified treated oil phase 24 being passed through the heat exchanger 2 on its way to storage.

[0028] In a preferred arrangement, the aqueous phase, or at least that part being fed out as effluent, is also treated with caustic solution.

Claims

1. Apparatus for treating waste oil including first means arranged to add water to the oil and second means arranged to add an acidic material to the oil after the water has been added.
2. Apparatus according to claim 1 wherein the first means is arranged so that the water forms a dispersion or emulsion with said oil.
3. Apparatus according to claim 2 wherein the first means includes a first mixing device or pump for forming said dispersion or emulsion.
4. Apparatus according to any preceding claim wherein at least one of said first means and said second means is a centrifugal pump.
5. Apparatus according to any preceding claim and including storage means arranged to allow the oil to react with the acidic material.
6. Apparatus according to any preceding claim and including means arranged to add a de-emulsifying and/or de-ashing chemical after the acidic material has been added, and means for separating the resulting phases to provide an output of a purified oil phase.
7. Apparatus according to claim 7 and including a flash evaporator arranged to receive the purified oil phase and to provide a purified oil product at its output.

8. Apparatus according to any preceding claim and including means prior to said first means for pretreating the oil by heating and/or by phase separation.
9. A method of oil treatment in which water is added to the oil prior to the addition of an acidic material. 5
10. The method according to claim 9 wherein the water is added in a manner such as to form an emulsion or dispersion with said oil prior to said addition of acidic material. 10
11. The method according to any preceding claim wherein said acidic material is sulphuric acid. 15
12. The method according to any preceding claim wherein the oil is permitted to react with the acidic material for at least 20 minutes, following which a purified oil phase and an aqueous phase are separated. 20
13. The method according to claim 12 wherein the oil is maintained at a temperature in the range 75-95° C from the addition of said water to the separation of the oil and aqueous phases. 25

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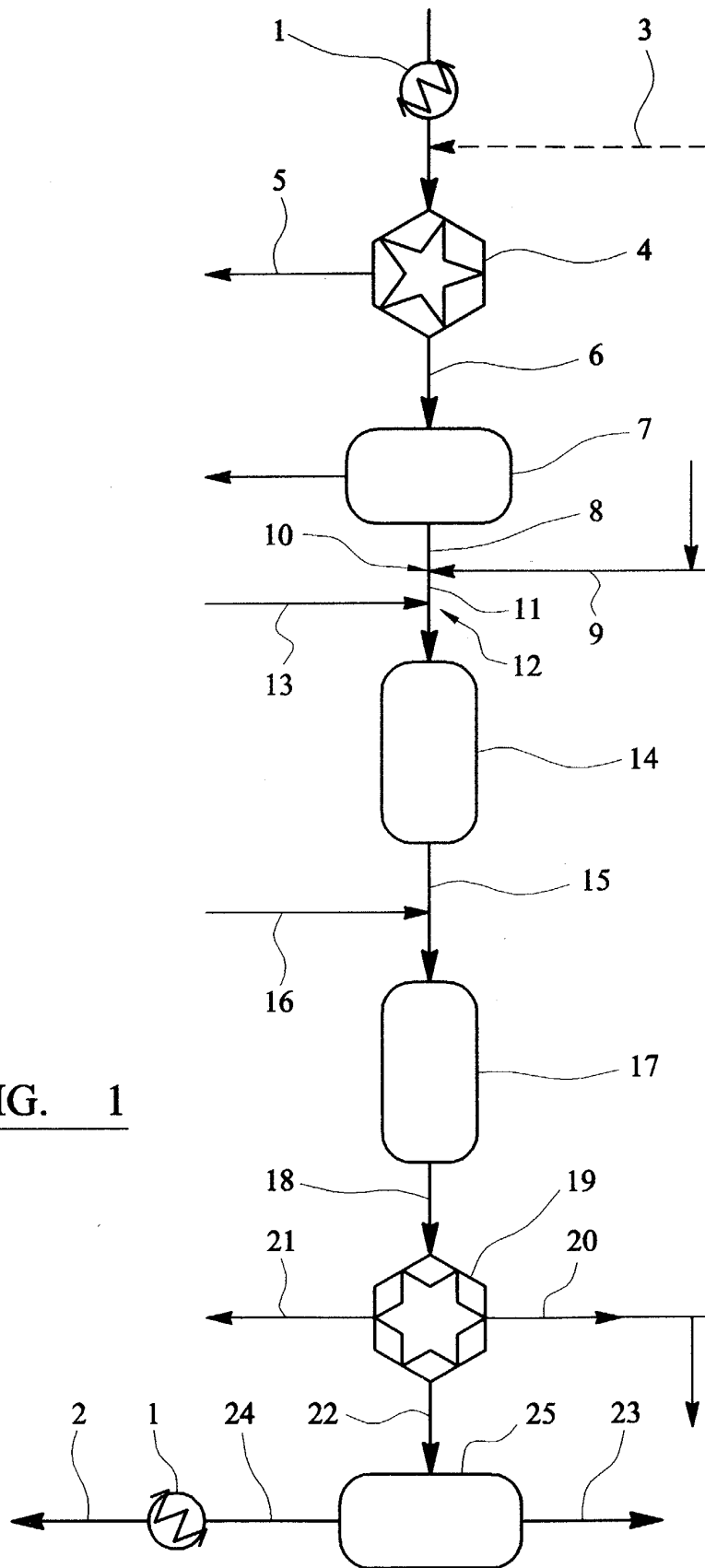


FIG. 1



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 04 25 0667

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.7)
X	WO 93/13190 A (S & D OIL TECHNICS BV) 8 July 1993 (1993-07-08) * page 2, line 1 - page 3, line 8; claim 1 *	1-13	C10G17/02 C10G31/08 C10M175/00
X	----- US 1 686 491 A (HUGHES WAYNE S ET AL) 2 October 1928 (1928-10-02) * claims 1,3,4 *	1-13	
X	----- US 2 434 528 A (WADLEY EDWARD F) 13 January 1948 (1948-01-13) * column 1, line 51 - line 54 * * column 2, line 33 - line 35; claims 1,3 *	1-13	
X	----- US 4 491 515 A (TIRTAATMADJA VIYADA ET AL) 1 January 1985 (1985-01-01) * claims 1,4; examples 5,6 *	1,5,9,11	
X	----- US 2 520 407 A (HUGHES EDWARD M) 29 August 1950 (1950-08-29) * claim 1; figure 2 *	1,9,11	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
X	----- GB 193 029 A (APOLLINE RIALLAND) 10 January 1924 (1924-01-10) * claim 1 *	1,9,11	C10G C10M
E	----- GB 2 393 448 A (OSS GROUP LTD) 31 March 2004 (2004-03-31) * the whole document *	1-13	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 23 June 2004	Examiner Deurinck, P
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			

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EPO FORM 1503 03.82 (P4/C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 04 25 0667

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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23-06-2004

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9313190	A	08-07-1993	NL 9200003 A	02-08-1993
			AU 3368693 A	28-07-1993
			CA 2061077 A1	04-07-1993
			NL 9200209 A	02-08-1993
			WO 9313190 A1	08-07-1993
			ZA 9201954 A	24-02-1993

US 1686491	A	02-10-1928	NONE	

US 2434528	A	13-01-1948	NONE	

US 4491515	A	01-01-1985	AU 557294 B2	18-12-1986
			CA 1177007 A1	30-10-1984
			EP 0084212 A1	27-07-1983
			AU 8165482 A	04-11-1982

US 2520407	A	29-08-1950	NONE	

GB 193029	A	10-01-1924	FR 557963 A	20-08-1923

GB 2393448	A	31-03-2004	NONE	
