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

(11) **EP 3 098 291 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
30.11.2016 Bulletin 2016/48

(51) Int Cl.:
C10M 175/00 *(2006.01)*

(21) Application number: **16164521.3**

(22) Date of filing: **08.04.2016**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA MD

(30) Priority: **28.05.2015 IT UB20151298**

(71) Applicant: **Viscolube S.r.l.**
26854 Pieve Fissiraga Lodi (IT)

(72) Inventor: **GALLO, Francesco**
26854 Pieve Fissiraga Lodi (IT)

(74) Representative: **Vatti, Francesco Paolo et al**
Fumero S.r.l
Pettenkofferstrasse 20/22
80336 Munich (DE)

(54) PROCESS FOR REGENERATING WASTE OILS

(57) A process for the regeneration of waste oils is disclosed, comprising a flash distillation step of the oil to be regenerated, a decanting step of the heavy fraction, a distillation step in a packed distillation column, allowing to produce an oil fraction to be sent to hydrorefining and a bitumen fraction. The bitumen fraction is ground, the liquid fraction obtained after grinding being separated and collected as bitumen and the remaining solid fraction being separated and recycled to said step of decanting of the heavy fraction.

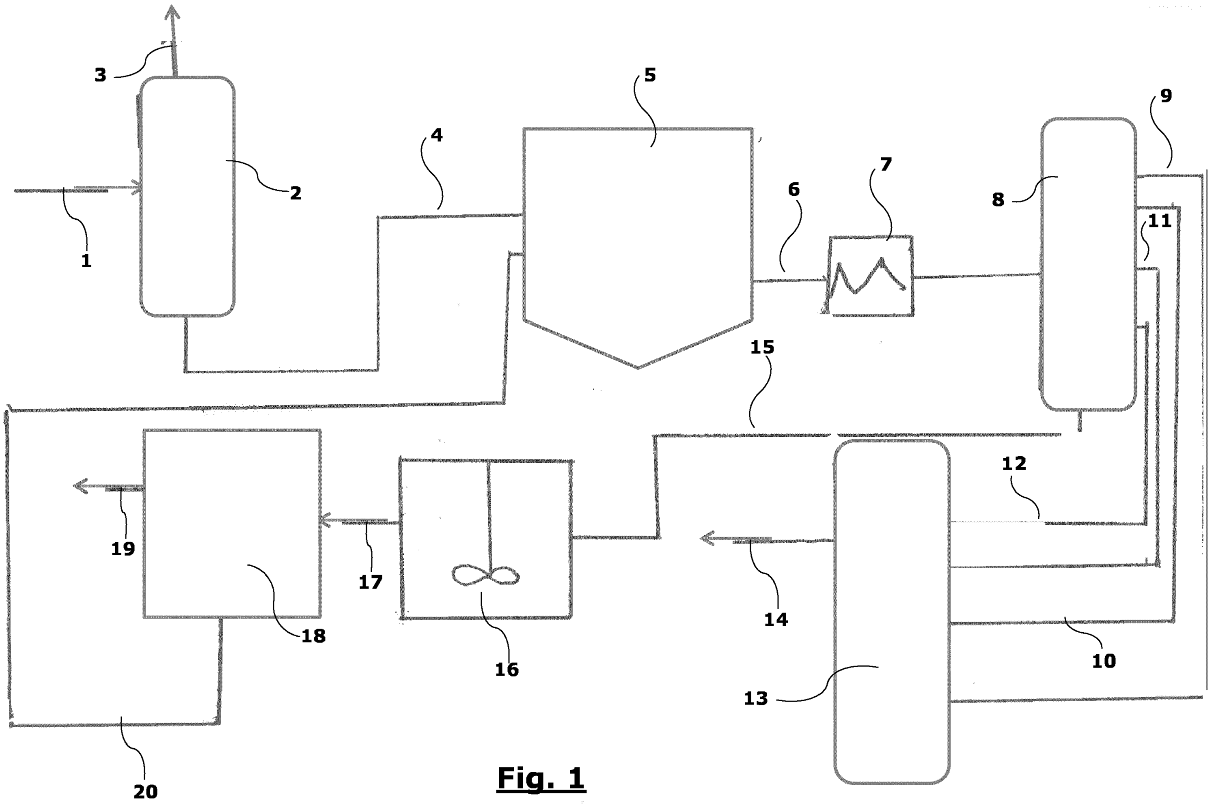

Fig. 1

EP 3 098 291 A1

Printed by Jouve, 75001 PARIS (FR)

Description

[0001] The present invention relates to a regeneration process for waste oils, in particular mineral oils, aimed at obtaining a particularly clean product, suitable to be used as a lubricant base, increasing the enhancement of waste oil compared to the prior art processes.

[0002] Lubricating oils are used in almost all the fields of mechanics to allow engine parts or the like to slide on each other. A classic example is that of oil used in internal combustion engines to help the sliding of the pistons in the cylinders, without the parts getting stuck into one another.

[0003] Lubricating oils are often used in machinery involving relative, very fast sliding movements of their parts. Because of this, in addition to other aspects, lubricating oils frequently undergo temperature changes, which are in some cases very remarkable. For this reason, oils undergo chemical reactions of various kinds and their nature is altered. So reactions such as cleavage, dehydration, dehydrogenation, condensation, etc. take place. An example of such a reaction is the dehydrogenation-dehydration of oils, which leads to the formation of carbon in the form of carbon black. In some cases, the formation of asphaltenes and bitumens also occurs. Furthermore, the oils can contact with other substances, such as, for example, metallic and/or ceramic particles, thus remaining inside the oil itself. Moreover, it is not uncommon that spurious substances, such as various types of polymers, get mixed with oils, since their use and/or collection after use do not always tale place in an appropriate manner and with precautions aimed at avoiding the introduction of foreign substances and obtaining a quality waste.

[0004] The above-mentioned and other transformations determine the deterioration of the physical and chemical characteristics of the oil, making it eventually even harmful for the machines inside which it is used, because the foreign substances inside the oil significantly increase friction. Therefore, it is appropriate to replace the oil with fresh oil after a certain period of use, so as to avoid performance reduction or even breakage of mechanisms.

[0005] Waste oil contains a number of toxic substances, for which reason it cannot be simply discharged into the environment, but must be treated to reduce its environmental impact. The regeneration of waste oils has thus emerged as a solution allowing to reduce waste and the resulting environmental impact.

[0006] The first plants for re-refining waste oils date back to the 60s of the twentieth century, when environmental awareness began to develop and spread. Given the high costs to obtain freshly refined oils and because of the increase in consumption of these oils, the regeneration of waste oils has been gaining important market shares over time.

[0007] The establishment of mandatory consortia responsible for the collection of waste oils has also made easily available the material to be treated, now widely accessible at a good price, although its quality is rather poor. This type of market has significantly expanded over the years. About a third of waste oil is properly collected by the consortia and sent to regeneration or to other treatments to make it harmless, the rest being improperly dispersed in an uncontrolled manner into the environment and being a source of pollution or, in any case, being lost in its service cycle, with economic damage as well.

[0008] The typical yield of a regeneration process, starting from 100 kg of waste oil to be sent to the process, is now around 60 kg of regenerated oil (base for lubricants), 20-25 kg of fuel and 20-25 kg of bitumen.

[0009] Historically, the first processes were those with sulphuric acid or with propane. In other words, oils are treated by adding sulphuric acid or propane, so as to eliminate a large part of impurities contained in waste oils. However, the process involving the use of acid has been virtually abandoned, due to the considerable pollution problems it entails.

[0010] The process with sulphuric acid causes the formation of acid sludge, which retains non-negligible amount of oil and also contains polymeric compounds and heavy metals. This sludge is difficult to dispose of; its disposal generally occurs in landfills, preferably after neutralisation, which, however, increases the volume of the same sludge. The solution of sludge combustion has been tested, but turned out to be impractical.

[0011] Other processes, starting from the already mentioned one that makes use of propane, were thus developed.

[0012] The step of acid treatment is completely replaced by clarification with liquid propane. The chosen hydrocarbon is propane for being easily liquefiable and having a low density once liquefied. It therefore acts as fluidifying agent on oils to which it is added, so as to allow the separation of a high-density phase - containing high molecular weight polymers and heavy metals - from a second fraction, constituted by clarified and dehydrated oils. The propane is then removed and recycled by mixing with the in-fed oils.

[0013] A hot filtration is then performed, allowing the recovery of a gaseous fraction. Discolouration and deodorisation of the content are the final steps.

[0014] However, this process allowing to achieve higher yields still has some disadvantages. First of all, handling propane can be dangerous for plant workers. Moreover, a part of the propane is trapped in the asphalt; this presence excludes the use of the obtained bitumen for the construction of roads, with considerable economic damage. As a result, the bitumen fraction in this process is simply a waste to dispose of and cannot be enhanced. Finally, the process itself is much more expensive than the process with sulphuric acid.

[0015] In more recent years, a new type of process has been introduced, according to which waste oils are sent to the axial rotor of a distillation column and are sprayed by said rotor on the inner walls of the column, kept at a high temperature by a diathermic fluid flowing through some ducts. In contact with the heated walls, the vaporisable fraction evaporates, while the heavier fraction remains in the liquid phase. Fractions are then collected and further fractioned in a subsequent fractioning column, which is divided in further cuts inside a subsequent fractioned distillation column. The yields of this process are important, but a pre-treatment is required to purify the waste oils.

[0016] EP 0 618 959, of the same Applicant, discloses a process for re-refining waste oils, in which said oils are contacted with a basic reagent and heated to remove contained water, polymers and heavy metals are separated and fractioned distillation is performed in a packed column in order to obtain one or more base fractions for lubricants, followed by discolouration. The basic reagent is a strong base, water is removed together with a more volatile fraction in a preliminary step of flash distillation, while polymers and heavy metals are removed mostly by decanting. However, the packed distillation column tends to become clogged by solid residues, still contained in the oil to be fed inside the same.

[0017] Recently, the same Applicant filed an Italian patent application for a process which, starting from that of EP 0 618 959, provides for a centrifugation step of the oil to be regenerated between the step of flash distillation and the step of packed column distillation. The pressure inside the packed distillation column is adjusted through a liquid-ring pump, obtaining a cleaner product and a reduced number of interventions to regenerate the distillation column.

[0018] WO2004/033 608 discloses a process and a device for the treatment of waste oils, which includes a preliminary separation by decanting of at least one fraction of the water and one fraction of solid particles (sediments), a preliminary heating of the oily phase from the decanting step and centrifugal separation of the oil, preheated to a temperature below the boiling point of water, followed by the separation of water and other pollutants. The product obtained, however, is not reused to produce new lubricant bases, but is fed to a combustion step, along with other hydrocarbons, therefore with no enhancement of the same.

[0019] WO96/00 273 discloses a process of reclamation of waste oils, with a view to their reuse. According to this document, waste oil undergoes a centrifugation as it is to remove solids; the output oil is then contacted with diammonium phosphate and/or oxalic acid at a temperature between 60 and 85-90°C and is then subjected to a new centrifugation to separate oil and water. There are no distillation steps.

[0020] CA 2 396 206 discloses a process for treating waste oils, comprising a dehydration step of waste oil, a subsequent fractioned distillation, managing the lowest plate of the column to a temperature between 370 and 390°C at a pressure comprised between 67 and 133 mbar, the intermediate plate at a temperature between 265 and 280°C at a pressure between 47 and 60 mbar and the top plate at a temperature between 100 and 110°C at a pressure between 40 and 53 mbar, recovering bitumen from the bottom of the column and extracting oil fractions of different density at the highest levels.

[0021] US2001/0 001 198 discloses a procedure for removing acidic compounds, colour, and polynuclear aromatic hydrocarbons from petroleum distillates using phase transfer catalysts, by adding suitable solvents and then removing them by distillation together with the contaminants.

[0022] In all the processes just examined, next to the base for lubricants - which is the most refined product - important quantities of bitumen and asphalt are obtained. This fraction is, in the above processes, of not particularly high quality and can only be sold at relatively low prices and for basic uses, such as for the construction of paved roads.

[0023] The object underlying the invention is to propose a regeneration process of waste oils, overcoming the mentioned disadvantages and allowing for further enhancement of process effluents. This object is achieved through a process for the regeneration of waste oils, comprising a step of flash of the oil to be regenerated, a step of decanting of the heavy fraction, a step of distillation in a packed distillation column, allowing to produce an oil fraction to be sent to hydrorefining and a bitumen fraction, characterised in that the bitumen fraction is ground, the liquid fraction obtained after grinding being separated and collected as bitumen and the remaining solid fraction being separated and recycled to the step of decanting of the heavy fraction. The dependent claims describe preferred features of the invention.

[0024] Further features and advantages of the invention will anyhow be more evident from the following detailed description of a preferred embodiment, given by mere way of non-limiting example and illustrated in the accompanying drawings, wherein:

fig. 1 is a block diagram illustrating the process according to the present invention;
fig. 2 is a block diagram representing a part of the process according to the present invention, according to an alternative embodiment; and
fig. 3 is a block diagram illustrating the process according to a second alternative embodiment.

[0025] As previously mentioned, a first embodiment of the process according to the present invention is represented as a block diagram in fig. 1. The oil to be regenerated arrives from the pipeline 1. In this pipeline, oil can be mixed with an alkaline substance. A strong base is generally used, preferably KOH, which gave the best results. The pipeline 1 feeds the oil to be regenerated to a flash distillation column 2. The pressure inside the column 2 is maintained at about 330 mbar and the temperature is slightly higher than the boiling temperature of water, preferably about 130-140°C. Thus, in the column 2, a substantial part of water contained in the oil, partly directly from waste oil, partly fed in 1 as the solvent of the basic substance, is vaporised. The vaporised water exits from a drain 3. The oil, still containing a minor portion of water, along with other impurities, mostly solid, exits from the pipeline 4 and is thus fed to a decanter 5. Only one decanter 5 is represented in fig. 1, but the person skilled in the art can find practical reasons for providing two or more, without thereby departing from the scope of the present invention. The further separation of oil from water and from a part of the solid particles contained in it occurs in the decanter. The fraction to be subjected to the subsequent steps exits the decanter 5 through the pipeline 6. The latter feeds the oil to be treated in a heat exchanger 7, preferably an oven, which brings the oil temperature to values above 300°C, preferably to values between 350° and 400°C, subsequently feeding it in a packed distillation column 8. Inside it, some useful fractions are separated, respectively transported by pipelines 9, 10, 11 and 12 to a reactor 13 where oil hydrorefining occurs, thereby obtaining the lubricant bases coming out from the plant at 14.

[0026] The column 8 also outputs a bituminous tail fraction which, in the processes according to the prior art, is usually sold directly as bitumen. According to the present invention, instead, the bituminous fraction exits the bottom of column 8 and is fed to a mixer 16 through a pipeline 15 in order to be homogenised. From the mixer 16, an outlet 17 feeds the mixed fraction to the grinding unit 18. The unit 18 can be any type of grinding device. A ball mill is particularly preferred, but wedge mills, disc grinders and others can be used as well.

[0027] The unit 18 chops the solid particles contained in the bitumen, opening them and thus making available more oil to be regenerated. A more liquid part and a part that remains more solid are obtained. Unit 18 has two outlets: an outlet 19, from which the liquid part of the product comes out, substantially a more liquid bitumen, containing less solid impurities than the one in the pipeline 15, thus having a higher value; and an outlet 20, from which the solid fraction comes out, containing, *inter alia,* the particles opened in the grinding step with the oil to be regenerated. The outlet 20 feeds the solid fraction back to the decanter 5, where it mixes with the oil flow from the column 2 and the process begins again, releasing more oil for regeneration. In this way, process yield increases, allowing to obtain a higher amount of lubricant base (fine fraction), up to 67-70% by weight, and lower amounts of fuel and bitumen (poorer fractions).

[0028] Fig. 2 represents a block diagram of an alternative embodiment of the present invention. Elements identical to those of Fig. 1 are indicated with the same reference numbers.

[0029] Flows 9, 10, 11 and 12, output from the packed distillation column 8, are fed to a tank 21 which acts as a buffer, to allow the subsequent operations to be carried out discontinuously, load-wise or batch-wise. From the tank 21, a pipeline 22 leads to microfiltration unit 23, of a type known per se. A flow 24 brings the liquid fraction to the reactor 13 to perform the hydrorefining and collect the produced lubricant base from the outlet 14.

[0030] A pipeline 15 carries the bitumen fraction from the packed distillation column 8. An additional flow from pipeline 25, output by the microfiltration unit 23, from which sediments separated during the microfiltration step are removed, joins this flow.

[0031] Also in this case, the pipeline 15, joined by the pipeline 25, carry the bitumen fraction, containing solid particles, to the mixer 16 and from there, through the pipeline 17, to the grinding unit 18. As already shown in the case of fig. 1, in this case as well, the pipeline 19 transports and discharges bitumen, more valuable than that obtainable according to the prior art, while the pipeline 20 recycles the solid part ground during the first process steps according to the present invention, bringing the lubricant base yield to higher levels.

[0032] According to this embodiment, in addition to an increase in higher quality products and the greater value of the poor products, the fraction fed to the reactor 13 is cleaner. The fact that the flow being treated in the reactor 13 is cleaner causes a significant extension of the useful life of the catalyst used in this step; given that, although used in small quantities, the catalysts for hydrorefining are normally based on precious metals, a certain cost saving is achieved, increased by the reduction of performance interruptions due to catalyst replacement.

[0033] Fig. 3 represents the block diagram of a further alternative embodiment. Even in this case, the steps already described in relation to fig. 1 will carry the same reference numbers and will not be further described. This embodiment depends on a patent application recently filed by the same Applicant.

[0034] The oil to be treated, exiting through pipeline 4 from the column 2 for flash distillation, is divided into two flows 4A and 4B, which feed respective decanters 5A and 5B, entirely similar to the decanter 5 described with reference to fig. 1. The fraction to be regenerated comes out from the decanters 5A, 5B through the pipelines 26A, 26B, and is fed to centrifugal separators 27A, 27B. The part still to be treated (oil to be regenerated) is carried by pipelines 28A, 28B, which then gather in the pipeline 28, to a decanter 29. The useful fraction output from the decanter 29 is then fed to the heat exchanger 7, usually an oven, where it is brought to a temperature higher than 300°C, typically between 350° and 400°C. The fraction is then fed to the packed distillation column 8. The column 8 is operated so as to have a tail pressure comprised between 10 and 20 mbar and a head pressure comprised between 2.5 and 9.5 mbar, in order to collect the best product. According to a preferred embodiment, pressure is adjusted, rather than by the ejectors commonly used for this purpose, by a liquid-ring pump. In this way, besides saving on costs related to steam and eliminating the need to manage a dedicated steam cycle, flows and pressure are more regular compared to what could be previously achieved with ejectors.

[0035] The column 8 outputs the useful product flows, through the pipelines 9, 10, 11 and 12, which go to the next step of hydrorefining, into the reactor 13; the produced lubricant bases are extracted from the reactor 13 through the pipeline 14. Using a liquid-ring pump to adjust pressure inside the column 8, the fraction fed to the reactor 13 is particularly clean and the life of the catalyst contained in the reactor 13 is significantly extended.

[0036] Column 8 also outputs the tail flow from the pipeline 15. This flow, containing the bitumen fraction, is joined by flows 30 and 31, output from centrifugal separators 27A, 27B and containing the solid sediments separated from the oil in regeneration.

[0037] The pipeline 15 carries the bituminous fluid to the mixer 16 and from here, via the pipeline 17, to the grinding unit 18.

[0038] The liquid fraction obtained after grinding is collected from the pipeline 19 and sold.

[0039] The solid fraction is collected from the pipeline 20, which is divided into two flows 20A, 20B, respectively feeding decanters 5A, 5B.

[0040] The two last alternative embodiments described can also be advantageously combined with each other.

[0041] The system used to implement the process according to the present invention is of the type comprising a flash distillation column 2, a number of decanters 5 or 5A, 5B, a packed distillation column 8 and a hydrorefining reactor 14 and also comprises a unit 18 for grinding the bitumen fractions and any process sediments. Normally, the grinding unit 18 is a ball mill.

[0042] The bitumen fraction that leaves the process through pipeline 19 has improved characteristics compared to that obtained by the processes of regeneration of waste oils according to the prior art. In particular, this bitumen - also thanks to its carbon black content - in addition to the common uses of bituminous fractions, such as the preparation of roads and the like, is also suitable for more refined uses. If this bitumen is mixed with polyethylene (for example, low-density polyethylene) or polypropylene, for example by making 10% bitumen and 90% polymer mixtures, it can be used for the creation of master batches. For example, it is possible to easily obtain a film thickness of about 60 microns.

[0043] Furthermore, this bitumen may be used for the production of inks, such as, for example, heatset or coldset inks.

[0044] The process and the plant according to the present invention allow to obtain a higher lubricant base yield (as seen, it changes from 60% by weight to about 67-70% by weight), increasing the enhancement of the initial waste and reducing process waste. Such enhancement is further increased by the fact that, as seen, even the least valuable product - bitumen - is enhanced.

[0045] It is understood, anyway, that the invention is not to be considered as limited by the particular arrangement illustrated above, which represents only an exemplary embodiment of the same, but different variants are possible, all within the reach of a person skilled in the art, without departing from the scope of the invention itself, as defined by the following claims.

LIST OF REFERENCE NUMERALS

[0046]

1	Pipeline
2	Flash distillation column
3	Drain (of 2)
4	Pipeline (of 2)
5	Decanter
5A	Decanter
5B	Decanter
6	Pipeline
7	Heat exchanger
8	Packed distillation column
9	Pipeline
10	Pipeline
11	Pipeline
12	Pipeline
13	Reactor
14	Output (of 13)
15	Pipeline
16	Mixer
17	Output (of 16)
18	Grinding unit
19	Liquid product output (of 18)
20	Solid fraction output (of 18)
21	Tank
22	Pipeline
23	Microfiltration unit
24	Flow
25	Pipeline
26A	Pipeline
26B	Pipeline
27A	Centrifugal separator
27B	Centrifugal separator
28	Pipeline
28A	Pipeline
28B	Pipeline
29	Decanter

Claims

1. Process for the regeneration of waste oils, comprising a step of flash distillation of the oil to be regenerated, a step of decanting of the heavy fraction, a step of distillation in a packed distillation column, allowing to produce an oil fraction to be sent to hydrorefining and a bitumen fraction, **characterised in that** the bitumen fraction is ground, the liquid fraction obtained after grinding being separated and collected as bitumen and the remaining solid fraction being separated and recycled to said step of decanting of the heavy fraction.

2. Process as in claim 1), **characterised in that** said grinding step of the bitumen fraction is preceded by a mixing step.

3. Process as in claims 1) and 2), **characterised in that** it provides a microfiltration step of the product resulting from packed column distillation, the sediment of which is sent to said grinding step.

4. Process as in any one of the preceding claims, **characterized in that**, before said packed column distillation step, a centrifugal separation step is provided, and **in that** the pressure within said packed distillation column is adjusted by a liquid-ring pump.

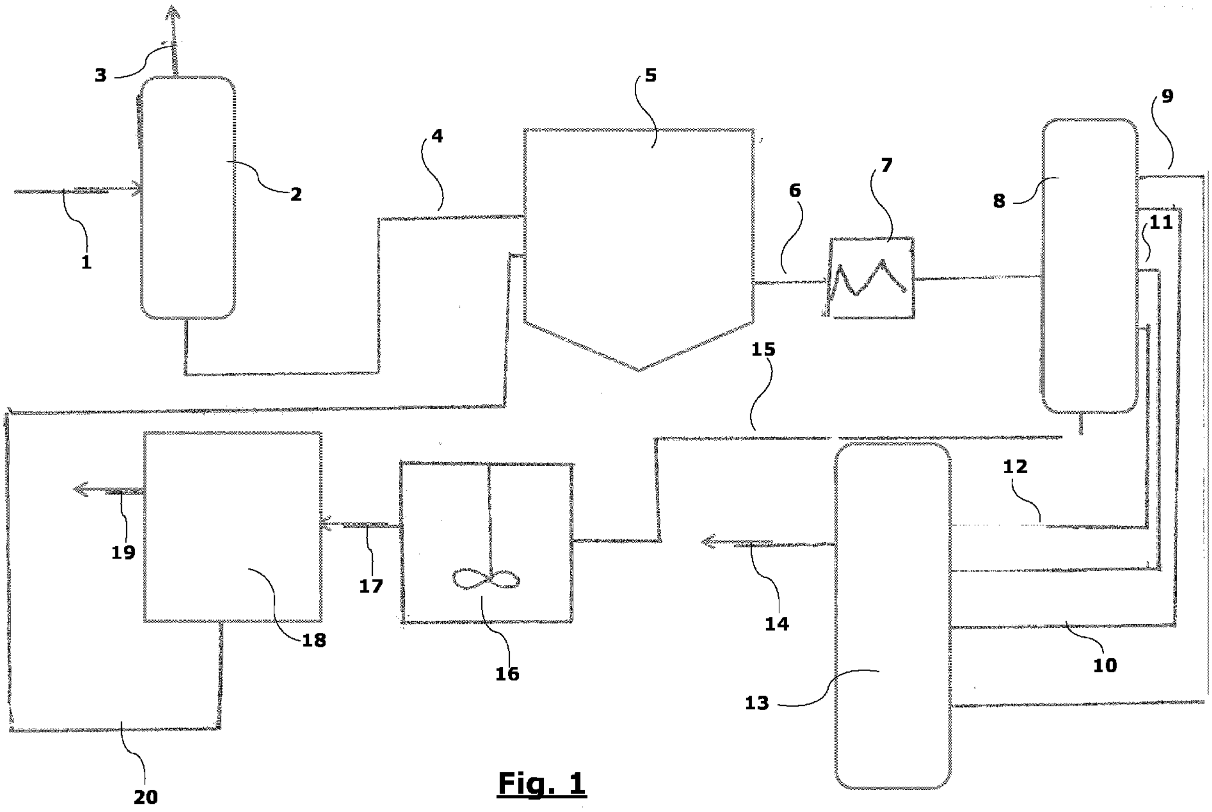

Fig. 1

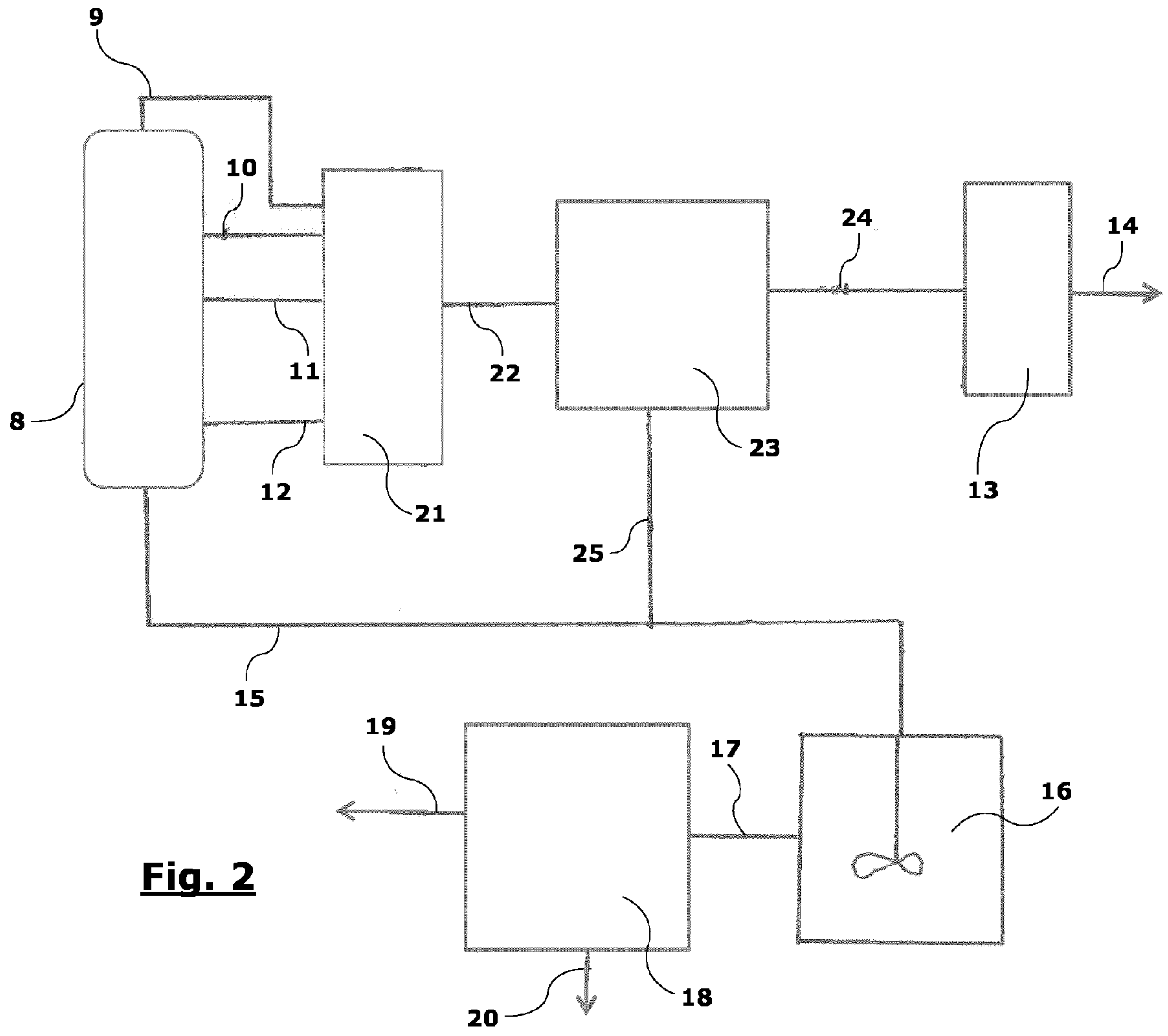

Fig. 2

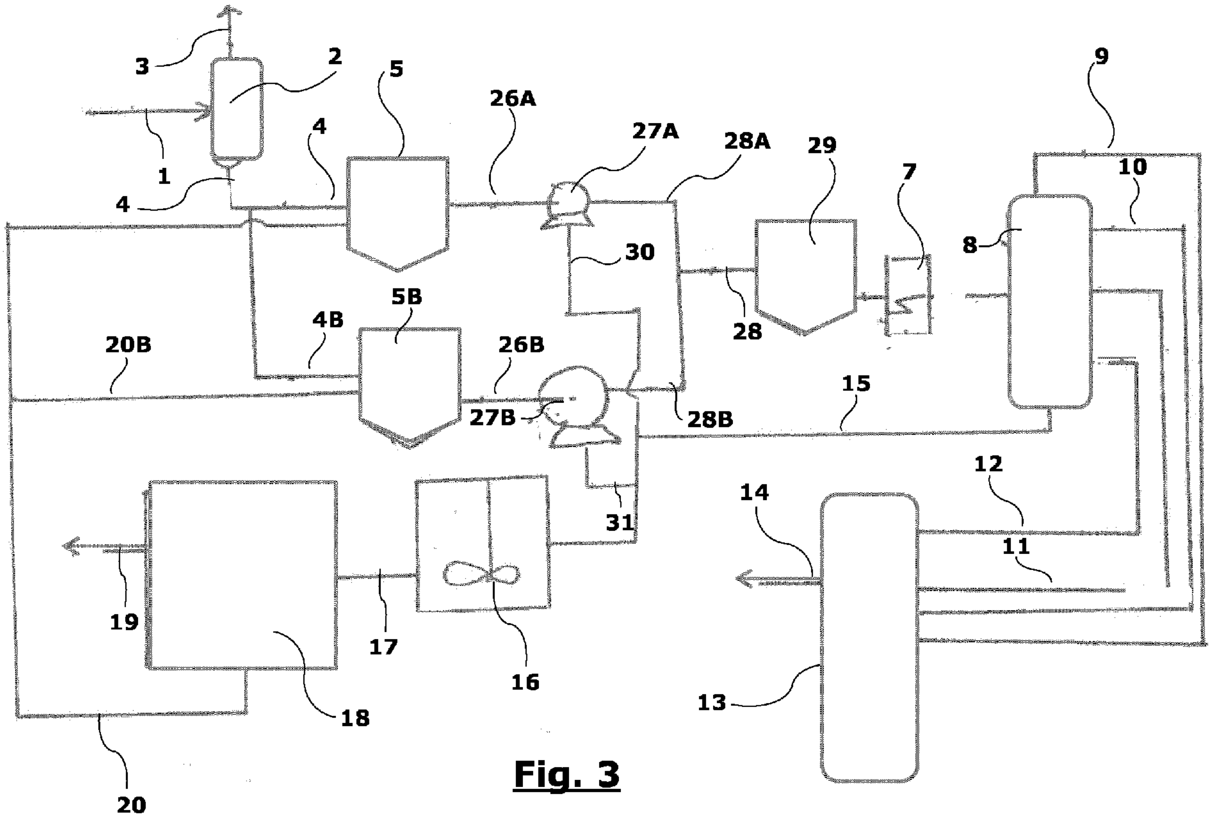
3
2
5
26A
27A
28A
29
7
9
10
1
4
4
8
30
28
5B
4B
20B
26B
27B
28B
15
12
14
31
11
19
17
16
13
18
20

Fig. 3

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 16 16 4521

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A,D	WO 94/07798 A1 (VISCOLUBE ITALIANA SPA [IT]; MINANA JOSE ANTONIO GOMEZ [ES]; SCHIEPPAT) 14 April 1994 (1994-04-14) * claims * -----	1-4	INV. C10M175/00
A	CA 2 396 206 A1 (FAKHRI NOUREDINE [CA]) 30 January 2004 (2004-01-30) * page 5, line 14 - line 28 * -----	1-4	
A	US 2001/001198 A1 (SHERMAN JEFFREY H [US] ET AL) 17 May 2001 (2001-05-17) * paragraphs [0023] - [0025] * -----	1-4	

TECHNICAL FIELDS SEARCHED (IPC)

C10M

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	30 June 2016	Keipert, Olaf

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 (P04C01)

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

EP 16 16 4521

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
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

30-06-2016

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9407798 A1	14-04-1994	AT 180009 T	15-05-1999
		CN 1086252 A	04-05-1994
		CZ 9401579 A3	15-12-1994
		DE 69324905 D1	17-06-1999
		DE 69324905 T2	11-11-1999
		DK 0618959 T3	29-11-1999
		EG 20181 A	30-09-1997
		EP 0618959 A1	12-10-1994
		ES 2132258 T3	16-08-1999
		GR 3030648 T3	29-10-1999
		HK 1013280 A1	12-05-2000
		HU 213650 B	29-09-1997
		IT 1255534 B	09-11-1995
		PL 297417 A1	05-04-1994
		RU 2099397 C1	20-12-1997
		TJ 335 B	01-07-2002
		WO 9407798 A1	14-04-1994
CA 2396206 A1	30-01-2004	AU 2003249818 A1	16-02-2004
		CA 2396206 A1	30-01-2004
		MA 26075 A1	01-04-2004
		US 2004173505 A1	09-09-2004
		WO 2004011579 A1	05-02-2004
US 2001001198 A1	17-05-2001	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- EP 0618959 A **[0016] [0017]**
- WO 2004033608 A **[0018]**
- WO 9600273 A **[0019]**
- CA 2396206 **[0020]**
- US 20010001198 A **[0021]**