

# (11) EP 2 175 010 A1

(12)

## **EUROPEAN PATENT APPLICATION**

(43) Date of publication: **14.04.2010 Bulletin 2010/15** 

(21) Application number: 08017792.6

(22) Date of filing: 10.10.2008

(51) Int Cl.: C10L 1/18<sup>(2006.01)</sup> C11D 1/66<sup>(2006.01)</sup>

C10L 10/02 (2006.01)

C10M 105/34 (2006.01) C23G 5/032 (2006.01) C10L 10/04 (2006.01)

(84) Designated Contracting States:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MT NL NO PL PT RO SE SI SK TR

**Designated Extension States:** 

AL BA MK RS

(71) Applicant: Eco Air S.r.I. 20077 Melegnano (MI) (IT) (72) Inventor: Grignani, Vittorio 20077 Melegnano (MI) (IT)

(74) Representative: Pipparelli, Claudio PIPPARELLI & PARTNERS Via Quadronno, 6 20122 Milano (IT)

## (54) Use of fatty acid esters as descaling and lubricating agents

(57) Use as descaling and lubricating agents of compositions of  $C_1$ - $C_2$  esters of monocarboxylic acids from  $C_6$  to  $C_{20}$ , particularly from  $C_8$  to  $C_{18}$ , the above-mentioned compositions being characterized by containing esters of monocarboxylic saturated acids  $C_{12}$ - $C_{16}$  in

quantity from 65% to 94% by weight, preferably from 68% to 90% by weight, compared to the total esters of monocarboxylic acids.

EP 2 175 010 A1

#### Description

**[0001]** The present invention concerns the use as descaling and lubricating agents of particular compositions of  $C_1$ - $C_2$  esters of monocarboxylic acids from  $C_6$  to  $C_{20}$ , particularly from  $C_8$  to  $C_{18}$ , with prevalence of esters of monocarboxylic acids from  $C_{12}$  to  $C_{16}$ .

**[0002]** It is well known that in general the mechanicals parts of any machines can operate in the long run in a non-optimal condition or can even get stuck. This is particularly valid for mechanical parts in movement. In most cases, the above-mentioned inconveniences are due to scales developing and accumulating in time. These scales can be of various types, of inorganic nature (i.e. rust, powders) or of carbonaceous nature (i.e. soot, residual hydrocarbons combustion, impurities contained in the alimentation fuel of diesel engines). Deteriorated mechanical parts can be particularly found in various parts of diesel engines, i.e, feed pumps, hydraulic head of diesel alimentation, injector, injector nozzle.

**[0003]** Therefore it is felt by skilled persons the need to be able to restore rapidly and efficiently the functionality of the above-mentioned mechanical parts, possibly keeping them lubricated at the same time.

**[0004]** It has been found that these problems can be solved by a particular composition of methyl and/or ethyl esters of monocarboxylic acids.

**[0005]** According to that, the present invention concerns the use as descaling and lubricating agents of compositions of  $C_1$ - $C_2$  esters of monocarboxylic acids from  $C_6$  to  $C_{20}$  particularly from  $C_8$  to  $C_{18}$ , the above-mentioned compositions being characterized by containing esters of monocarboxylic saturated acids  $C_{12}$ - $C_{16}$  in quantity from 65% to 94% by weight, preferably from 68% to 90% by weight, compared to the total esters of monocarboxylic acids.

**[0006]** The compositions of the present invention arc then methyl and/or ethyl esters, preferably methyl, of the above-mentioned monocarboxylic acids.

**[0007]** Main components of the above-mentioned compositions are methyl and/or ethyl esters of lauric acid ( $C_{12}$ ), myristic acid ( $C_{14}$ ) and palmitic acid ( $C_{16}$ ). Between these three esters, it is usually prevalent the one derived from the lauric acid.

**[0008]** Other components of the compositions in the present invention are usually esters  $C_1$ - $C_2$  of monocarboxylic saturated acids  $C_6$  (hexanoic acid),  $C_8$  (caprylic acid),  $C_{10}$  (capric acid),  $C_{18}$  (stearic acid) and unsaturated acids  $C_{18}$  (oleic acid and linoleic acid), with prevalence of the last ones.

**[0009]** These composition conditions arc satisfied by the methyl and /or ethyl esters of particular vegetable oils, as Babassu oil, Coconut oil, Palm Kernel oil. The preferred composition of the present invention is constituted by methyl and/or ethyl ester of Babassu oil.

[0010] The table 1 reproduces the composition in % by weight of the three above-mentioned vegetable oils.

Table 1 - Vegetable oils composition

	Table 1 Vege	cable ons comp	OSITION
	Babassu Oil	Coconut Oil	Palm Kernel Oil
C 6.0	ND	ND-0.7	ND-0.8
C 8.0	2.6-7.3	4.6-10.0	2.4-6.2
C 10.0	1.2-7.6	5.0-8.0	2.6-5.0
C 12.0	40.0-55.0	45.1-53.2	45.0-55.0
C 14.0	11.0-27.0	16.8-21.0	14.0-18.0
C 16.0	5.2-11.0	7.5-10.2	6.5-10.0
C 16.1	ND	ND	ND-0.2
C 17.0	ND	ND	ND
C 17.1	ND	ND	ND
C 18.0	1.8-7.4	2.0-4.0	1.0-3.0
C 18.1	9.0-20.0	5.0-10.0	12.0-19.0
C 18.2	1.4-6.6	1.0-2.5	1.0-3.5
C 18.3	ND	ND-0.2	ND-0.2
C 20.0	ND	ND-0.2	ND-0.2
C 20.1	ND-0.2	ND-0.1	ND-0.2
C 20.2	ND	ND	ND

35

30

20

40

45

50

55

(continued)

	Babassu Oil	Coconut Oil	Palm Kernel Oil
C 22.0	ND	ND	ND-0.2
C 24.0	ND	ND	ND

5

10

15

20

25

30

35

40

45

50

55

**[0011]** The above reported vegetable oils are under the form of mono, di- and tri- glycerides, for which it is necessary a transesterification reaction with methyl and/or ethyl alcohol in order to obtain the present invention composition.

**[0012]** The transesterification reaction is carried out in presence of basic catalysts, preferably chosen between sodium hydroxide, potassium hydroxide, sodium or potassium methylate, sodium or potassium carbonate, mixed carbonates of sodium and methyl, or potassium and methyl. The last ones can be obtained bubbling  $CO_2$  in a solution of sodium or potassium chloride dissolved in methanol.

**[0013]** The transesterification reaction is carried out at the alcohol boiling temperature and the alcohol and catalyst quantities are function of the composition of the vegetable oil to esterify.

**[0014]** As it will be demonstrated in the experimental part, the used process allows the reaction completeness and then the absence of free fatty acids in the final product. Moreover the synthesized ester is nearly free of free glycerol and alcohol.

**[0015]** In table 2 are reported the characteristics of various Babassu oil samples esterified with methanol according to the above described process and illustrated in the experimental part.

Table 2 - Characteristics of the methyl ester of the Babassu oil

Parameters	Measure	Lin	nits
		Min	Max
Aspect	Visual	Transparent slig	htly yellow liquid
Ester content	% w/w	96.5	
Viscosity at 40 °C	mm <sup>2</sup> /sec	3.5	5
Flash point	°C	125	
Pour point	°C		-9
Water content	mg/kg		500
Acidity Value	mg KOH/g		0.5
Free Glycerol	% w/w		0.02
Methanol content	% w/w		0.2
Saponification Number	mg KOH/g		170
Caprylic acid C 8.0	%	2	6
Capric acid C 10.0	%	3	7
Lauric acid C 12.0	%	42	54
Myristic acid C 14.0	%	15	25
Palmitic acid C 16.0	%	8	15
Stearic acid C 18.0	%	2	6
Oleic acid C 18.1	%	12	20
Linoleic acid C 18.2	%	2	6

**[0016]** As previously stated, the present invention composition is particularly useful as descaling and lubricating agent, especially for mechanical parts, more in particular for mechanical parts of diesel engines, on which scales and/or deposits of different kind are present. The above-mentioned scales can be of different kind, i.e. rust, powders, carbonaceous residuals, asphaltenes, soot.

[0017] The present invention compositions can be used as such or diluted with hydrocarbon diluents as diesel, petrol,

naphtha. It is preferable that the above-mentioned diluents will lead to homogeneous mixtures once blended with the present invention compositions. In the case that the esters of the present invention compositions are used diluted with hydrocarbon diluents, it is preferable that the weight ratio between the esters compositions and the hydrocarbon diluent will not be lower than 5/95 weight/weight, preferably 20/80.

[0018] The present invention compositions work placing the scaled parts in contact with the present invention compositions (as such or diluted) for the time necessary to restore the functionality of the above-mentioned mechanical parts. Obviously, this time will be function of the scales quantity and type and of the dilution degree of the present invention composition.

**[0019]** Finally the present invention compositions can be added to the feed oil of diesel engines, particularly with the purpose of cleaning the injectors and the feeding system. In this case, the ester composition of the present invention will preferably be contained in a quantity of at least 0.05% by weight, more preferably of at least 0.1% by weight compared with the diesel oil weight.

[0020] The following examples are reported for a better comprehension of the present invention.

**[0021]** Example 1 refers to a typical esterification of the Babassu oil, while examples 2-6 refer to applications of the esterified product obtained in the example 1.

#### EXAMPLE 1 - Synthesis of the Babassu oil methyl ester

[0022] In a 500ml coated reactor, equipped with a bubble cooler, temperature drill and magnetic stirrer, gr 260 of refined Babassu oil are loaded; then a solution of gr 80 of soda dissolved in gr 110 of methanol is added.

[0023] The system is brought at 64°C and is kept under agitation for 1 hour.

[0024] During the reaction, the temperature decreases slightly (62-63°) as the methanol reacts.

[0025] After one hour, the agitation is stopped and it is left to decant.

**[0026]** The lower part is left in the reactor, the upper part containing the esters, part of the methanol, the catalyst and also a glycerine quote is submitted to 60° C water extraction.

[0027] The hydrophilic part contains glycerine, water, methanol and catalyst.

[0028] The hydrophobic part contains esters, traces of methanol and water.

[0029] The methanol is stripped under vacuum and then recuperated.

[0030] Analyses show absence of starting acids.

30 [0031] A composition of methyl esters is obtained, whose characteristics fall in the range reported in table 2.

## **EXAMPLE 2**

15

20

35

40

45

50

**[0032]** Object: BOSH C 0681200502 EFEP 60 H 952. Pumping tool, of manual use for verifying the injectors good functioning.

[0033] <u>Problem</u>: The pump kept on jamming, despite the repeated maintenance interventions, during which it was dismantled, washed with diesel and petrol and lubricated with motor car oil Esso 10/40. Unfortunately, 2 weeks without use were enough to find it again blocked.

**[0034]** Solution: The tool has been dismantled, cleaned and lubricated with the product of example 1 and since then it has not needed maintenance works and always worked well. Two years have nearly passed from that..

## **EXAMPLE 3**

[0035] Object: Hydraulic head of ZEXEL diesel pump

[0036] Problem: The pump piston presented difficulties in sliding.

**[0037]** It has already been done a washing treatment with diesel and petrol and then the pump was lubricated with motor oil Esso 10/40, but the head was newly blocked after a couple of hours being left unused. It has been tested even a specific additive of Winn's<sup>(R)</sup> brand, "Diesel Power 3", without valuable results. Before testing our product, the mechanic showed that he could not displace the piston neither with a plier help.

[0038] Solution: Some drops of the product of example 1 have been placed on the piston in the point where it looked blocked and immediately with only one finger pressure, the piston moved until the stroke end. From that moment it has been possible to let it glide to and from without the least friction-taking place. The pump had been left exposed in the garage at air and dust for two months without the piston fluency suffering any limitations in time.

#### 55 EXAMPLE 4

[0039] Object: Diesel pump ZEXEL

[0040] Problem: The pump was kept accelerated because of fluency difficulties of its slider.

**[0041]** Solution: It has been prepared a mixture of 2 litres of diesel and 500 ml of the product of example 1. Only the entrance and exit tubes of the pump had been removed and their openings had been submerged in a vessel containing the mixture. The pump had been set in motion and maintained in function in order to keep the mixture circulating in its inside for 1 hour. The washing and the lubricating done in this way had restored the perfect functioning to the pump, without being necessary to remove and dismantle it.

**[0042]** The interventions previously realized consisted in removing and dismantling the pump, then it was washed with diesel and petrol and tried to introduce in the fluency slits of the critical points one of the finest and thinnest sandpaper in order to attempt to remove as much as possible of the scales; at the end the pump was washed again with diesel and petrol and lubricated with motor oil Esso 10/40. Although the intervention complexity and care, the functioning never resulted completely recovered. Attempts were made also using specific products Winn's<sup>(R)</sup>, with even more disappointing results.

#### **EXAMPLE 5**

10

20

25

30

35

15 [0043] Object: DELPHI injector mounted on Micra DCI Common Rail.

[0044] Problem: Nozzle micro holes completely obstructed.

**[0045]** Solution: The nozzle has been removed and completely submerged in about 10 ml of the product in object. Recovered and dried after some hours, the nozzle resulted completely cleaned from scales and the micro holes resulted completely descaled. Before the use of the product in object there were no solution known able to recover the part that was substituted with a new one.

#### **EXAMPLE 6**

[0046] Object: Automotive vehicle Terrano II

[0047] Problem: The car misfired and emitted smoke from the exhaust pipes.

[0048] Solution: 500 ml of the product in object had been poured into the tank in addition to diesel, before putting back into circulation the car. At its return to the garage, after a distance covered of about 100 km, the engine resulted perfectly functioning and the exhausting normalized. The use of the Winn's<sup>(R)</sup> "Diesel Power 3" additive has not given clear results and then it would have been necessary remove the injection system in order to dismantle it, wash it with diesel and petrol and lubricate it with motor oil Esso 10/40, thus obtaining a functioning recover not comparable with that one obtainable with the product in object which results as the only mean able to give back to the system its entire restoration.

#### **Claims**

- Use of compositions of C<sub>1</sub>-C<sub>2</sub> esters of monocarboxylic acids from C<sub>6</sub> to C<sub>20</sub> as descaling and lubricating agents, the above mentioned compositions being characterized by containing esters of saturated monocarboxylic acids C<sub>12</sub>-C<sub>16</sub> in quantity from 65% to 94% by weight compared to the total monocarboxylic acids esters.
- 2. Use according to claim 1, in which the compositions are esters C<sub>1</sub> of monocarboxylic acids.
  - 3. Use according to claim 1, in which the compositions are esters of monocarboxylic acids from C<sub>8</sub> to C<sub>18</sub>.
- **4.** Use according to claim 1, in which the esters of saturated monocarboxylic acids C<sub>12</sub>-C<sub>16</sub> are contained in the above mentioned compositions in quantity from 68% to 90% by weight.
  - **5.** Use according to claim 1, in which the compositions arc selected from esters C<sub>1</sub>-C<sub>2</sub>, preferably C<sub>1</sub>, of the vegetable oils selected between Babassu oil, coconut oil, Palm Kernel oil, preferably Babassu oil.
- 6. Use according to claim 1, in which the compositions are diluted with hydrocarbon compounds.
  - 7. Use according to claim 6, in which the weight ratio between the compositions and the hydro carbon compounds is not less than 5/95 weight/weight, preferably than 20/80 weight/weight.
- 55 **8.** Use according to claims from 1 to 7, as descaling and lubricating agents of mechanical parts, particularly in diesel engines.
  - 9. Use according to the claims from 1 to 8, characterized by the fact that the composition is added to the feeding

diesel of a diesel engine in quantity of at least 0.05% by weight, more preferably of at least 0.1% by weight compared

	to the diesel weight.
5	
10	
15	
20	
25	
30	
35	
40	
45	
50	
55	



## **EUROPEAN SEARCH REPORT**

Application Number EP 08 01 7792

Category	Citation of document with in	ndication, where appropriate,	Relevant	CLASSIFICATION OF THE
Jalegory	of relevant pass		to claim	APPLICATION (IPC)
Х	AL) 8 April 2003 (2 abstract		1-7	INV. C10L1/18 C10M105/34 C11D1/66 C23G5/032
X	WO 2007/087003 A (UCIOLETTI KENNETH R [US]) 2 August 2007 * paragraphs [0019] 1,3-5,15,17; exampl	(2007-08-02) - [0021]; claims	1-5	ADD. C10L10/02 C10L10/04
X	1 May 1990 (1990-05	- column 5, line 63;	1-9	
X	EP 0 635 558 A (EUR 25 January 1995 (19 * page 3, line 1 - 1,2,9,10 *		1-9	TECHNICAL FIELDS SEARCHED (IPC)
Х	BDI ANLAGENBAU GES MICHAEL) 3 February * page 3, line 22 -	2005 (2005-02-03)	1-9	C10L C10M C11D C23G
	The present search report has	•		
	Place of search	Date of completion of the search		Examiner
	Munich	10 March 2009	Pöl	lmann, Klaus
X : parti Y : parti docu A : tech	ATEGORY OF CITED DOCUMENTS cularly relevant if taken alone cularly relevant if combined with anotiment of the same category nological background written disclosure	L : document cited fo	ument, but publice the application rother reasons	shed on, or

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

EP 08 01 7792

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.

10-03-2009

	Patent document ed in search report		Publication date		Patent family member(s)		Publication date
US	6544349	B1	08-04-2003	NONE	Ε		1
WO	2007087003	Α	02-08-2007	US	2007010414	A1	11-01-200
US	4920691	Α	01-05-1990	NONE	E		
EP	0635558	A	25-01-1995	AT AU CA DE DE DK ES FI IT JP NO SG	69414770 635558	B2 A A1 D1 T2 T3 T3 A A1 A	15-12-199 14-11-199 02-02-199 22-01-199 20-05-199 09-08-199 16-01-199 22-01-199 23-01-199 23-01-199 21-12-199
WO	2005010130	A	03-02-2005	AT AU CA CN EP US	504745 2004259773 2533657 1860209 1648984 2006213118	A1 A1 A A1	15-07-200 03-02-200 03-02-200 08-11-200 26-04-200 28-09-200