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(71) Applicant: **Tecnored Desenvolvimento Tecnologico S.A.**
12422-281, Pindamonhangaba, SP (BR)

(72) Inventors:
- **DE OLIVEIRA, Ronald, Lopes**
  12405-278 Pindamonhangaba, SP (BR)
- **GONÇALVES, Guilherme Francisco**
  12412-520 Pindamonhangaba, SP (BR)
- **POTTER, Stephen Michael**
  22250-145 Rio de Janeiro, RJ (BR)
- **SOARES, Álvaro, Guedes**
  13800-384 Mogi Mirim, SP (BR)
- **DE ALMEIDA, Ewerton, Giovani**
  12604-120 Lorena, SP (BR)
- **DE MOURA, Leonardo, Caputo**
  22250-080 Rio de Janeiro, RJ (BR)
- **RIBEIRO, Rilei, Vilaça**
  30840-500 Belo Horizonte, MG (BR)

(74) Representative: **Zacco Denmark A/S**
Arne Jacobsens Allé 15
2300 Copenhagen S (DK)

(54) OILY BIOFUEL SUSPENSION AND METHOD FOR MANUFACTURING SAME

(57) The present invention is related to biofuel oily suspensions that use biocarbon in their composition. In this scenario, the present invention provides a biofuel oily suspension, comprising 5 to 50% by weight of micronized biocarbon and 50 to 95% by weight of oil. The biofuel oily suspension of the present invention is better adapted to compression internal combustion engines (diesel type) currently on the market, dispensing with major adaptations to them. Furthermore, the biofuel oily suspension of the present invention is highly sustainable and has an energy volumetric density and viscosity compared to liquid fossil fuels currently on the market.

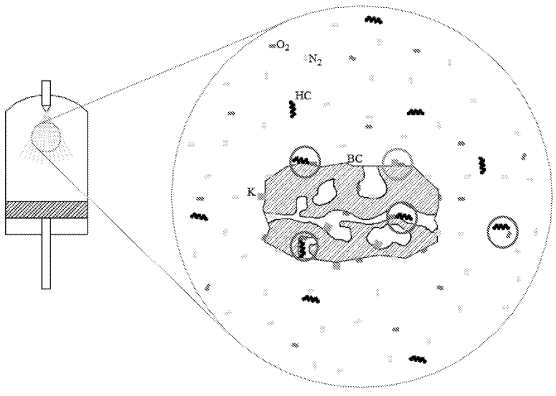

FIG. 1

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Description

FIELD OF INVENTION

[0001] The present invention relates to fuels. More specifically, the present invention is related to biofuel oily suspensions that employ solid biocarbon in their composition.

BACKGROUND OF THE INVENTION

[0002] Internal combustion engines are widely used in industries covering segments such as machine movement, cogeneration, and transport, covering a wide range of capacities. They are applied in different modes of transport, in large, medium, and small machines, and in the naval, railway, and road sectors. Compression-burning internal combustion engines, commonly called diesel engines in honor of their inventor, Rudolph Diesel, are of great relevance.

[0003] Liquid fossil fuels from petroleum distillation are usually used in compression internal combustion engines. In general, for large engines, higher viscosity fuels called heavy fuel oil (HFO - Heavy Fuel Oil or HFOLS - Heavy Fuel Oil Low Sulphur), normally called bunker oil, are used, and for medium and small engines they are used lower viscosity fuels were used, called diesel oil and gas oil.

[0004] Although the fossil fuels mentioned above are currently in widespread use, the world is rapidly moving towards changing the energy matrix, which will imply an agenda of bold commitments towards an economy with zero carbon emissions. To achieve this goal of reducing Greenhouse Gases - GHGs in the transport sector, countries will have to adopt a set of measures simultaneously. Biofuels are among the main protagonists in reducing carbon emissions in the transport sector in several countries.

[0005] As an example, the European Union (EU) recently launched a bold plan to reduce GGE emissions by at least 55% by 2030, known as the "Fit for 55" Package, which will contribute so that member countries can meet the objective of a carbon neutral EU by 2050, under of the Paris Agreement. The plan includes the transport sectors, including aviation and maritime - currently responsible for almost 40% of all emissions. The commitment of these modes to the goals assumed will be fundamental for the European continent to achieve a rapid reduction in CO_2 emissions.

[0006] Additionally, it is proposed to ban the use of conventional diesel, gasoline, gas, or even hybrid technology, in new vehicles by 2035, creating a space for electric or biodiesel-powered vehicles.

[0007] In this scenario, which is gradually spreading throughout the world, biodiesel plays a very important role in providing an energy alternative to entirely fossil fuel, as it generally contains raw materials of vegetable origin in its composition, such as soybean oils, cotton, castor beans, sunflower, babassu, peanuts, palm oil, etc.

[0008] In addition to the conventional biodiesel composition previously described, recent studies show the possibility of using coal, especially of mineral origin, in micronized form (particle size less than 50 μm) mixed with a liquid, such as water, forming an aqueous suspension.

[0009] However, the use of micronized mineral coal for the manufacture of aqueous suspensions still faces several technical barriers for its practical application, as its physical-chemical properties (calorific power, viscosity, and inorganic content) differ from the fuels used today, which requires adaptations to the engines currently on the market.

[0010] Furthermore, solid coal has a hydrophobic chemical nature, which makes its stability difficult when mixed with water. Another relevant point is that experimental results show that the calorific value of the aqueous coal suspension, and therefore, the energy density, is considerably lower than that of fuels currently on the market.

[0011] Finally, the presence of inorganics in the composition of micronized carbons used in state-of-the-art biofuels commonly generate problems of scale and wear due to abrasion of internal engine components.

[0012] In the context of seeking sustainability in production processes, biomass pyrolysis technology has been recognized by the technical and scientific community as a powerful tool for transforming biomass into new products such as charcoal, synthesis gas (*syngas*), and liquids such as tar and pyroligneous extract. Precisely to characterize the biomass pyrolysis process carried out rigorously under aspects of operational safety and respect for the environment, charcoal began to receive other names in the literature such as *biochar* or biocarbon. This last term is what will be adopted in this invention to designate the solid product obtained from biomass pyrolysis.

[0013] The proposed invention solves the prior art problems described above simply and efficiently.

SUMMARY OF THE INVENTION

[0014] The present invention's first objective is to provide a biocarbon-based biofuel oily suspension better adapted to compression internal combustion engines currently on the market, dispensing with major adaptations to them.

[0015] The present invention has as a second objective to provide an oily biofuel suspension based on highly sustainable biocarbon with calorific value, energy density, and viscosity compared to fuels currently present on the market.

[0016] To achieve the objectives described above, the present invention provides a biofuel oily suspension, comprising 5 to 50% by mass of micronized biocarbon and 50 to 95% by mass of suspension base liquid.

[0017] The invention also provides a process for man-

ufacturing the aforementioned biofuel oily suspension comprising the steps of (i) micronizing biocarbon to a maximum diameter of 50 μm and (ii) mixing 5 to 50% by mass of micronized biocarbon to 50 to 95% in mass of suspension base liquid.

BRIEF DESCRIPTION OF THE FIGURES

[0018] The detailed description presented below makes reference to the attached figure and their respective reference numbers.

Figure 1 illustrates a schematic diagram of the interaction between the various molecules around a biocarbon particle in the biofuel oily suspension of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0019] Preliminarily, it should be noted that the following description will start from preferred embodiments of the invention. As will be evident to anyone skilled in the art, however, the invention is not limited to these particular embodiments.

[0020] The present invention therefore provides an oily biofuel suspension, comprising 5 to 50% by mass of micronized biocarbon and 50 to 95% by mass of the liquid base of the suspension. For the purposes of this description, micronized biocarbon is any charcoal of vegetable origin, produced according to sustainable standards, with a maximum diameter of 50 μm. Preferably, this biocarbon has a low inorganic content (less than 1%).

[0021] Preferably, the liquid base of the aforementioned suspension is at least one of (i) bunker oil (also known as HFO - *Heavy Fuel Oil*), (ii) marine diesel oil (MDO - *Marine Diesel Oil* or MGO - *Marine Gasoil*), (iii) hydrotreated vegetable oil (HVO - *Hydrotreated Vegetable Oil*), (iv) hydrotreated pyrolysis oil (HPO - *Hydrotreated Pyrolysis Oil*), and (v) vegetable tar (also called PO - Oil of Pyrolysis or *Pyrolysis Oil*).

[0022] More preferably, the liquid base of the suspension used in the present invention may be a mixture of at least two of the above-mentioned oils in suitable proportions to generate a biofuel with viscosity and energy density equivalent to fuel oils found on the market.

[0023] In a first embodiment of the present invention, the following composition is used:

5 to 50% by mass of micronized biocarbon;
50 to 95% by mass of bunker oil; and
0 to 30% marine diesel oil or gas oil.

[0024] In this first embodiment, biocarbon is mixed with bunker oil. The engineering of large combustion engines is already prepared to operate with a viscosity typical of bunker oil. Naturally, as solid biocarbon particles are introduced into the suspension, its viscosity tends to increase. Another oily base, diesel oil or gas oil, is then introduced to adjust the viscosity of the suspension and return it to values close to the original viscosity of the bunker. This is a suspension characterized by the partial replacement of fossil fuel (bunker) with green fuel (biocarbon). It is a highly optimized suspension in terms of technical (burning) and logistical aspects since the introduction of biocarbon can be carried out in different proportions and implemented gradually.

[0025] In a second embodiment of the present invention, 100% sustainable, the following composition is used:

5 to 50% by mass of micronized biocarbon;
50 to 95% by mass of hydrotreated vegetable oil; and
0 to 50% vegetable tar.

[0026] In this second embodiment, the biocarbon is mixed with a completely green oily base, which may be HVO (Hydrotreated Vegetable Oil) or vegetable tar (PO Pyrolysis Oil) or a mixture of these components. This suspension is characterized by lower viscosity compared to the bunker and, in this case, there is a suspension composed only of sustainable products, that is, of renewable origin.

[0027] In a third embodiment of the present invention, also 100% sustainable, the following composition is used:

5 to 50% by mass of micronized biocarbon; and
50 to 95% by mass of hydrotreated pyrolysis oil.

[0028] In this third embodiment, the suspension is composed of biocarbon and the oily base HPO (Hydrotreated Pyrolysis Oil) and, like the second embodiment, is completely sustainable.

[0029] The three aforementioned embodiments have one characteristic in common: the use of micronized biocarbon in the composition. Aiming for suspensions that result in the lowest level of wear due to abrasion in diesel engines, it is preferable to produce biocarbon from biomass with low ash content, such as eucalyptus, preferably without the bark, which has a higher inorganic content compared to the wood core itself.

[0030] The present invention also provides a process for manufacturing the biofuel oily suspension described above, comprising the steps of (i) micronizing biocarbon to a maximum diameter of 50 μm and (ii) mixing 5 to 50% by mass of micronized biocarbon at 50 to 95 % by mass of liquid base of the suspension.

[0031] The present invention refers to an oily biofuel suspension whose composition contains a portion of biocarbon from the carbonization of biomass in micronized form (particles smaller than 50 μm). The presence of biocarbon provides advantages in the ecological aspect, such as a reduction in greenhouse gas and SO_x emissions, in marketing aspects, by bringing cost reduction through the use of cheaper fuel raw materials and in technical aspects.

[0032] The main technical advantages arise from the catalytic effects due to the presence of solid biocarbon particles in the reacting atmosphere, inside the engine's combustion chamber. **Figure 1** presents an illustration of these catalytic phenomena, bringing an allusion to the molecular interactions that occur in this reactant medium.

[0033] Firstly, the internal surface area associated with porosity, as well as the external surface area of biocarbon particles, favors the process of physical adsorption of oxygen molecules and other liquid fuels, promoting chemical interaction between them, which characterizes a catalytic effect in the process of combustion. More specifically, biocarbon is a product with a high concentration of carbon, typically greater than 80%, depending on the raw material and operational conditions in which it is produced. It is, therefore, a friable and porous product, and these pores can be closed or open. Associated with the degree of micronization, the external specific surface area of the particles is generated and associated with porosity, the internal specific surface area of the particles is generated. Both the external and internal specific surface area contribute to the phenomenon of heterogeneous catalysis during the combustion process. This effect is illustrated in **Figure 1,** where the **HC** liquid fuel molecules interact more significantly and more frequently with the $\mathbf{O_2}$ oxygen molecules precisely on the internal and external surfaces of the **BC** biocarbon particles. Such interactions are highlighted in **figure 1** with a blue circle.

[0034] Additionally, the catalytic effect of the injection of potassium salts in the burning of solid, liquid and gaseous fuels is known. It is also known from the relevant literature that, during the biomass carbonization process, the migration of inorganic elements present in the precursor biomass occurs, forming pockets of SiO_2 and KCl crystals on the surface of the biocarbon particle. Biomass and its respective biocarbon contain micronutrients in their composition, including potassium salts. In this way, the heterogeneous suspension containing biocarbon is an intrinsic way of seeking this catalytic action of potassium in the combustion process. This effect, where potassium reduces the activation energy and catalyzes the reaction of oxygen with the carbon surface of the biocarbon itself, is illustrated in **figure 1** and is highlighted with an orange circle.

[0035] Optionally, the present invention also provides for the introduction of additives into the biocarbon-based biofuel oily suspension, such as surfactant agents, to improve the stabilization of the solution and its handling, transport and storage properties. Additives can be used in small proportions, typically less than 5%.

[0036] In addition to the innovative effects listed above, the following advantages are observed in the biofuel of the present invention:

1) The friability of biocarbon allows grinding to obtain particles with typical dimensions of less than 50 μm at relatively competitive operating costs;

2) Preferably, the biocarbon is micronized to achieve a bimodal particle size distribution, which favors the preparation of the oily suspension of this invention;

3) Biocarbon has a low ash and sulfur content when compared to other carbonaceous materials, such as mineral coal;

4) The catalytic processes associated with biocarbon improve the burning properties of the suspension and, in this way, increase the performance of the diesel engine;

5) The burning times of porous biocarbon microparticles are low, typically the stroke times of many diesel cycle engines of interest in terms of industrial application of the present invention, such as, for example, low-speed engines used in maritime transport. This provides complete solid fuel burning efficiency and low level of particulate emissions;

6) The catalytic optimization of the combustion processes of the oily phase of the suspension and the biocarbon particle itself allows the engine to operate at lower compression levels and, in this way, leads to greater thermal efficiency of the engine;

7) Better performance concerning atmospheric emissions of contaminants such as particulates and NO_x due to the catalytic combustion process associated with biocarbon particles;

8) As it is renewable, partially or completely, the biofuel oily suspension of the present invention promotes a reduction in greenhouse gas emissions in the form of CO_2 into the atmosphere.

[0037] The biofuel of the present invention has its viscosity, calorific value, and energy density adjustable to its applications. This way, it can be adjusted to replace any types of diesel oils currently on the market. By way of example, the present invention can be used very efficiently to replace bunker oil for applications in low-speed engines, such as marine engines. However, its application is not limited to this specific application, and can also be used in engines used in rail, road, air transport, machine movement, and cogeneration.

[0038] Thus, as explained above, the present invention provides a biofuel oily suspension better adapted to diesel engines currently on the market, dispensing with major adaptations to them. Furthermore, the biofuel oily suspension of the present invention is highly sustainable and has a calorific value, energy density and viscosity compared to fuels currently on the market.

[0039] Numerous variations affecting the scope of protection of this order are permitted. In this way, the fact is reinforced that the present invention is not limited to the particular configurations/embodiments described above.

Claims

1. Biofuel oily suspension, **characterized by** comprising:

5 to 50% by mass of micronized biocarbon; and
50 to 95% by mass of liquid suspension base.

2. Biofuel oily suspension according to claim 1, **characterized in that** the liquid base of the suspension is at least one of:

bunker oil;
marine diesel oil or gas oil;
hydrotreated vegetable oil;
hydrotreated pyrolysis oil; and
vegetable tar.

3. Biofuel oily suspension according to claim 2, **characterized in that** the liquid base of the suspension is a suspension of at least two of:

bunker oil;
marine diesel oil;
hydrotreated vegetable oil;
hydrotreated pyrolysis oil; and
vegetable tar.

4. Biofuel oily suspension according to claim 2 or 3, **characterized by** comprising:

5 to 50% by mass of micronized biocarbon;
50 to 95% by mass of bunker oil; and
0 to 30% marine diesel oil.

5. Biofuel oily suspension according to claim 2 or 3, **characterized by** comprising:

5 to 50% by mass of micronized biocarbon;
50 to 95% by mass of hydrotreated vegetable oil; and
0 to 50% vegetable tar.

6. Biofuel oily suspension according to claim 2 or 3, **characterized by** comprising:

5 to 50% by mass of micronized charcoal; and
50 to 95% by mass of hydrotreated pyrolysis oil;

7. Process of manufacturing of a biofuel oily suspension, **characterized by** comprising the steps of:

micronize biocarbon to a maximum diameter of 50 μm;
mix 5 to 50% by mass of micronized biocarbon to 50 to 95% by mass of liquid suspension base.

8. Process according to claim 7, **characterized in that** the biocarbon has a bimodal particle size distribution.

9. Process according to claim 7 or 8, **characterized in that** the liquid base of the suspension is at least one of:

bunker oil;
marine diesel oil;
hydrotreated vegetable oil;
hydrotreated pyrolysis oil; and
vegetable tar.

10. Process according to claim 9, **characterized in that** the liquid base of the suspension is at least two of:

bunker oil;
marine diesel oil;
hydrotreated vegetable oil;
hydrotreated pyrolysis oil; and
vegetable tar.

11. Process according to any one of claims 7 to 10, **characterized in that** it additionally comprises a step of adding at least one surface-active additive to the biofuel oily suspension.

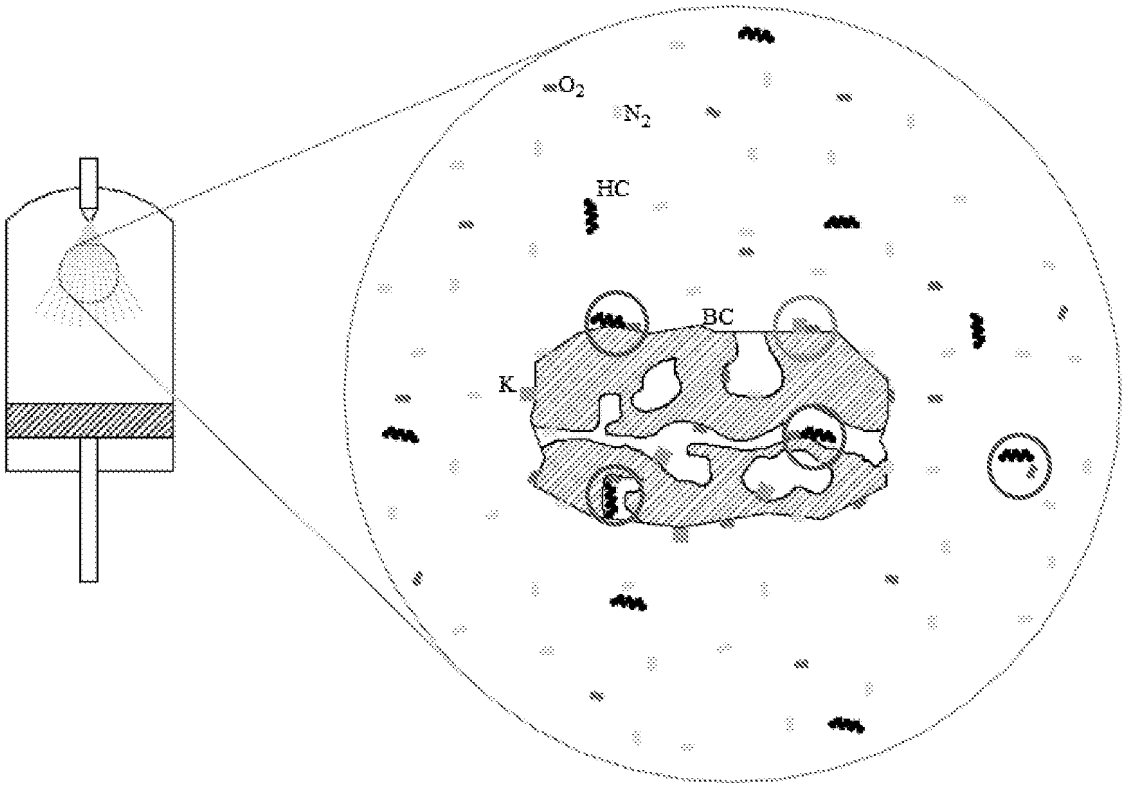

FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/BR2023/050054

A. CLASSIFICATION OF SUBJECT MATTER
IPC: C10L 08/00 (2006.01)
CPC: C10L 08/00 (2006.01)
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10L 08/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

BASE DE DADOS DO INPI, PORTAL CAPES, LATTES

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAPLUS, COMPENDEX, INSPEC, EPODOC, DERWENT INNOVATION

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US2016137939 Al (SEIDNER MARC [US]; SEIDNER LEO [US]; SEIDNER HANYA [US]) 19 May 2016 (2016-05-19) The whole document	1-7, 9-10 8, 11
X Y	HAMMERTON, J. M.; LI, H.; ROSS, A. B.: "Char-Diesel Slurry Fuels for Microgeneration: Emission Characteristics and Engine performance". University of Leeds https://eprints.whiterose.ac.Uk/l 63870/3/Char%20slurry%20accepted%20version.pdf 30 June 2020 (2020-06-30) The whole document	1-3, 5-7, 9-11 4, 8

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19/03/2023	**29/03/2023**
Name and mailing address of the ISA/ BR Facsimile No.	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/BR2023/050054

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	LONG, J. M.; BOYETTE, M. D.: "Analysis of Micronized Charcoal for Use in a Liquid Fuel Slurry". Energies, 10, 25 https://www.researchgate.net/publication/311957544_Analysis_of_Micronized_Charcoal_for_Use_in_a_Liquid_Fuel_Slurry 27 December 2016 (2016-12-27) The whole document	1, 7 2-6, 8-11
X Y	SOLOIU, V. et al.: "Combustion Characteristics of a Charcoal Slurry in a Direct Injection Diesel Engine and the Impact on the Injection System Performance". Energy, 36, 7, 4353-4371 https://doi.org/! 0.1016/j.energy.2011.04.006 14 May 2011 (2011-05-14) The whole document	1, 7 2-6, 8-11
X Y	LONG, J. M.; BOYETTE, M. D.: "Development of a Charcoal Slurry for Compression Ignition Internal Combustion Engines". American Society of Agricultural and Biological Engineers Annual International Meeting 29 July 2015 (2015-07-29) The whole document	1 2-11
Y	RYAN, T. W.; DODGE, L. G.: "Diesel Engine Injection and Combustion of Slurries of Coal Charcoal, and Coke in Diesel Fuel". SAE Transactions, 93, 1, 703-719 https://www.jstor.org/stable/44468054 01 January 1984 (1984-01-01) The whole document	1-11
Y	LONG, J. M.: "Development of a Charcoal Slurry for Compression Ignition Internal Combustion Engines". https://repository.lib.ncsu.edu/bitstream/handle/! 840.16/9655/etd.pdf?sequence=2&isAllowed=y 01 January 2014 (2014-01-01) The whole document	1-11
Y	MARSHALL, H. P.; WALTERS, D. C.: "An Experimental Investigation of a Coal-Slurry Fueled Diesel Engine". SAE Mobilus (preview) https://saemobilus.sae.org/content/770795/ 01 February 1977 (1977-02-01) The whole document	1-11

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/BR2023/050054

US2016137939 A1	2016-05-19	US9758738 B2	2017-09-12
		US2017369806 A1	2017-12-28
		WO2016077631 A1	2016-05-19

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