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### (54) COMPOSITION

ZUSAMMENSETZUNG

COMPOSITION

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**Description**

**[0001]** The present invention relates to a composition. In particular the present invention relates to fuel compositions having reduced nitrogen oxide emissions when combusted.

**[0002]** As discussed in US 7,491,247 environmental considerations and government regulations have increased the need to reduce nitrogen oxide (NOx) production. Nitrogen oxides comprise a major irritant in smog and are believed to contribute to tropospheric ozone which is a known threat to health. Relatively high flame temperatures reached in internal combustion engines, for example diesel-fuelled engines, increase the tendency for the production of nitrogen oxides (NOx). These are formed from both the combination of nitrogen and oxygen in the combustion chamber and from the oxidation of organic nitrogen species in the fuel.

**[0003]** Various methods for reducing NOx production include the use of catalytic converters, engine timing changes, exhaust recirculation, and the burning of "clean" fuels. These methods are generally too expensive and/or too complicated to be placed in widespread use. The rates at which NOx are formed is related to the flame temperature; a small reduction in flame temperature can result in a large reduction in the production of nitrogen oxides.

**[0004]** It has been shown that introducing water into the combustion zone can lower the flame temperature and thus lower NOx production, however; the direct injection of water requires costly and complicated changes in engine design. Further attempts to use water to reduce flame temperature include the use of aqueous fuels, i.e., incorporating both water and fuel into an emulsion. Problems that may occur from long-term use of aqueous fuels include precipitate depositions include coalescing ionic species resulting in filter plugging and inorganic post combustion deposits resulting in turbo fouling. Another problem related to aqueous fuel compositions is that they often require substantial engine modifications, such as the addition of in-line homogenizers, thereby limiting their commercial utility.

**[0005]** Another method for introducing water into the combustion area is to use fuel emulsions in which water is emulsified into a fuel continuous phase, i.e., invert fuel emulsions. A problem with these invert fuel emulsions is obtaining and maintaining the stability of the emulsion under conventional use conditions. Gravitational phase separation (during storage) and high temperature high pressure/shear flow rate phase separation (in a working engine) of these emulsions present the major hurdle preventing their commercial use.

**[0006]** DE-A-3229918 teaches the preparation of emulsions of 25 wt. of water in diesel oil using emulsifier which are polyesters of saturated or unsaturated fatty acids having 8-22 carbon atoms. The emulsifiers include polyglycerol esters, sorbitan esters or diacetyltartaric acid esters of glycerol esters of the fatty acids. The emulsifiers are dosed in the fuel compositions in amounts of 0.65 to 1.6 wt.%. The diesel emulsions are taught to be stable for at least 6 months and, as compared with pure diesel oil used in engines, give a better fuel economy, less coke deposition and a lower content of CO and hydrocarbons in the exhaust gas. In such a system, the emulsifier is potentially the most expensive component and dosage at the high levels of this document, such as at 1.6 wt.% would be expensive in use and potentially not commercially viable.

**[0007]** JP-A-2003 201485 discloses a fuel composition containing a burning temperature lowering agent, such as water, and one or more polyhydric-alcohol hydroxy-fatty acid ester, for reducing NOx emissions.

**[0008]** The present invention addresses the problems associated with the use of fuel emulsion compositions by providing a stable fuel emulsion composition with the beneficial reduction in NOx emissions using commercially viable amounts of emulsifier.

**[0009]** The present invention alleviates the problems of the prior art.

**[0010]** The invention is disclosed in and by the appended claims.

**[0011]** In one aspect a fuel composition is provided comprising:

(a) a fuel; and

(b) a polyglycerol ester of a fatty acid;

wherein the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises a mixture of diglycerol in an amount of 11.0 to 34.0 weight% based on the combined weight of the polyglycerols; triglycerol in an amount of 9.5 to 24.5 weight% based on the combined weight of the polyglycerols; tetraglycerol in an amount of 6.0 to 21.0 weight% based on the combined weight of the polyglycerols; pentaglycerol in an amount of 3.5 to 19.0 weight% based on the combined weight of the polyglycerols; hexaglycerol in an amount of 6.0 to 13.5 weight% based on the combined weight of the polyglycerols; heptaglycerol in an amount of 5.0 to 13.0 weight% based on the combined weight of the polyglycerols; octaglycerol in an amount of 3.0 to 12.0 weight% based on the combined weight of the polyglycerols; nonaglycerol in an amount of 1.5 to 10.0 weight% based on the combined weight of the polyglycerols; decaglycerol in an amount of 0.0 to 8.0 weight% based on the combined weight of the polyglycerols; and unadecaglycerol in an amount of 0.0 to 7.0 weight% based on the combined weight of the polyglycerols.

**[0012]** In one aspect is provided a method for improving the stability of a fuel composition containing (a) fuel and (c) water, the method comprising mixing with the fuel and water, (b) a polyglycerol ester of a fatty acid;

wherein the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises a mixture of diglycerol in an amount of 11.0 to 34.0 weight% based on the combined weight of the polyglycerols; triglycerol in an amount of 9.5 to 24.5 weight% based on the combined weight of the polyglycerols; tetraglycerol in an amount of 6.0 to 21.0 weight% based on the combined weight of the polyglycerols; pentaglycerol in an amount of 3.5 to 19.0 weight% based on the combined weight of the polyglycerols; hexaglycerol in an amount of 6.0 to 13.5 weight% based on the combined weight of the polyglycerols; heptaglycerol in an amount of 5.0 to 13.0 weight% based on the combined weight of the polyglycerols; octaglycerol in an amount of 3.0 to 12.0 weight% based on the combined weight of the polyglycerols; nonaglycerol in an amount of 1.5 to 10.0 weight% based on the combined weight of the polyglycerols; decaglycerol in an amount of 0.0 to 8.0 weight% based on the combined weight of the polyglycerols; and unadecaglycerol in an amount of 0.0 to 7.0 weight% based on the combined weight of the polyglycerols.

**[0013]** In one aspect is provided a kit for preparing a fuel composition as defined herein, the kit comprising a polyglycerol ester of a fatty acid as described herein; together with instructions for use to prepare a fuel composition containing fuel and water.

**[0014]** In one aspect is provided the use of a polyglycerol ester of a fatty acid for improving the stability of a fuel composition containing fuel and water;

wherein the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises a mixture of diglycerol in an amount of 11.0 to 34.0 weight% based on the combined weight of the polyglycerols; triglycerol in an amount of 9.5 to 24.5 weight% based on the combined weight of the polyglycerols; tetraglycerol in an amount of 6.0 to 21.0 weight% based on the combined weight of the polyglycerols; pentaglycerol in an amount of 3.5 to 19.0 weight% based on the combined weight of the polyglycerols; hexaglycerol in an amount of 6.0 to 13.5 weight% based on the combined weight of the polyglycerols; heptaglycerol in an amount of 5.0 to 13.0 weight% based on the combined weight of the polyglycerols; octaglycerol in an amount of 3.0 to 12.0 weight% based on the combined weight of the polyglycerols; nonaglycerol in an amount of 1.5 to 10.0 weight% based on the combined weight of the polyglycerols; decaglycerol in an amount of 0.0 to 8.0 weight% based on the combined weight of the polyglycerols; and unadecaglycerol in an amount of 0.0 to 7.0 weight% based on the combined weight of the polyglycerols.

**[0015]** We have shown that when a polyglycerol composition is used which has predominantly one polyglycerol present, such as diglycerol or triglycerol, then the polyglycerol composition must be present in a significantly higher amount to provide a fuel/water emulsion which is stable during storage. In contrast we have surprisingly found that having a broad range of polyglycerols present in a polyglycerol composition, and in particular the specific ranges recited herein, then a lower and therefore commercially viable amount of emulsifiers may be used while still providing a fuel and water emulsion which is stable over the period required in use, such as 3 hours. The "flat" distribution of polyglycerols allows for this enhanced effect at low dosages. By flat distribution it is meant that the polyglycerols contain a broad range of polyglycerols chain lengths and the broad range of polyglycerols are present in an amount such that only a few polyglycerol chain lengths dominate the distribution of polyglycerols. For example in a flat distribution one or two polyglycerol chain lengths do not make up 70 or 80% of the total amount of polyglycerols.

**[0016]** For ease of reference these and further aspects of the present invention are now discussed under appropriate section headings. However, the teachings under each section are not necessarily limited to each particular section.

## **Composition**

**[0017]** As previously mentioned, in one aspect is provided a fuel composition comprising:

- (a) a fuel; and
- (b) a polyglycerol ester of a fatty acid;

wherein the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises a mixture of diglycerol in an amount of 11.0 to 34.0 weight% based on the combined weight of the polyglycerols; triglycerol in an amount of 9.5 to 24.5 weight% based on the combined weight of the polyglycerols; tetraglycerol in an amount of 6.0 to 21.0 weight% based on the combined weight of the polyglycerols; pentaglycerol in an amount of 3.5 to 19.0 weight% based on the combined weight of the polyglycerols; hexaglycerol in an amount of 6.0 to 13.5 weight% based on the combined weight of the polyglycerols; heptaglycerol in an amount of 5.0 to 13.0 weight% based on the combined weight of the polyglycerols; octaglycerol in an amount of 3.0 to 12.0 weight% based on the combined weight of the polyglycerols; nonaglycerol in an amount of 1.5 to 10.0 weight% based on the combined weight of the polyglycerols; decaglycerol in an amount of 0.0 to 8.0 weight% based on the combined weight of the polyglycerols; and unadecaglycerol in an amount of 0.0 to 7.0 weight% based on the combined weight of the polyglycerols.

Polyglycerol Ester of a Fatty Acid

**[0018]** As is understood by one skilled in the art polyglycerol ester of a fatty acid is an emulsifier comprising a polyglycerol 'backbone' onto which fatty acid side chains are attached.

**[0019]** Polyglycerol esters of fatty acids are typically prepared by polymerisation of glycerol to provide one or more polyglycerols to which the fatty acids are then attached. The fatty acids are generally attached by one of two routes. A first route involves the direct attachment of the fatty acid to the polyglycerol. The second route involves inter-esterifying a polyglycerol and a triglyceride thereby transferring fatty acids from the triglyceride to the polyglycerol. The polymerisation of glycerol typically provides a mixture of polyglycerols of different degrees of polymerisation. The mixture of polyglycerols of different degrees of polymerisation is described herein as a polyglycerol composition. It will be understood by one skilled in the art that references to a polyglycerol composition having particular polyglycerol components requires only that those components be present in the amount specified. It will be appreciated by one skilled in the art that because of the nature of polymerisation of glycerol, the polyglycerol composition may contain other polyglycerols having degrees of polymerisation not recited herein. In determining the amounts of polyglycerols in the polyglycerol composition, the total amount of all polyglycerols (irrespective of degree of polymerisation) is determined to provide the total weight of the polyglycerol composition. Materials which are not a polyglycerol do not form part of the polyglycerol composition and their weight is not considered when determining the total weight of the polyglycerol composition.

**[0020]** References in the present specification to "the combined weight of the polyglycerols" encompass the total combined weight of all polyglycerols, irrespective of their chain length and irrespective of whether the polyglycerol is recited in the listing of polyglycerols.

**[0021]** As discussed here in the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises a mixture of diglycerol in an amount of 11.0 to 34.0 weight% based on the combined weight of the polyglycerols; triglycerol in an amount of 9.5 to 24.5 weight% based on the combined weight of the polyglycerols; tetraglycerol in an amount of 6.0 to 21.0 weight% based on the combined weight of the polyglycerols; pentaglycerol in an amount of 3.5 to 19.0 weight% based on the combined weight of the polyglycerols; hexaglycerol in an amount of 6.0 to 13.5 weight% based on the combined weight of the polyglycerols; heptaglycerol in an amount of 5.0 to 13.0 weight% based on the combined weight of the polyglycerols; octaglycerol in an amount of 3.0 to 12.0 weight% based on the combined weight of the polyglycerols; nonaglycerol in an amount of 1.5 to 10.0 weight% based on the combined weight of the polyglycerols; decaglycerol in an amount of 0.0 to 8.0 weight% based on the combined weight of the polyglycerols; and undecaglycerol in an amount of 0.0 to 7.0 weight% based on the combined weight of the polyglycerols.

**[0022]** It will be appreciated by one skilled in the art that polyglycerols may be either in the form of a cyclic polyglycerol or an acyclic polyglycerol. Acyclic polyglycerols are straight chain and branched chain polyglycerols, that is acyclic polyglycerols are formed entirely from glycerol groups linked such that no rings are formed. Cyclic polyglycerols contain a ring structure. References in the present specification to a polyglycerol of a particular degree of polymerisation, for example triglycerol referring to a polyglycerol having a degree of polymerisation of 3, include both the polyglycerol in cyclic form and in acyclic form. We have further determined the preferred amounts of cyclic and acyclic polyglycerols for each of diglycerol, triglycerol, tetraglycerol and pentaglycerol. In one preferred aspect the diglycerol comprises acyclic diglycerol in an amount of 6.0 to 25.0 weight% based on the combined weight of the polyglycerols, and cyclic diglycerol in an amount of 5.0 to 13.0 weight% based on the combined weight of the polyglycerols. In one preferred aspect the triglycerol comprises acyclic triglycerol in an amount of 7.0 to 21.0 weight% based on the combined weight of the polyglycerols, and cyclic triglycerol in an amount of 2.5 to 9.5 weight% based on the combined weight of the polyglycerols. In one preferred aspect the tetraglycerol comprises acyclic tetraglycerol in an amount of 5.5 to 15.0 weight% based on the combined weight of the polyglycerols, and cyclic tetraglycerol in an amount of 0.5 to 8.0 weight% based on the combined weight of the polyglycerols. In one preferred aspect the pentaglycerol comprises acyclic pentaglycerol in an amount of 3.0 to 11.0 weight% based on the combined weight of the polyglycerols, and cyclic pentaglycerol in an amount of 0.5 to 8.0 weight% based on the combined weight of the polyglycerols.

**[0023]** In one preferred aspect

the diglycerol comprises acyclic diglycerol in an amount of 6.0 to 25.0 weight% based on the combined weight of the polyglycerols, and cyclic diglycerol in an amount of 5.0 to 13.0 weight% based on the combined weight of the polyglycerols;

the triglycerol comprises acyclic triglycerol in an amount of 7.0 to 21.0 weight% based on the combined weight of the polyglycerols, and cyclic triglycerol in an amount of 2.5 to 9.5 weight% based on the combined weight of the polyglycerols;

the tetraglycerol comprises acyclic tetraglycerol in an amount of 5.5 to 15.0 weight% based on the combined weight of the polyglycerols, and cyclic tetraglycerol in an amount of 0.5 to 8.0 weight% based on the combined weight of the polyglycerols; and

the pentaglycerol comprises acyclic pentaglycerol in an amount of 3.0 to 11.0 weight% based on the combined











weight of the polyglycerols, and cyclic pentaglycerol in an amount of 3.8 to 4.6 weight% based on the combined weight of the polyglycerols.

**[0038]** In one preferred aspect

the diglycerol comprises acyclic diglycerol in an amount of 9.1 to 11.4 weight% based on the combined weight of the polyglycerols, and cyclic diglycerol in an amount of 8.5 to 9.5 weight% based on the combined weight of the polyglycerols;  
the triglycerol comprises acyclic triglycerol in an amount of 10.0 to 11.8 weight% based on the combined weight of the polyglycerols, and cyclic triglycerol in an amount of 5.9 to 6.3 weight% based on the combined weight of the polyglycerols;  
the tetraglycerol comprises acyclic tetraglycerol in an amount of 8.4 to 9.5 weight% based on the combined weight of the polyglycerols, and cyclic tetraglycerol in an amount of 4.1 to 4.4 weight% based on the combined weight of the polyglycerols; and  
the pentaglycerol comprises acyclic pentaglycerol in an amount of 6.7 to 7.6 weight% based on the combined weight of the polyglycerols, and cyclic pentaglycerol in an amount of 3.8 to 4.6 weight% based on the combined weight of the polyglycerols.

**[0039]** In one preferred aspect the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises a mixture of

acyclic diglycerol in an amount of 9.1 to 11.4 weight% based on the combined weight of the polyglycerols, and cyclic diglycerol in an amount of 8.5 to 9.5 weight% based on the combined weight of the polyglycerols;  
acyclic triglycerol in an amount of 10.0 to 11.8 weight% based on the combined weight of the polyglycerols, and cyclic triglycerol in an amount of 5.9 to 6.3 weight% based on the combined weight of the polyglycerols;  
acyclic tetraglycerol in an amount of 8.4 to 9.5 weight% based on the combined weight of the polyglycerols, and cyclic tetraglycerol in an amount of 4.1 to 4.4 weight% based on the combined weight of the polyglycerols; and  
acyclic pentaglycerol in an amount of 6.7 to 7.6 weight% based on the combined weight of the polyglycerols, and cyclic pentaglycerol in an amount of 3.8 to 4.6 weight% based on the combined weight of the polyglycerols.  
the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises hexaglycerol in an amount of 9.3 to 10.1 weight% based on the combined weight of the polyglycerols;  
the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises heptaglycerol in an amount of 8.6 to 9.9 weight% based on the combined weight of the polyglycerols;  
the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises octaglycerol in an amount of 7.3 to 8.9 weight% based on the combined weight of the polyglycerols;  
the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises nonaglycerol in an amount of 5.5 to 6.4 weight% based on the combined weight of the polyglycerols;  
the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises decaglycerol in an amount of 2.9 to 4.5 weight% based on the combined weight of the polyglycerols; and  
the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises unadecaglycerol in an amount of 1.8 to 3.7 weight% based on the combined weight of the polyglycerols.

**[0040]** In one preferred aspect the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises diglycerol in an amount of 18.0 to 32.0 weight% based on the combined weight of the polyglycerols. In one preferred aspect the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises triglycerol in an amount of 16.0 to 24.0 weight% based on the combined weight of the polyglycerols. In one preferred aspect the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises tetraglycerol in an amount of 12.0 to 16.0 weight% based on the combined weight of the polyglycerols. In one preferred aspect the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises pentaglycerol in an amount of 8.0 to 12.0 weight% based on the combined weight of the polyglycerols. In one preferred aspect the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises hexaglycerol in an amount of 7.0 to 11.0 weight% based on the combined weight of the polyglycerols. In one preferred aspect the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises heptaglycerol in an amount of 5.0 to 10.0 weight% based on the combined weight of the polyglycerols. In one preferred aspect the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises octaglycerol in an amount of 3.0 to 9.0 weight% based on the combined weight of the polyglycerols. In one preferred aspect the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises nonaglycerol in an amount of 1.5 to 7.0 weight% based on the combined weight of the polyglycerols. In one preferred aspect the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises decaglycerol in an amount of 0.0 to 4.5 weight% based on the combined weight of the polyglycerols. In one preferred aspect the polyglycerol composition used to form the polygly-





the pentaglycerol comprises acyclic pentaglycerol in an amount of 6.5 to 9.5 weight% based on the combined weight of the polyglycerols, and cyclic pentaglycerol in an amount of 1.5 to 4.0 weight% based on the combined weight of the polyglycerols.

**[0051]** In one preferred aspect the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises a mixture of

acyclic diglycerol in an amount of 20.0 to 26.0 weight% based on the combined weight of the polyglycerols, and cyclic diglycerol in an amount of 6.5 to 8.0 weight% based on the combined weight of the polyglycerols;  
acyclic triglycerol in an amount of 18.0 to 21.0 weight% based on the combined weight of the polyglycerols, and cyclic triglycerol in an amount of 2.5 to 5.0 weight% based on the combined weight of the polyglycerols;  
acyclic tetraglycerol in an amount of 11.0 to 14.5 weight% based on the combined weight of the polyglycerols, and cyclic tetraglycerol in an amount of 1.5 to 4.0 weight% based on the combined weight of the polyglycerols;  
acyclic pentaglycerol in an amount of 6.5 to 9.5 weight% based on the combined weight of the polyglycerols, and cyclic pentaglycerol in an amount of 1.5 to 4.0 weight% based on the combined weight of the polyglycerols;  
hexaglycerol in an amount of 6.0 to 10.0 weight% based on the combined weight of the polyglycerols;  
heptaglycerol in an amount of 4.5 to 7.5 weight% based on the combined weight of the polyglycerols;  
octaglycerol in an amount of 2.5 to 5.5 weight% based on the combined weight of the polyglycerols;  
nonaglycerol in an amount of 1.0 to 3.0 weight% based on the combined weight of the polyglycerols;  
decaglycerol in an amount of 0.0 to 1.0 weight% based on the combined weight of the polyglycerols; and  
unadecaglycerol in an amount of 0.0 to 0.5 weight% based on the combined weight of the polyglycerols.

**[0052]** The fatty acid side chains attached to the polyglycerol may be of any suitable length. The polyglycerol ester of a fatty acid may be a polyglycerol ester of a single fatty acid, or polyglycerol ester of a mixture of fatty acids. The fatty chain lengths of the fatty acids of the polyglycerol ester need not be of the same length. Typically the polyglycerol ester of a fatty acid is an ester of a fatty acid of a C12 to C22 fatty acid. Preferably the polyglycerol ester of a fatty acid is an ester of a C16 or C22 fatty acid. Preferably the polyglycerol ester of a fatty acid is an ester of a C16 or C18 fatty acid. Preferably the polyglycerol ester of a fatty acid is an ester of a C18 fatty acid.

**[0053]** The fatty acid of the polyglycerol ester of a fatty acid may be saturated fatty acid, unsaturated fatty acid or a mixture of saturated fatty acid and unsaturated fatty acid. In one aspect the fatty acid of the polyglycerol ester of a fatty acid is an unsaturated fatty acid. The fatty acid of the polyglycerol ester of a fatty acid may be mono- or di-unsaturated fatty acid. Preferably the fatty acid of the polyglycerol ester of a fatty acid is a mono-unsaturated fatty acid.

**[0054]** A highly preferred fatty acid of the polyglycerol ester of a fatty acid is oleic acid ((9Z)-Octadec-9-enoic acid).

**[0055]** The fatty acids attached to the polyglycerol may be provided from any suitable source. Thus in one aspect, the polyglycerol fatty acid ester is prepared from fatty acids from oils selected from rape seed oil, high oleic rape seed oil, soy oil, high oleic sunflower oil, tall oil and mixtures thereof.

**[0056]** In one preferred aspect the polyglycerol composition used to form the polyglycerol ester of a fatty acid has a hydroxyl value of from 880 to 1230 mg KOH/g. In one preferred aspect the polyglycerol composition used to form the polyglycerol ester of a fatty acid has a hydroxyl value of from 1130 to 1230 mg KOH/g. In one preferred aspect the polyglycerol composition used to form the polyglycerol ester of a fatty acid has a hydroxyl value of from 880 to 1060 mg KOH/g. In a further preferred aspect the polyglycerol composition used to form the polyglycerol ester of a fatty acid has a hydroxyl value of from 950 to 990 mg KOH/g.

**[0057]** In one preferred aspect the polyglycerol composition used to form the polyglycerol ester of a fatty acid has a refractive index at 50°C of from 1.4860 to 1.4925. In one preferred aspect the polyglycerol composition used to form the polyglycerol ester of a fatty acid has a refractive index at 50°C of from 1.4895 to 1.4925. In a further preferred aspect the polyglycerol composition used to form the polyglycerol ester of a fatty acid has a refractive index at 50°C of from 1.4900 to 1.4920. In a further preferred aspect the polyglycerol composition used to form the polyglycerol ester of a fatty acid has a refractive index at 50°C of from 1.4900 to 1.4910. In one preferred aspect the polyglycerol composition used to form the polyglycerol ester of a fatty acid has a refractive index at 25°C of from 1.4855 to 1.4935.

**[0058]** In one preferred aspect the polyglycerol ester of a fatty acid has a viscosity of less than 700 mPa s at 20°C, such as less than 600 mPa s at 20°C, such as less than 500 mPa s at 20°C, such as less than 400 mPa s at 20°C, such as less than 350 mPa s at 20°C, such as less than 300 mPa s at 20°C, such as less than 250 mPa s at 20°C, such as less than 200 mPa s at 20°C. We have found that during the preparation of a fuel emulsion in accordance with the present invention a low viscosity, such as that described above, and preferably less than 200 mPa s at 20°C, is an important factor in the preparation of an effective emulsion.

**[0059]** We have found that a means by which the viscosity the polyglycerol ester of a fatty acid may be controlled is by control of the ratio of the polyol to triglyceride source when preparing the present polyglycerol ester of a fatty acid, as well as the fatty acid profile which is described in detail herein. The effect of ratio of the polyol to triglyceride source

is shown in Figure 8. Thus in one aspect the polyglycerol ester of a fatty acid is prepared by reacting a polyglycerol and a fatty acid triglyceride in a ratio of polyglycerol to fatty acid triglyceride of from 1:1 to 1:10. Preferably the polyglycerol ester of a fatty acid is prepared by reacting a polyglycerol and a fatty acid triglyceride in a ratio of polyglycerol to fatty acid triglyceride of from 1:1 to 1:9, such as from 1:1 to 1:8, such as from 1:1 to 1:7, such as from 1:1 to 1:6, such as from 1:1 to 1:5, such as from 1:1 to 1:4, such as from 1:2 to 1:4, such as from 1:2 to 1:3, such as approximately 1:2.8, such as from 1:4 to 1:9, such as from 1:4 to 1:8, such as from 1:4 to 1:7, such as from 1:4 to 1:6, such as from 1:4 to 1:5, such as from 1:5 to 1:7, such as from 1:6 to 1:7, such as approximately 1:6.7.

#### Fuel Composition

**[0060]** When a polyglycerol ester of a fatty acid prepared from a mixture of polyglycerols as described herein is provided the polyglycerol ester may be dosed in the water and fuel composition in any suitable amount to provide an emulsion of desired stability. In one aspect the fuel composition comprises a polyglycerol ester of a fatty acid prepared from a mixture of polyglycerols as described herein in an amount of from 0.1 to 2.0 wt.% based on the total fuel composition. In a further aspect the fuel composition comprises a polyglycerol ester of a fatty acid prepared from a mixture of polyglycerols as described herein in an amount of from 0.1 to 1.0 wt.% based on the total fuel composition. In a further aspect the fuel composition comprises a polyglycerol ester of a fatty acid prepared from a mixture of polyglycerols as described herein in an amount of from 0.1 to 0.5 wt.% based on the total fuel composition. In a further aspect the fuel composition comprises a polyglycerol ester of a fatty acid prepared from a mixture of polyglycerols as described herein in an amount of less than 0.5 wt.% based on the total fuel composition. In a further aspect the fuel composition comprises a polyglycerol ester of a fatty acid prepared from a mixture of polyglycerols as described herein in an amount of less than 0.3 wt.% based on the total fuel composition.

**[0061]** According to the invention, the fuel composition comprises a polyglycerol ester of a fatty acid prepared from a mixture of polyglycerols as described herein in an amount of less than 0.25 wt.% based on the total fuel composition. In a further aspect the fuel composition comprises a polyglycerol ester of a fatty acid prepared from a mixture of polyglycerols as described herein in an amount of less than 0.2 wt.% based on the total fuel composition. In a further aspect the fuel composition comprises a polyglycerol ester of a fatty acid prepared from a mixture of polyglycerols as described herein in an amount of less than 0.15 wt.% based on the total fuel composition. In a further aspect the fuel composition comprises a polyglycerol ester of a fatty acid prepared from a mixture of polyglycerols as described herein in an amount of less than 0.1 wt.% based on the total fuel composition.

**[0062]** As discussed herein we have identified that by use of the "flat" composition of polyglycerols the emulsifier may be used in lower amounts than required in the prior art. Thus in the preferred aspect the polyglycerol ester of a fatty acid is present in an amount of less than 0.25 wt.%. The improved activity of the composition of polyglycerol esters of the present invention allows for the emulsifier to be dosed at lower amounts than had previously been required in the prior art. This is advantageous both for reasons of cost and also for storage. These materials are dosed in use and therefore must be transported by the user. Minimising the amount of material required to achieve the desired effect is important for end users. Although the present composition allows for use at lower levels than the prior art, the present composition may be dosed at any level, for example it may be dosed at a higher level in a demanding application. It is appreciated by one skilled in the art that depending on the required use and stability time desired the polyglycerol ester of a fatty acid may be dosed at any amount.

#### Fuel

**[0063]** As discussed herein, the emulsifiers described allow for the preparation of an emulsion of fuel and water. A fuel suitable for preparing into an emulsion but which has yet to be combined with water is hereby disclosed. According to the invention the fuel containing the emulsifiers is combined with water and the fuel composition comprises (c) water. It will be appreciated that in this aspect the fuel composition may be prepared by first dosing the polyglycerol ester of a fatty acid into the fuel, such as marine gasoil (MGO), after which water is dosed into the fuel/emulsifier blend.

**[0064]** The amount of water may be selected based on the requirements of the combustion system. According to the invention the fuel composition further comprises (c) water in an amount of from 10 to 70 wt.% based on the total fuel composition. Preferably the water is present in an amount of from 30 to 60 wt.% based on the total fuel composition. Preferably the water is present in an amount of from 33 to 50 wt.% based on the total fuel composition.

**[0065]** The composition according to the present invention may comprise one or more additives for example, to improve various aspects of the fuel to which the composition is typically added or to improve various aspects of the combustion system performance. Suitable additional additives include detergents, carrier oils, anti-oxidants, corrosion inhibitors, colour stabilisers, metal deactivators, cetane number improvers, other combustion improvers, antifoams, pour point depressants, cold filter plugging point depressants, wax anti-settling additives, dispersants, deodorants, dyes, smoke suppressants, lubricity agents, and other particulate filter regeneration additives.

**[0066]** The fuel may be any fuel suitable for combustion where reduction of NO<sub>x</sub> is desired. In one aspect the fuel is a fuel for spark ignition engines such as a gasoline engine. Preferably the fuel is a fuel for a high compression spontaneous ignition engine. In one aspect the fuel is selected from diesel, heavy fuel oil, marine gasoil (MGO) and kerosene. The diesel may be biodiesel, low sulphur diesel and ultra-low sulphur diesel. Preferably the fuel is marine gasoil. The marine gasoil may be any suitable marine gasoil. In one aspect it is a fuel having a (i) a density of 0.85-0.89g/cm<sup>3</sup>, a cetane Number of approximately 45; and a flash point of greater than 55°C.

**[0067]** Aspects of the invention are defined in the appended claims.

**[0068]** The present invention will now be described in further detail in the following examples in which:

Figures 1, 3a, 3b, 7 to 9 and 13 show graphs; and  
Figures 2, 3c, 4, 5, 6, 10, 11, 12 and 14 show images.

## EXAMPLES

### Example 1

**[0069]** Four polyglycerol esters were prepared and tested. Two were broad range polyglycerol (BRPG) esters in accordance with the present invention - one based on soya bean oil and one based on oleic acid. Two were triglycerol esters prepared as a comparison - one based on soya bean oil and one based on oleic acid.

#### Manufacture of polyglycerol:

Glycerol: 1250 kg  
50% NaOH in water: 9.17 kg

**[0070]** Glycerol and NaOH solution is added to the reactor. Heated to 240°C while taking care with columns and condensers not to distill off glycerol. The heating to 240°C takes about 3h. Then the pressure is lowered carefully to about 30 mbar to remove reaction water from the polymerisation of glycerol. After about 7-14 hours at 240°C samples

are withdrawn from the reactor for measurement of refractive index at 50.0°C,  $(n_D^{50.0})$ .

**[0071]** The refractive index is used to determine the termination of the reaction. The refractive index should be in the interval of 1.4900-1.4920. If the refractive index is not yet in the interval, the reaction is continued for further 1 hour and another sample is withdrawn for measurement. This continues until the refractive index is within the interval. When the polyglycerol is within the stop-interval the temperature is lowered to 120°C.

**[0072]** The glycerol and polyglycerol content of the BRPG samples was determined. The details of this analysis are given below.

Polyglycerol composition	BRPG Batch 1	BRPG Batch 2	BRPG Batch 3 (reanalysis in [ ])	BRPG Batch 4
%Glycerol	4.81	5.49	4.22 [4.24]	5.15
% CY-Diglycerol	8.68	8.42	9.14 [9.14]	8.13
% Diglycerol	10.04	10.85	8.68 [8.67]	10.58
% CY-Triglycerol	5.94	5.58	6.00 [6.02]	5.70
% Triglycerol	10.57	11.15	9.47 [9.46]	11.00
% CY-Tetraglycerol	4.20	3.90	3.93 [4.24]	4.06
% Tetraglycerol	8.76	9.12	8.00 [8.00]	9.06
% CY-Pentaglycerol	4.13	3.60	4.44 [4.38]	3.59
% Pentaglycerol	6.95	7.20	6.44 [6.53]	6.40
% Hexaglycerol	9.36	8.98	8.89 [9.22]	9.58
% Heptaglycerol	8.71	8.15	8.63 [8.96]	9.44
% Octaglycerol	7.27	7.02	8.52 [7.57]	7.02
% Nonaglycerol	5.58	5.20	6.07 [5.80]	5.36

(continued)

Polyglycerol composition	BRPG Batch 1	BRPG Batch 2	BRPG Batch 3 (reanalysis in [ J ])	BRPG Batch 4
% Decaglycerol	3.31	3.51	4.20 [4.25]	2.76
% Undecaglycerol	1.69	1.82	3.38 [3.54]	2.17
Normalised from	95.89	97.02	95.59 [95.06]	98.53

[0073] Specifications of the hydroxyl values and the refractive index for the broad range polyglycerol of the present invention and the triglycerol used for the esters below are given below:

#### Broad range polyglycerol

##### [0074]

Hydroxyl value (OHV): 950-990  
Refractive index at 50°C: 1.4900-1.4920

#### Triglycerol

##### [0075]

Hydroxyl value (OHV): 1090-1190  
Refractive index (20°C): 1.4930-1.4970

#### Manufacture of Triglycerol and Polyglycerol esters:

##### [0076]

##### Polyglycerol PGE 24401198:

Soyabean oil:	700g
Polyglycerol:	203.2g
50% NaOH in water:	3.80g

[0077] The polyglycerol was prepared in accordance with the above process.

[0078] All ingredients are charged to a 3-necked flask with mechanical stirring, condenser, temperature control, nitrogen protection is used, vacuum pump is connected to the set-up.

[0079] Temperature is raised to 90°C. Pressure is lowered to about 50 mBar when the mixture reaches 90°C. Temperature is then raised to 230°C and held at that temperature for 30 min. Cooled to about 90°C. Pressure equalised with nitrogen at 90°C. The product is clear.

[0080] Analysis: Acid value: 0.3; Saponification value: 146.2; Hydroxyl value: 219.2.

##### Polyglycerol PGE 2528/160:

Oleic acid 90%:	340g
Polyglycerol:	102g
Glycerol:	37g
50% NaOH in water:	1.75g

[0081] The polyglycerol was prepared in accordance with the above process.

[0082] All ingredients are charged to a 3-necked flask with mechanical stirring, vigreux column, condenser, temperature control, nitrogen protection is used, vacuum pump is connected to the set-up.

[0083] Temperature is raised gradually to 235°C. At 208°C reaction water is distilled off. After 80 min. the mixture is clear and the temperature is 235°C. The reaction mixture is reacted for further 1h.

The pressure is lowered gradually to 75 mBar. Then the mixture reacts for further 1h. A sample is withdrawn for acid value measurement.

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When the acid value is below 2 the product is finished and the temperature is lowered to 90°C. Pressure equalised with nitrogen. The product is clear.

**[0084]** Analysis: Acid value: 0.5; Saponification value: 145.5; Hydroxyl value: 214.9; Alcaline number: 7.4.

### ***Triglycerol PGE 2528/072 (Comparative):***

Soyabean oil:	700g
Triglycerol:	215g
50% NaOH in water:	3.80g

**[0085]** The triglycerol was obtained from Solvay.

**[0086]** All ingredients are charged to a 3-necked flask with mechanical stirring, condenser, temperature control, nitrogen protection is used, vacuum pump is connected to the set-up.

**[0087]** Pressure is lowered to about 50 mBar when the mixture reaches 90°C. Temperature is raised from room temperature to 230°C in 85 min. The reaction mixture is held at 230°C for 2.5h, then cooled to 90°C and pressure equalised with nitrogen. The product is clear.

**[0088]** Analysis: Acid value: 0.2; Saponification value: 142.6; Iodine value: 95.2; Color 5 1/4", Total: 3.0 yellow: 15 red: 1.5.

### ***Triglycerol PGE 2526/159 (Comparative):***

Oleic acid 90%:	340g
Triglycerol:	108g
Glycerol:	37g
50% NaOH in water:	1.75g

**[0089]** The triglycerol was obtained from Solvay.

**[0090]** All ingredients are charged to a 3-necked flask with mechanical stirring, vigreux column, condenser, temperature control, nitrogen protection is used, vacuum pump is connected to the set-up.

**[0091]** Temperature is raised gradually to 235°C. At 208°C reaction water is observed. After 65 min. the mixture is clear and the temperature is 235°C. The reaction mixture is reacted for further 1h. The pressure is lowered gradually to 75 mBar, then the mixture reacts for further 1h. A sample is withdrawn for acid value measurement. When the acid value is below 2 the product is finished and the temperature is lowered to 90°C. Pressure equalised with nitrogen. The product is clear.

**[0092]** Analysis: Acid value: 0.8; Saponification value: 143.6; Hydroxyl value: 262.8; Alcaline number: 4.6.

**[0093]** Four polyglycerol esters based on either soy oil or oleic acid and either triglycerol or broad range polyglycerol (BRPG) esters were tested in water-in-fuel emulsion (WIF-emulsion) with 50% water content at 55°C with focus on water droplet size distribution, stability and emulsion viscosity.

**[0094]** The results of the investigations show that BRPG esters provides smaller water droplets and reduced water droplet sedimentation during storage compared to triglycerol esters.

**[0095]** Four samples were tested with two polyol distributions (triglycerol vs. BRPG) and two fatty acid sources (soy oil vs. pure oleic acid). The main focus of the test was the effect of reduced emulsifier addition on the emulsion stability.

## **EXPERIMENTAL**

**[0096]** Four emulsifiers were tested in water-in-fuel emulsions, WIF-emulsions, with 50% water content at 55°C. The emulsifiers are listed in table 1. Dosages 0.5%, 0.25% and 0.1% based on the emulsion. The emulsions (200 g) were prepared by slowly adding the water phase to the fuel (MGO) during homogenization with Ultra Turrex at 20500 rpm for 64 s. Both the MGO and the water were heated to 55°C prior to emulsification.

**[0097]** The following analyses were carried out immediately after preparation of the emulsion:

1. Water droplet size distribution by NMR.
2. Microscopy by CLSM.
3. Emulsion stability during 3 hours storage at 55°C by imaging and image analysis.



Table 1 \* The low polyol percentage is due to the fatty acid source.

Polyglycerol Type	Material	Fatty acid composition	Polyglycerol %
BRPG	2440/198	soy oil	23.8*
BRPG	2526/160	Oleate	27.0
Triglycerol	2528/072	soy oil	23.8*
Triglycerol	2526/159	Oleate	28.6

[0098] The marine gasoil (diesel) used in the testing was Shell Thermo heating oil.

## RESULTS

[0099] The water droplet size distribution is shown in Table 2. Note the significant increase in water droplet size at low emulsifier concentration.

Table 2 Water droplet size distribution.

Emulsifier	Conc % Emulsion	Conc % Diesel	Water % Emulsion	Temp °C	D2.5 μm	D50.0 μm
2440/198 BRPG-soy	0.50	1.00	50	55	0.6	7.7
	0.25	0.50	50	55	3.3	16.6
	0.10	0.20	50	55	4.2	63.0
2526/160 BRPG - oleate	0.50	1.00	50	55	0.5	7.1
	0.25	0.50	50	55	3.7	18.6
	0.10	0.20	50	55	6.7	47.0
2528/072 Triglycerol - soy	0.50	1.00	50	55	0.4	6.6
	0.25	0.50	50	55	2.7	17.8
	0.10	0.20	50	55	2.8	87.8
2526/159 Triglycerol - oleate	0.50	1.00	50	55	0.5	7.4
	0.25	0.50	50	55	1.9	14.9
	0.10	0.20	50	55	4.5	72.7

[0100] The D50.0 values are compared in Figure 1, where the huge increase in droplet size at 0.1 % dosage level is clearly seen. The graph also shows that at very stressing conditions (0.1% emulsifier dosage) PGE based on BRPG (broad range polyglycerol) results in smaller water droplets than PGE based on triglycerol. At the same time PGE based on fatty acids from soy oil results in larger droplets than PGE based on pure oleic acid.

[0101] The droplet size distribution by CLSM is seen below with a comparison between 0.5% and 0.1% emulsifier dosage. The huge increase in droplet size at low emulsifier dosage is clearly seen on the pictures. Pictures of samples with 0.25% emulsifier addition are shown in Figure 2. Pictures of samples with 0.1%, 0.25% and 0.5% emulsifier addition are shown in Figure 6.

[0102] In Figure 3a, 3b and 3c are shown the degree of water droplet sedimentation in the emulsions during 3 hours storage at 55°C with 0.5%, 0.25% and 0.1% emulsifier addition. The degree of sedimentation is expressed as the free diesel oil on top of the samples in percentage of the total samples height. The values were generated by image analysis. The difference in the degree of sedimentation between the dosage levels is to be noted. At 0.1% dosage the sedimentation is ten-fold larger than at 0.5% dosage level.

[0103] The ester of triglycerol and soy oil performs poorly at low concentration. Hence the performance of this emulsifier is more sensitive to dosage reduction compared to the broad range polyglycerol ester emulsifiers of the present invention.

[0104] At low concentration the two emulsifiers based on BRPG of the present invention perform better than the emulsifiers based on triglycerol. This is in agreement with the difference in water droplet size illustrated in Figure 1.

[0105] Pictures of the samples are available in Figures 4 and 5.

## CONCLUSION

[0106] It is clearly documented that polyglycerol esters based on broad range polyglycerols results in smaller water

droplet and reduced water droplet sedimentation during storage as compared to polyglycerolesters based on triglycerol. This effect is seen at very low emulsifier addition (0.1%) representing stressing conditions, which most like a real life situation. Furthermore it is concluded that a fatty acids composition with high oleic acid content is superior to a composition with high linoleic acid (soy oil) based on above attributes.

## Example 2

[0107] Four further polyglycerol esters were prepared and tested. Each was a broad range polyglycerol (BRPG) esters in accordance with the present invention and each was based on rape seed oil. Two were triglycerol esters and two were hexaglycerol esters.

[0108] The esters in accordance with the present invention were compared against a comparison prepared from triglycerol and soy oil (REF PGE or REF).

## EXPERIMENTAL

### [0109]

#### PGE 2680/060 with polyol 13%:

Rapeseed oil:	920g
Broad Range Hexaglycerol (BRHG):	138g
50% NaOH in water:	1.92g

[0110] The hexaglycerol was prepared by polymerisation in the same manner as described in Example 1.

[0111] All ingredients are charged to a 3-necked flask with mechanical stirring, condenser, temperature control, nitrogen protection is used, vacuum pump is connected to the set-up.

[0112] Pressure is lowered to 50 - 100 mBar when the mixture reaches 235°C and is clear. Temperature is raised from room temperature to 235°C in 50 min. The reaction mixture is held at 235°C for 2.5h, then cooled to 100°C and pressure equalised with nitrogen. The product is clear.

[0113] Analysis: Acid value: 0.2; Saponification value: 161.8; Hydroxyl value: 125; Alkaline number: 3.9

#### PGE 2680/065 with polyol 10%:

Rapeseed oil:	960g
Broad Range Hexaglycerol (BRHG):	106.6g
50% NaOH in water:	2.4g

[0114] The hexaglycerol was prepared by polymerisation in the same manner as described in Example 1.

[0115] All ingredients are charged to a 3-necked flask with mechanical stirring, condenser, temperature control, nitrogen protection is used, vacuum pump is connected to the set-up.

[0116] Pressure is lowered to 50 - 100 mBar when the mixture reaches 235°C and is clear. Temperature is raised from room temperature to 235°C in 50 min. The reaction mixture is held at 235°C for 2.5h, then cooled to 100°C and pressure equalised with nitrogen. The product is clear.

[0117] Analysis: Acid value: 0.2; Saponification value: 168.6; Hydroxyl value: 100.2; Alkaline number: 4.1

#### PGE 2680/062 with polyol 23%:

Rapeseed oil:	450g
Broad Range Triglycerol (BRTG):	135g
50% NaOH in water:	0.82g

[0118] The triglycerol was prepared by polymerisation in the same manner as described in Example 1 except the refractive index was at 25°C was changed from 1.4855 to 1.4935.

[0119] All ingredients are charged to a 3-necked flask with mechanical stirring, condenser, temperature control, nitrogen protection is used, vacuum pump is connected to the set-up.

[0120] Pressure is lowered to 50 - 100 mBar when the mixture reaches 235°C and is clear. Temperature is raised from room temperature to 235°C in 50 min. The reaction mixture is held at 235°C for 2.5h, then cooled to 100°C and pressure equalised with nitrogen. The product is clear.

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**[0121]** Analysis: Acid value: 0.1; Saponification value: 144.9; Hydroxyl value: 241.4; Alcaline number: 5.0

### ***PGE 2680/073 with polyol 13%:***

Rapeseed oil: 500g  
Broad Range Triglycerol (BRTG): 75g  
50% NaOH in water: 0.8g

**[0122]** The triglycerol was prepared by polymerisation in the same manner as described in Example 1 except the refractive index was at 25°C was changed from 1.4855 to 1.4935.

**[0123]** All ingredients are charged to a 3-necked flask with mechanical stirring, condenser, temperature control, nitrogen protection is used, vacuum pump is connected to the set-up.

**[0124]** Pressure is lowered to 50 - 100 mBar when the mixture reaches 235°C and is clear. Temperature is raised from room temperature to 235°C in 50 min. The reaction mixture is held at 235°C for 2.5h, then cooled to 100°C and pressure equalised with nitrogen. The product is clear.

**[0125]** Analysis: Acid value: 0.2; Saponification value: 163.9; Hydroxyl value: 147.5; Alcaline number: 3.7

### **Polyol Distribution**

**[0126]** The polyol distribution of the polyol used in the preparation of each of 2680/062 and 2680/073 was analysed. The analyses was performed twice and an average taken. The results of this analysis are given in Table 3 below.

Table 3 - Polyol duplicate analysis

	Analysis 1	Analysis 2	Average of 2 Analyses	Polyol % based on total Polyols
%Glycerol	11.08	10.9998	11.03	
% CY-Diglycerol	6.42	6.37	6.4	7.19%
% Diglycerol	21.56	21.51	21.54	24.20%
% CY-Triglycerol	2.96	3	2.98	3.35%
% Triglycerol	17.74	17.89	17.8182	20.02%
% CY-Tetraglycerol	1.98	2.06	2.02	2.27%
% Tetraglycerol	11.52	11.79	11.6566	13.10%
% CY-Pentaglycerol	2.78	2.7	2.74	3.08%
% Pentaglycerol	6.8	6.93	6.87	7.72%
% Hexaglycerol	6.53	6.67	6.6	7.42%
% Heptaglycerol	4.84	4.89	4.87	5.47%
% Octaglycerol	3.15	3	3.07	3.45%
% Nonaglycerol	1.9	1.62	1.76	1.98%
% Decaglycerol	0.74	0.58	0.66	0.74%
% Undecaglycerol	0	0	0	0.00%

**[0127]** The polyglycerol esters synthesized are summarised in Table 4. Three types of polyglycerol were included in series, they were two triglycerols and one hexaglycerol The fatty acid source was either soy oil or rape seed oil.

Table 4. BRHG / BRTG: Broad range Hexa/Tri-Glycerol

Sample	Polyol type	Wt. % Polyol	Oil Type
REF PGE	Tri	23.8	Soy
J 2680/053	BRHG	19.0	Soy
J 2680/054	BRHG	16.0	rape seed

(continued)

Sample	Polyol type	Wt. % Polyol	Oil Type
J 2680/060	BRHG	13.0	rape seed
J 2680/062	BRTG	23.1	rape seed
J 2680/065	BRHG	10.0	rape seed
J 2680/073	BRTG	13.0	rape seed

**[0128]** The difference in polyol composition is shown below

**[0129]** The polyol distribution of samples REF PGE, the BRTG used in the preparation of 2680/073 and the BRHG used in the preparation of 2680/060 are shown in Table 5.

Table 5. polyol distribution of samples

	REF PGE	BRTG	BRHG
%Glycerol	0.1	11	5.2
% CY-Diglycerol	0	6.4	9
% Diglycerol	27	21.5	9.7
% CY-Triglycerol	2.5	3	5.7
% Triglycerol	44.2	17.8	10.3
% CY-Tetraglycerol	4.1	2	4
% Tetraglycerol	12.4	11.7	8.5
% CY-Pentaglycerol	1.6	2.7	4.1
% Pentaglycerol	4.2	6.9	6.8
% Hexaglycerol	2.5	6.6	9.2
% Heptaglycerol	1.2	4.9	8.5
% Octaglycerol	0	3.1	7
% Nonaglycerol	0	1.8	5.4
% Decaglycerol	0	0.7	3.6
%Undecaglycerol	0	0	3.1

**[0130]** The viscosity of each emulsifier was measured on a Physica Rheometer using the following setup: Temp: 60°C to -10°C (1 °C/min), Shear rate : 23 1/s, Measuring system: DG26.7 7-SN711; d=0mm

**[0131]** Selected emulsifiers (REF PGE, J2680/060, J2680/065, J2680/073) were further tested in WIF-emulsions with 50% water content at 55°C at 0.1% and 0.2% dosage. Diesel quality: MGO.

**[0132]** WIF-samples were prepared as described in Example 1.

## RESULTS

**[0133]** The droplet size distribution is shown in Table 6 and graphically in Figure 9 for D50.0 values. Samples 2680/065 and 2680/073 were not stable enough to allow NMR measurement.

Table 6 water droplet size distribution

Sample	Dosage %	D2.5 µm	D50.0 µm	comments
REF PGE	0.1	1.6	81.0	
J 2680/060	0.1	5.3	100.0	
J 2680/065	0.1	-	-	Too fast sedimentation

(continued)

Sample	Dosage %	D2.5 $\mu\text{m}$	D50.0 $\mu\text{m}$	comments
J 2680/073	0.1	-	-	Water phase separation
REFPGE	0.2	4.2	19.3	
J 2680/060	0.2	7.9	32.6	
J 2680/065	0.2	3.7	100.0	
J 2680/073	0.2	-	-	Water phase separation

**[0134]** The CLSM pictures of the emulsion are shown in Figure 10. The images were recorded immediately after emulsification. Samples 2680/065 and 2680/073 both provides much bigger water droplets at both emulsifier dosage levels as compared to the reference (REF PGE) and 2680/060..

**[0135]** The CLSM images of Figure 11 show a dramatic increase in the water droplet size at low emulsifier dosage for samples 2680/065 and 2680/073 as a sign of reduced functionality. Also at 0.2% dosage level, the droplets are clearly larger than for samples REF PGE and 2680/060.

**[0136]** Sedimentation and water phase separation after 1h, 2, and 3h storage at 55°C for sample 2680/073 are shown in Figure 12. Such pronounced water separation is unusual with WIF-emulsions. Sedimentation at rest however is not a problem as a homogeneous emulsion will be reformed during flow

**[0137]** Images of the emulsions are shown in Figure 14.

**[0138]** The degree of water droplet sedimentation in the emulsions expressed as the amount of free oil on top formed during 3 hours of storage at 55°C is shown in Figure 13.

## Claims

### 1. A fuel composition comprising:

- (a) a fuel;
- (b) a polyglycerol ester of a fatty acid, wherein the polyglycerol ester of a fatty acid is present in an amount no greater than 0.25 wt% based on the total fuel composition; and
- (c) water in an amount of from 10 to 70 wt% based on the total fuel composition;

wherein the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises, based on the combined weight of the polyglycerols, a mixture of

diglycerol in an amount of 11.0 to 34.0 weight%;  
 triglycerol in an amount of 9.5 to 24.5 weight%;  
 tetraglycerol in an amount of 6.0 to 21.0 weight%;  
 pentaglycerol in an amount of 3.5 to 19.0 weight%;  
 hexaglycerol in an amount of 6.0 to 13.5 weight%;  
 heptaglycerol in an amount of 5.0 to 13.0 weight%;  
 octaglycerol in an amount of 3.0 to 12.0 weight%;  
 nonaglycerol in an amount of 1.5 to 10.0 weight%;  
 decaglycerol in an amount of 0.0 to 8.0 weight; and  
 unadecaglycerol in an amount of 0.0 to 7.0 weight%.

### 2. A fuel composition according to claim 1 wherein the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises, based on the combined weight of the polyglycerols, a mixture of

diglycerol in an amount of 11.0 to 28.0 weight%;  
 triglycerol in an amount of 9.5 to 24.5 weight%;  
 tetraglycerol in an amount of 6.0 to 21.0 weight%;  
 pentaglycerol in an amount of 3.5 to 19.0 weight%;  
 hexaglycerol in an amount of 6.0 to 13.5 weight%;  
 heptaglycerol in an amount of 5.0 to 13.0 weight%;

octaglycerol in an amount of 4.0 to 12.0 weight%;  
 nonaglycerol in an amount of 2.0 to 10.0 weight%;  
 decaglycerol in an amount of 0.5 to 8.0 weight%; and  
 unadecaglycerol in an amount of 0.1 to 7.0 weight%.

3. A fuel composition according to claim 1 wherein, based on the combined weight of the polyglycerols,

the diglycerol comprises acyclic diglycerol in an amount of 6.0 to 25.0 weight%, and cyclic diglycerol in an amount of 5.0 to 13.0 weight%;  
 the triglycerol comprises acyclic triglycerol in an amount of 7.0 to 21.0 weight%, and cyclic triglycerol in an amount of 2.5 to 9.5 weight%;  
 the tetraglycerol comprises acyclic tetraglycerol in an amount of 5.5 to 15.0 weight%, and cyclic tetraglycerol in an amount of 0.5 to 8.0 weight%; and  
 the pentaglycerol comprises acyclic pentaglycerol in an amount of 3.0 to 11.0 weight% and cyclic pentaglycerol in an amount of 0.5 to 8.0 weight%.

4. A fuel composition according to claim 2 wherein, based on the combined weight of the polyglycerols,

the diglycerol comprises acyclic diglycerol in an amount of 6.0 to 15.0 weight%, and cyclic diglycerol in an amount of 5.0 to 13.0 weight%;  
 the triglycerol comprises acyclic triglycerol in an amount of 7.0 to 15.0 weight%, and cyclic triglycerol in an amount of 2.5 to 9.5 weight%;  
 the tetraglycerol comprises acyclic tetraglycerol in an amount of 5.0 to 13.0 weight%, and cyclic tetraglycerol in an amount of 1.0 to 8.0 weight%; and  
 the pentaglycerol comprises acyclic pentaglycerol in an amount of 3.0 to 11.0 weight%, and cyclic pentaglycerol in an amount of 0.5 to 8.0 weight%.

5. A fuel composition according to any one of the preceding claims wherein the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises, based on the combined

weight of the polyglycerols, a mixture of  
 diglycerol in an amount of 15.0 to 23.5 weight%;  
 triglycerol in an amount of 13.5 to 20.5 weight%;  
 tetraglycerol in an amount of 10.0 to 17.0 weight%;  
 pentaglycerol in an amount of 8.0 to 14.5 weight%;  
 hexaglycerol in an amount of 8.0 to 11.5 weight%;  
 heptaglycerol in an amount of 7.5 to 11.0 weight%;  
 octaglycerol in an amount of 6.5 to 10.0 weight%;  
 nonaglycerol in an amount of 4.0 to 8.0 weight%;  
 decaglycerol in an amount of 1.5 to 6.0 weight%; and  
 unadecaglycerol in an amount of 0.5 to 5.0 weight%.

6. A fuel composition according to any one of the preceding claims wherein the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises, based on the combined

weight of the polyglycerols, a mixture of  
 diglycerol in an amount of 17.6 to 21.0 weight%;  
 triglycerol in an amount of 15.9 to 18.1 weight%;  
 tetraglycerol in an amount of 12.5 to 14.0 weight%;  
 pentaglycerol in an amount of 10.5 to 12.2 weight%;  
 hexaglycerol in an amount of 9.3 to 10.1 weight%;  
 heptaglycerol in an amount of 8.6 to 9.9 weight%;  
 octaglycerol in an amount of 7.3 to 8.9 weight%;  
 nonaglycerol in an amount of 5.5 to 6.4 weight%;  
 decaglycerol in an amount of 2.9 to 4.5 weight%; and  
 unadecaglycerol in an amount of 1.8 to 3.7 weight%.

7. A fuel composition according to claim 1 wherein in the polyglycerol composition, based on

the combined weight of the polyglycerols, used to form the polyglycerol ester of a fatty acid  
 the diglycerol comprises acyclic diglycerol in an amount of 9.0 to 24.5 weight%, and cyclic diglycerol in an  
 amount of 6.5 to 10.0 weight%;  
 the triglycerol comprises acyclic triglycerol in an amount of 9.0 to 20.5 weight%, and cyclic triglycerol in an  
 amount of 3.5 to 6.5 weight%;  
 the tetraglycerol comprises acyclic tetraglycerol in an amount of 8.0 to 13.5 weight%, and cyclic tetraglycerol  
 in an amount of 2.0 to 4.5 weight%; and  
 the pentaglycerol comprises acyclic pentaglycerol in an amount of 6.0 to 9.0 weight%, and cyclic pentaglycerol  
 in an amount of 2.0 to 5.0 weight%.

8. A fuel composition according to claim 6 wherein in the polyglycerol composition, based on

the combined weight of the polyglycerols, used to form the polyglycerol ester of a fatty acid  
 the diglycerol comprises acyclic diglycerol in an amount of 20.0 to 26.0 weight%, and cyclic diglycerol in an  
 amount of 6.5 to 8.0 weight%;  
 the triglycerol comprises acyclic triglycerol in an amount of 18.0 to 21.0 weight%, and cyclic triglycerol in an  
 amount of 2.5 to 5.0 weight%;  
 the tetraglycerol comprises acyclic tetraglycerol in an amount of 11.0 to 14.5 weight%, and cyclic tetraglycerol  
 in an amount of 1.5 to 4.0 weight%; and  
 the pentaglycerol comprises acyclic pentaglycerol in an amount of 6.5 to 9.5 weight%, and cyclic pentaglycerol  
 in an amount of 1.5 to 4.0 weight%.

9. A fuel composition according to any one of the preceding claims wherein the polyglycerol composition used to form  
 the polyglycerol ester of a fatty acid has a hydroxyl value of from 880 to 1230 mg KOH/g.

10. A fuel composition according to any one of the preceding claims wherein the polyglycerol composition used to form  
 the polyglycerol ester of a fatty acid has a refractive index at 50°C of from 1.4860 to 1.4925.

11. A fuel composition according to any one of the preceding claims wherein the (b) a polyglycerol ester of a fatty acid  
 is present in an amount of no greater than 0.1wt% based on the total fuel composition.

12. A fuel composition according to any one of the preceding claims wherein the fuel is marine gasoil.

13. A method for improving the stability of a fuel composition containing (a) fuel and (c) water, the method comprising  
 mixing with the fuel and water,  
 (b) a polyglycerol ester of a fatty acid, wherein the polyglycerol ester of a fatty acid is present in an amount no greater  
 than 0.25 wt% based on the total fuel composition;  
 and wherein the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises, based on  
 the combined weight of the polyglycerols, a mixture of

diglycerol in an amount of 11.0 to 34.0 weight%;  
 triglycerol in an amount of 9.5 to 24.5 weight%;  
 tetraglycerol in an amount of 6.0 to 21.0 weight%;  
 pentaglycerol in an amount of 3.5 to 19.0 weight%;  
 hexaglycerol in an amount of 6.0 to 13.5 weight%;  
 heptaglycerol in an amount of 5.0 to 13.0 weight%;  
 octaglycerol in an amount of 3.0 to 12.0 weight%;  
 nonaglycerol in an amount of 1.5 to 10.0 weight%;  
 decaglycerol in an amount of 0.0 to 8.0 weight%; and  
 undecaglycerol in an amount of 0.0 to 7.0 weight%.

14. Use of a polyglycerol ester of a fatty acid for improving the stability of a fuel composition containing fuel and water,  
 wherein the polyglycerol ester of a fatty acid is present in an amount no greater than 0.25 wt% based on the total  
 fuel composition;  
 and wherein the polyglycerol composition used to form the polyglycerol ester of a fatty acid comprises, based on  
 the combined weight of the polyglycerols, a mixture of

diglycerol in an amount of 11.0 to 34.0 weight%;

triglycerol in an amount of 9.5 to 24.5 weight%;  
 tetraglycerol in an amount of 6.0 to 21.0 weight%;  
 pentaglycerol in an amount of 3.5 to 19.0 weight%;  
 hexaglycerol in an amount of 6.0 to 13.5 weight%;  
 heptaglycerol in an amount of 5.0 to 13.0 weight%;  
 octaglycerol in an amount of 3.0 to 12.0 weight%;  
 nonaglycerol in an amount of 1.5 to 10.0 weight%;  
 decaglycerol in an amount of 0.0 to 8.0 weight%; and  
 undecaglycerol in an amount of 0.0 to 7.0 weight%.

## Patentansprüche

### 1. Kraft- oder Brennstoffzusammensetzung, umfassend:

- (a) einen Kraft- oder Brennstoff;
- (b) einen Polyglycerinester einer Fettsäure, wobei der Polyglycerinester einer Fettsäure in einer Menge von nicht mehr als 0,25 Gew.-%, bezogen auf die gesamte Kraft- oder Brennstoffzusammensetzung, vorliegt; und
- (c) Wasser in einer Menge von 10 bis 70 Gew.-%, bezogen auf die gesamte Kraft- oder Brennstoffzusammensetzung;

wobei die zur Bildung des Polyglycerinesters einer Fettsäure verwendete Polyglycerinzusammensetzung, bezogen auf das kombinierte Gewicht der Polyglycerine, ein Gemisch von

Diglycerin in einer Menge von 11,0 bis 34,0 Gew.-%;  
 Triglycerin in einer Menge von 9,5 bis 24,5 Gew.-%;  
 Tetraglycerin in einer Menge von 6,0 bis 21,0 Gew.-%;  
 Pentaglycerin in einer Menge von 3,5 bis 19,0 Gew.-%;  
 Hexaglycerin in einer Menge von 6,0 bis 13,5 Gew.-%;  
 Heptaglycerin in einer Menge von 5,0 bis 13,0 Gew.-%;  
 Octaglycerin in einer Menge von 3,0 bis 12,0 Gew.-%;  
 Nonaglycerin in einer Menge von 1,5 bis 10,0 Gew.-%;  
 Decaglycerin in einer Menge von 0,0 bis 8,0 Gew.-%; und  
 Undecaglycerin in einer Menge von 0,0 bis 7,0 Gew.-%

umfasst.

### 2. Kraft- oder Brennstoffzusammensetzung nach Anspruch 1, wobei die zur Bildung des Polyglycerinesters einer Fettsäure verwendete Polyglycerinzusammensetzung, bezogen auf das kombinierte Gewicht der Polyglycerine, ein Gemisch von

Diglycerin in einer Menge von 11,0 bis 28,0 Gew.-%;  
 Triglycerin in einer Menge von 9,5 bis 24,5 Gew.-%;  
 Tetraglycerin in einer Menge von 6,0 bis 21,0 Gew.-%;  
 Pentaglycerin in einer Menge von 3,5 bis 19,0 Gew.-%;  
 Hexaglycerin in einer Menge von 6,0 bis 13,5 Gew.-%;  
 Heptaglycerin in einer Menge von 5,0 bis 13,0 Gew.-%;  
 Octaglycerin in einer Menge von 4,0 bis 12,0 Gew.-%;  
 Nonaglycerin in einer Menge von 2,0 bis 10,0 Gew.-%;  
 Decaglycerin in einer Menge von 0,5 bis 8,0 Gew.-%; und  
 Undecaglycerin in einer Menge von 0,1 bis 7,0 Gew.-%

umfasst.

### 3. Kraft- oder Brennstoffzusammensetzung nach Anspruch 1, wobei, bezogen auf das kombinierte Gewicht der Polyglycerine,

das Diglycerin acyclisches Diglycerin in einer Menge von 6,0 bis 25,0 Gew.-% und cyclisches Diglycerin in einer



Menge von 5,0 bis 13,0 Gew.-% umfasst; das Triglycerin acyclisches Triglycerin in einer Menge von 7,0 bis 21,0 Gew.-% und cyclisches Triglycerin in einer Menge von 2,5 bis 9,5 Gew.-% umfasst;  
das Tetraglycerin acyclisches Tetraglycerin in einer Menge von 5,5 bis 15,0 Gew.-% und cyclisches Tetraglycerin in einer Menge von 0,5 bis 8,0 Gew.-% umfasst; und  
das Pentaglycerin acyclisches Pentaglycerin in einer Menge von 3,0 bis 11,0 Gew.-% und cyclisches Pentaglycerin in einer Menge von 0,5 bis 8,0 Gew.-% umfasst.

4. Kraft- oder Brennstoffzusammensetzung nach Anspruch 2, wobei, bezogen auf das kombinierte Gewicht der Polyglycerine,

das Diglycerin acyclisches Diglycerin in einer Menge von 6,0 bis 15,0 Gew.-% und cyclisches Diglycerin in einer Menge von 5,0 bis 13,0 Gew.-% umfasst; das Triglycerin acyclisches Triglycerin in einer Menge von 7,0 bis 15,0 Gew.-% und cyclisches Triglycerin in einer Menge von 2,5 bis 9,5 Gew.-% umfasst;  
das Tetraglycerin acyclisches Tetraglycerin in einer Menge von 5,0 bis 13,0 Gew.-% und cyclisches Tetraglycerin in einer Menge von 1,0 bis 8,0 Gew.-% umfasst; und  
das Pentaglycerin acyclisches Pentaglycerin in einer Menge von 3,0 bis 11,0 Gew.-% und cyclisches Pentaglycerin in einer Menge von 0,5 bis 8,0 Gew.-% umfasst.

5. Kraft- oder Brennstoffzusammensetzung nach einem der vorhergehenden Ansprüche, wobei die zur Bildung des Polyglycerinesters einer Fettsäure verwendete Polyglycerinzusammensetzung, bezogen auf das kombinierte Gewicht der Polyglycerine, ein Gemisch von

Diglycerin in einer Menge von 15,0 bis 23,5 Gew.-%;  
Triglycerin in einer Menge von 13,5 bis 20,5 Gew.-%;  
Tetraglycerin in einer Menge von 10,0 bis 17,0 Gew.-%;  
Pentaglycerin in einer Menge von 8,0 bis 14,5 Gew.-%;  
Hexaglycerin in einer Menge von 8,0 bis 11,5 Gew.-%;  
Heptaglycerin in einer Menge von 7,5 bis 11,0 Gew.-%;  
Octaglycerin in einer Menge von 6,5 bis 10,0 Gew.-%;  
Nonaglycerin in einer Menge von 4,0 bis 8,0 Gew.-%;  
Decaglycerin in einer Menge von 1,5 bis 6,0 Gew.-%; und  
Undecaglycerin in einer Menge von 0,5 bis 5,0 Gew.-%

umfasst.

6. Kraft- oder Brennstoffzusammensetzung nach einem der vorhergehenden Ansprüche, wobei die zur Bildung des Polyglycerinesters einer Fettsäure verwendete Polyglycerinzusammensetzung, bezogen auf das kombinierte Gewicht der Polyglycerine, ein Gemisch von

Diglycerin in einer Menge von 17,6 bis 21,0 Gew.-%;  
Triglycerin in einer Menge von 15,9 bis 18,1 Gew.-%;  
Tetraglycerin in einer Menge von 12,5 bis 14,0 Gew.-%;  
Pentaglycerin in einer Menge von 10,5 bis 12,2 Gew.-%;  
Hexaglycerin in einer Menge von 9,3 bis 10,1 Gew.-%;  
Heptaglycerin in einer Menge von 8,6 bis 9,9 Gew.-%;  
Octaglycerin in einer Menge von 7,3 bis 8,9 Gew.-%;  
Nonaglycerin in einer Menge von 5,5 bis 6,4 Gew.-%;  
Decaglycerin in einer Menge von 2,9 bis 4,5 Gew.-%; und  
Undecaglycerin in einer Menge von 1,8 bis 3,7 Gew.-%

umfasst.

7. Kraft- oder Brennstoffzusammensetzung nach Anspruch 1, wobei in der zur Bildung des Polyglycerinesters einer Fettsäure verwendeten Polyglycerinzusammensetzung, bezogen auf das kombinierte Gewicht der Polyglycerine,

das Diglycerin acyclisches Diglycerin in einer Menge von 9,0 bis 24,5 Gew.-% und cyclisches Diglycerin in einer Menge von 6,5 bis 10,0 Gew.-% umfasst; das Triglycerin acyclisches Triglycerin in einer Menge von 9,0 bis 20,5 Gew.-% und cyclisches Triglycerin in einer Menge von 3,5 bis 6,5 Gew.-% umfasst;

das Tetraglycerin acyclisches Tetraglycerin in einer Menge von 8,0 bis 13,5 Gew.-% und cyclisches Tetraglycerin in einer Menge von 2,0 bis 4,5 Gew.-% umfasst; und  
das Pentaglycerin acyclisches Pentaglycerin in einer Menge von 6,0 bis 9,0 Gew.-% und cyclisches Pentaglycerin in einer Menge von 2,0 bis 5,0 Gew.-% umfasst.

8. Kraft- oder Brennstoffzusammensetzung nach Anspruch 6, wobei in der zur Bildung des Polyglycerinesters einer Fettsäure verwendeten Polyglycerinzusammensetzung, bezogen auf das kombinierte Gewicht der Polyglycerine,

das Diglycerin acyclisches Diglycerin in einer Menge von 20,0 bis 26,0 Gew.-% und cyclisches Diglycerin in einer Menge von 6,5 bis 8,0 Gew.-% umfasst;  
das Triglycerin acyclisches Triglycerin in einer Menge von 18,0 bis 21,0 Gew.-% und cyclisches Triglycerin in einer Menge von 2,5 bis 5,0 Gew.-% umfasst;  
das Tetraglycerin acyclisches Tetraglycerin in einer Menge von 11,0 bis 14,5 Gew.-% und cyclisches Tetraglycerin in einer Menge von 1,5 bis 4,0 Gew.-% umfasst; und  
das Pentaglycerin acyclisches Pentaglycerin in einer Menge von 6,5 bis 9,5 Gew.-% und cyclisches Pentaglycerin in einer Menge von 1,5 bis 4,0 Gew.-% umfasst.

9. Kraft- oder Brennstoffzusammensetzung nach einem der vorhergehenden Ansprüche, wobei die zur Bildung des Polyglycerinesters einer Fettsäure verwendete Polyglycerinzusammensetzung eine Hydroxylzahl von 880 bis 1230 mg KOH/g aufweist.

10. Kraft- oder Brennstoffzusammensetzung nach einem der vorhergehenden Ansprüche, wobei die zur Bildung des Polyglycerinesters einer Fettsäure verwendete Polyglycerinzusammensetzung einen Brechungsindex bei 50 °C von 1,4860 bis 1,4925 aufweist.

11. Kraft- oder Brennstoffzusammensetzung nach einem der vorhergehenden Ansprüche, wobei (b) der Polyglycerinester einer Fettsäure in einer Menge von nicht mehr als 0,1 Gew.-%, bezogen auf die gesamte Kraft- oder Brennstoffzusammensetzung, vorliegt.

12. Kraft- oder Brennstoffzusammensetzung nach einem der vorhergehenden Ansprüche, wobei es sich bei dem Kraft- oder Brennstoff um Marinegasöl handelt.

13. Verfahren zur Verbesserung der Stabilität einer Kraft- oder Brennstoffzusammensetzung, die (a) Kraft- oder Brennstoff und (c) Wasser umfasst, bei dem man mit dem Kraft- oder Brennstoff und dem Wasser  
(b) einen Polyglycerinester einer Fettsäure mischt, wobei der Polyglycerinester einer Fettsäure in einer Menge von nicht mehr als 0,25 Gew.-%, bezogen auf die gesamte Kraft- oder Brennstoffzusammensetzung, vorliegt; und wobei die zur Bildung des Polyglycerinesters einer Fettsäure verwendete Polyglycerinzusammensetzung, bezogen auf das kombinierte Gewicht der Polyglycerine, ein Gemisch von

Diglycerin in einer Menge von 11,0 bis 34,0 Gew.-%;  
Triglycerin in einer Menge von 9,5 bis 24,5 Gew.-%;  
Tetraglycerin in einer Menge von 6,0 bis 21,0 Gew.-%;  
Pentaglycerin in einer Menge von 3,5 bis 19,0 Gew.-%;  
Hexaglycerin in einer Menge von 6,0 bis 13,5 Gew.-%;  
Heptaglycerin in einer Menge von 5,0 bis 13,0 Gew.-%;  
Octaglycerin in einer Menge von 3,0 bis 12,0 Gew.-%;  
Nonaglycerin in einer Menge von 1,5 bis 10,0 Gew.-%;  
Decaglycerin in einer Menge von 0,0 bis 8,0 Gew.-%; und  
Undecaglycerin in einer Menge von 0,0 bis 7,0 Gew.-%

umfasst.

14. Verwendung eines Polyglycerinesters einer Fettsäure zur Verbesserung der Stabilität einer Kraft- oder Brennstoffzusammensetzung, die Kraft- oder Brennstoff und Wasser enthält, wobei der Polyglycerinester einer Fettsäure in einer Menge von nicht mehr als 0,25 Gew.-%, bezogen auf die gesamte Kraft- oder Brennstoffzusammensetzung, vorliegt; und wobei die zur Bildung des Polyglycerinesters einer Fettsäure verwendete Polyglycerinzusammensetzung, bezogen auf das kombinierte Gewicht der Polyglycerine, ein Gemisch von

Diglycerin in einer Menge von 11,0 bis 34,0 Gew.-%;  
 Triglycerin in einer Menge von 9,5 bis 24,5 Gew.-%;  
 Tetraglycerin in einer Menge von 6,0 bis 21,0 Gew.-%;  
 Pentaglycerin in einer Menge von 3,5 bis 19,0 Gew.-%;  
 5 Hexaglycerin in einer Menge von 6,0 bis 13,5 Gew.-%;  
 Heptaglycerin in einer Menge von 5,0 bis 13,0 Gew.-%;  
 Octaglycerin in einer Menge von 3,0 bis 12,0 Gew.-%;  
 Nonaglycerin in einer Menge von 1,5 bis 10,0 Gew.-%;  
 10 Decaglycerin in einer Menge von 0,0 bis 8,0 Gew.-%; und  
 Undecaglycerin in einer Menge von 0,0 bis 7,0 Gew.-%

umfasst.

## 15 Revendications

### 1. Composition de combustible comprenant :

- (a) un combustible ;  
 20 (b) un ester de polyglycérol d'un acide gras, l'ester de polyglycérol d'un acide gras étant présent en une quantité inférieure ou égale à 0,25% en poids sur la base de la composition totale de combustible ; et  
 (c) de l'eau une quantité de 10 jusqu'à 70% en poids sur la base de la composition totale de combustible ;

la composition de polyglycérol utilisée pour former l'ester de polyglycérol d'un acide gras comprenant, sur la base  
 25 du poids combiné des polyglycérols, un mélange de

diglycérol en une quantité de 11,0 jusqu'à 34,0% en poids ;  
 triglycérol en une quantité de 9,5 jusqu'à 24,5% en poids ;  
 tétraglycérol en une quantité de 6,0 jusqu'à 21,0% en poids ;  
 30 pentaglycérol en une quantité de 3,5 jusqu'à 19,0% en poids ;  
 hexaglycérol en une quantité de 6,0 jusqu'à 13,5% en poids ;  
 heptaglycérol en une quantité de 5,0 jusqu'à 13,0% en poids ;  
 octaglycérol en une quantité de 3,0 jusqu'à 12,0% en poids ;  
 nonaglycérol en une quantité de 1,5 jusqu'à 10,0% en poids ;  
 35 décaglycérol en une quantité de 0,0 jusqu'à 8,0% en poids ;  
 undécaglycérol en une quantité de 0,0 jusqu'à 7,0% en poids.

### 2. Composition de combustible selon la revendication 1, la composition de polyglycérol utilisée pour former l'ester de polyglycérol d'un acide gras comprenant, sur la base du poids combiné des polyglycérols, un mélange de

40 diglycérol en une quantité de 11,0 jusqu'à 28,0% en poids ;  
 triglycérol en une quantité de 9,5 jusqu'à 24,5% en poids ;  
 tétraglycérol en une quantité de 6,0 jusqu'à 21,0% en poids ;  
 pentaglycérol en une quantité de 3,5 jusqu'à 19,0% en poids ;  
 45 hexaglycérol en une quantité de 6,0 jusqu'à 13,5% en poids ;  
 heptaglycérol en une quantité de 5,0 jusqu'à 13,0% en poids ;  
 octaglycérol en une quantité de 4,0 jusqu'à 12,0% en poids ;  
 nonaglycérol en une quantité de 2,0 jusqu'à 10,0% en poids ;  
 50 décaglycérol en une quantité de 0,5 jusqu'à 8,0% en poids ;  
 undécaglycérol en une quantité de 0,1 jusqu'à 7,0% en poids.

### 3. Composition de combustible selon la revendication 1,

le diglycérol comprenant le diglycérol acyclique en une quantité de 6,0 jusqu'à 25,0% en poids et le diglycérol  
 55 cyclique en une quantité de 5,0 jusqu'à 13,0% en poids ;  
 le triglycérol comprenant le triglycérol acyclique en une quantité de 7,0 jusqu'à 21,0% en poids et le triglycérol cyclique en une quantité de 2,5 jusqu'à 9,5% en poids ;  
 le tétraglycérol comprenant le tétraglycérol acyclique en une quantité de 5,5 jusqu'à 15,0% en poids et le

tétraglycérol cyclique en une quantité de 0,5 jusqu'à 8,0% en poids ;  
 le pentaglycérol comprenant le pentaglycérol acyclique en une quantité de 3,0 jusqu'à 11,0% en poids et le  
 pentaglycérol cyclique en une quantité de 0,5 jusqu'à 8,0% en poids,  
 sur la base du poids combiné des polyglycérols.

5  
 4. Composition de combustible selon la revendication 2,

le diglycérol comprenant le diglycérol acyclique en une quantité de 6,0 jusqu'à 15,0% en poids et le diglycérol  
 cyclique en une quantité de 5,0 jusqu'à 13,0% en poids ;  
 10 le triglycérol comprenant le triglycérol acyclique en une quantité de 7,0 jusqu'à 15,0% en poids et le triglycérol  
 cyclique en une quantité de 2,5 jusqu'à 9,5% en poids ;  
 le tétraglycérol comprenant le tétraglycérol acyclique en une quantité de 5,5 jusqu'à 13,0% en poids et le  
 tétraglycérol cyclique en une quantité de 1,0 jusqu'à 8,0% en poids ;  
 15 le pentaglycérol comprenant le pentaglycérol acyclique en une quantité de 3,0 jusqu'à 11,0% en poids et le  
 pentaglycérol cyclique en une quantité de 0,5 jusqu'à 8,0% en poids,  
 sur la base du poids combiné des polyglycérols.

5. Composition de combustible selon l'une quelconque des revendications précédentes, la composition de polyglycérol  
 utilisée pour former l'ester de polyglycérol d'un acide gras comprenant, sur la base du poids combiné des polygly-  
 cérols, un mélange de  
 20

diglycérol en une quantité de 15,0 jusqu'à 23,5% en poids ;  
 triglycérol en une quantité de 13,5 jusqu'à 20,5% en poids ;  
 tétraglycérol en une quantité de 10,0 jusqu'à 17,0% en poids ;  
 25 pentaglycérol en une quantité de 8,0 jusqu'à 14,5% en poids ;  
 hexaglycérol en une quantité de 8,0 jusqu'à 11,5% en poids ;  
 heptaglycérol en une quantité de 7,5 jusqu'à 11,0% en poids ;  
 octaglycérol en une quantité de 6,5 jusqu'à 10,0% en poids ;  
 nonaglycérol en une quantité de 4,0 jusqu'à 8,0% en poids ;  
 30 décaglycérol en une quantité de 1,5 jusqu'à 6,0% en poids ;  
 undécaglycérol en une quantité de 0,5 jusqu'à 5,0% en poids.

6. Composition de combustible selon l'une quelconque des revendications précédentes, la composition de polyglycérol  
 utilisée pour former l'ester de polyglycérol d'un acide gras comprenant, sur la base du poids combiné des polygly-  
 cérols, un mélange de  
 35

diglycérol en une quantité de 17,6 jusqu'à 21,0% en poids ;  
 triglycérol en une quantité de 15,9 jusqu'à 18,1% en poids ;  
 tétraglycérol en une quantité de 12,5 jusqu'à 14,0% en poids ;  
 40 pentaglycérol en une quantité de 10,5 jusqu'à 12,2% en poids ;  
 hexaglycérol en une quantité de 9,3 jusqu'à 10,1% en poids ;  
 heptaglycérol en une quantité de 8,6 jusqu'à 9,9% en poids ;  
 octaglycérol en une quantité de 7,3 jusqu'à 8,9% en poids ;  
 nonaglycérol en une quantité de 5,5 jusqu'à 6,4% en poids ;  
 45 décaglycérol en une quantité de 2,9 jusqu'à 4,5% en poids ;  
 undécaglycérol en une quantité de 1,8 jusqu'à 3,7% en poids.

7. Composition de combustible selon la revendication 1,

le diglycérol comprenant le diglycérol acyclique en une quantité de 9,0 jusqu'à 24,5% en poids et le diglycérol  
 cyclique en une quantité de 6,5 jusqu'à 10,0% en poids ;  
 le triglycérol comprenant le triglycérol acyclique en une quantité de 9,0 jusqu'à 20,5% en poids et le triglycérol  
 cyclique en une quantité de 3,5 jusqu'à 6,5% en poids ;  
 le tétraglycérol comprenant le tétraglycérol acyclique en une quantité de 8,0 jusqu'à 13,5% en poids et le  
 55 tétraglycérol cyclique en une quantité de 2,0 jusqu'à 4,5% en poids ;  
 le pentaglycérol comprenant le pentaglycérol acyclique en une quantité de 6,0 jusqu'à 9,0% en poids et le  
 pentaglycérol cyclique en une quantité de 2,0 jusqu'à 5,0% en poids, sur la base du poids combiné des poly-  
 glycérols, dans la composition de polyglycérol utilisée pour former l'ester de polyglycérol d'un acide gras.

## 8. Composition de combustible selon la revendication 6,

le diglycérol comprenant le diglycérol acyclique en une quantité de 20,0 jusqu'à 26,0% en poids et le diglycérol cyclique en une quantité de 6,5 jusqu'à 8,0% en poids ;  
 le triglycérol comprenant le triglycérol acyclique en une quantité de 18,0 jusqu'à 21,0% en poids et le triglycérol cyclique en une quantité de 2,5 jusqu'à 5,0% en poids ;  
 le tétraglycérol comprenant le tétraglycérol acyclique en une quantité de 11,0 jusqu'à 14,5% en poids et le tétraglycérol cyclique en une quantité de 1,5 jusqu'à 4,0% en poids ;  
 le pentaglycérol comprenant le pentaglycérol acyclique en une quantité de 6,5 jusqu'à 9,5% en poids et le pentaglycérol cyclique en une quantité de 1,5 jusqu'à 4,0% en poids, sur la base du poids combiné des polyglycérols, dans la composition de polyglycérol utilisée pour former l'ester de polyglycérol d'un acide gras.

## 9. Composition de combustible selon l'une quelconque des revendications précédentes, la composition de polyglycérol utilisée pour former l'ester de polyglycérol d'un acide gras possédant un indice d'hydroxyle de 880 jusqu'à 1230 mg de KOH/g.

## 10. Composition de combustible selon l'une quelconque des revendications précédentes, la composition de polyglycérol utilisée pour former l'ester de polyglycérol d'un acide gras possédant un indice de réfraction à 50°C de 1,4860 jusqu'à 1,4925.

## 11. Composition de combustible selon l'une quelconque des revendications précédentes, le (b) ester de polyglycérol d'un acide gras étant présent en une quantité inférieure ou égale à 0,1% en poids sur la base de composition totale de combustible.

## 12. Composition de combustible selon l'une quelconque des revendications précédentes, le combustible étant du gazole marin.

13. Procédé pour l'amélioration de la stabilité d'une composition de combustible contenant (a) du combustible et (c) de l'eau, le procédé comprenant le mélange, avec le combustible et l'eau, de  
 (b) un ester de polyglycérol d'un acide gras, l'ester de polyglycérol d'un acide gras étant présent en une quantité inférieure ou égale à 0,25% en poids sur la base de la composition totale de combustible ;  
 et  
 la composition de polyglycérol utilisée pour former l'ester de polyglycérol d'un acide gras comprenant, sur la base du poids combiné des polyglycérols, un mélange de

diglycérol en une quantité de 11,0 jusqu'à 34,0% en poids ;  
 triglycérol en une quantité de 9,5 jusqu'à 24,5% en poids ;  
 tétraglycérol en une quantité de 6,0 jusqu'à 21,0% en poids ;  
 pentaglycérol en une quantité de 3,5 jusqu'à 19,0% en poids ;  
 hexaglycérol en une quantité de 6,0 jusqu'à 13,5% en poids ;  
 heptaglycérol en une quantité de 5,0 jusqu'à 13,0% en poids ;  
 octaglycérol en une quantité de 3,0 jusqu'à 12,0% en poids ;  
 nonaglycérol en une quantité de 1,5 jusqu'à 10,0% en poids ;  
 décaglycérol en une quantité de 0,0 jusqu'à 8,0% en poids ;  
 undécaglycérol en une quantité de 0,0 jusqu'à 7,0% en poids.

14. Utilisation d'un ester de polyglycérol d'un acide gras pour l'amélioration de la stabilité d'une composition de combustible contenant du combustible et de l'eau,  
 l'ester de polyglycérol d'un acide gras étant présent en une quantité inférieure ou égale à 0,25% en poids sur la base de la composition totale de combustible ;  
 et  
 la composition de polyglycérol utilisée pour former l'ester de polyglycérol d'un acide gras comprenant, sur la base du poids combiné des polyglycérols, un mélange de

diglycérol en une quantité de 11,0 jusqu'à 34,0% en poids ;  
 triglycérol en une quantité de 9,5 jusqu'à 24,5% en poids ;  
 tétraglycérol en une quantité de 6,0 jusqu'à 21,0% en poids ;  
 pentaglycérol en une quantité de 3,5 jusqu'à 19,0% en poids ;

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hexaglycérol en une quantité de 6,0 jusqu'à 13,5% en poids ;  
heptaglycérol en une quantité de 5,0 jusqu'à 13,0% en poids ;  
octaglycérol en une quantité de 3,0 jusqu'à 12,0% en poids ;  
nonaglycérol en une quantité de 1,5 jusqu'à 10,0% en poids ;  
décaglycérol en une quantité de 0,0 jusqu'à 8,0% en poids ;  
undécaglycérol en une quantité de 0,0 jusqu'à 7,0% en poids.

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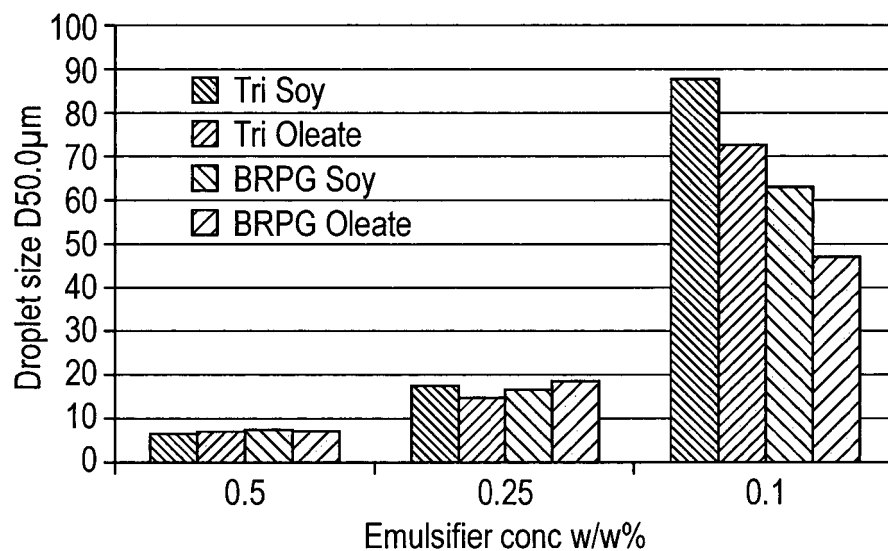
35

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45

50

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Water droplet size (D50.0) depending on emulsifier addition

FIG. 1

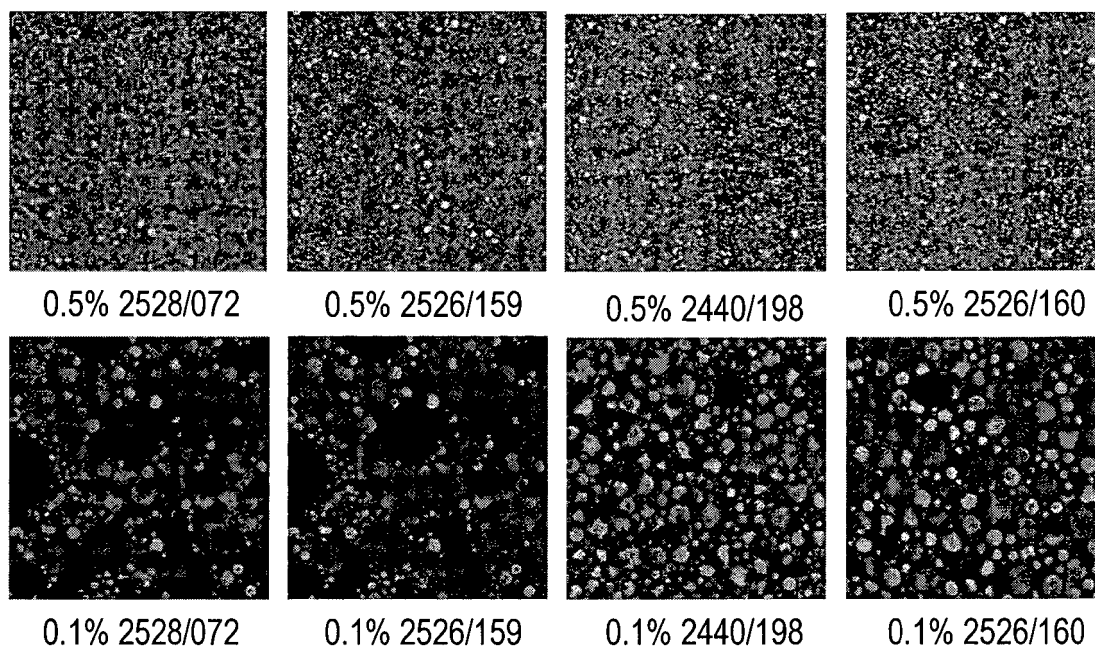
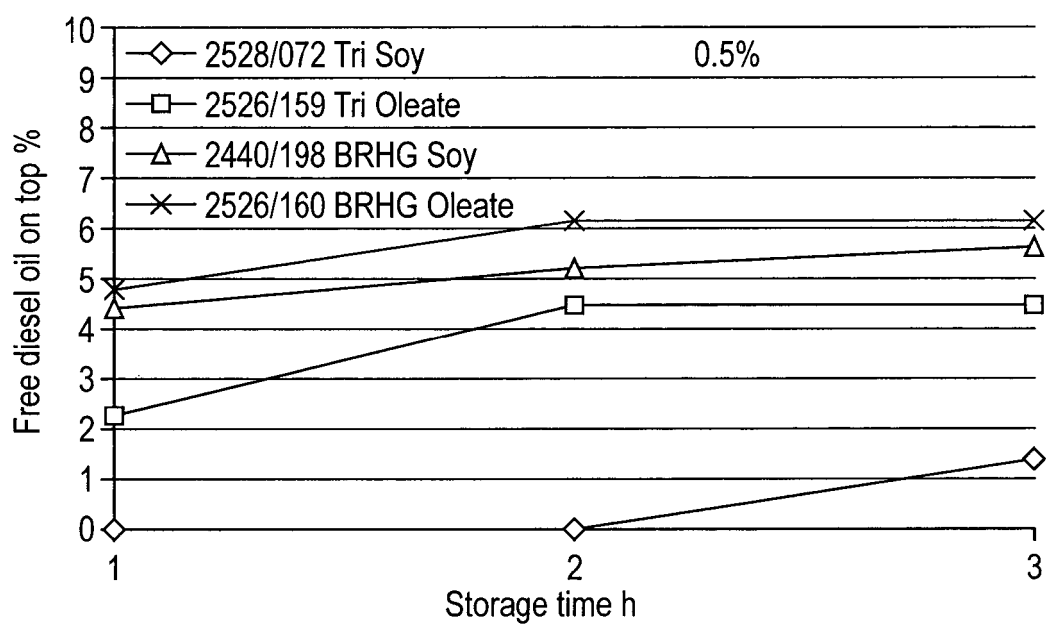
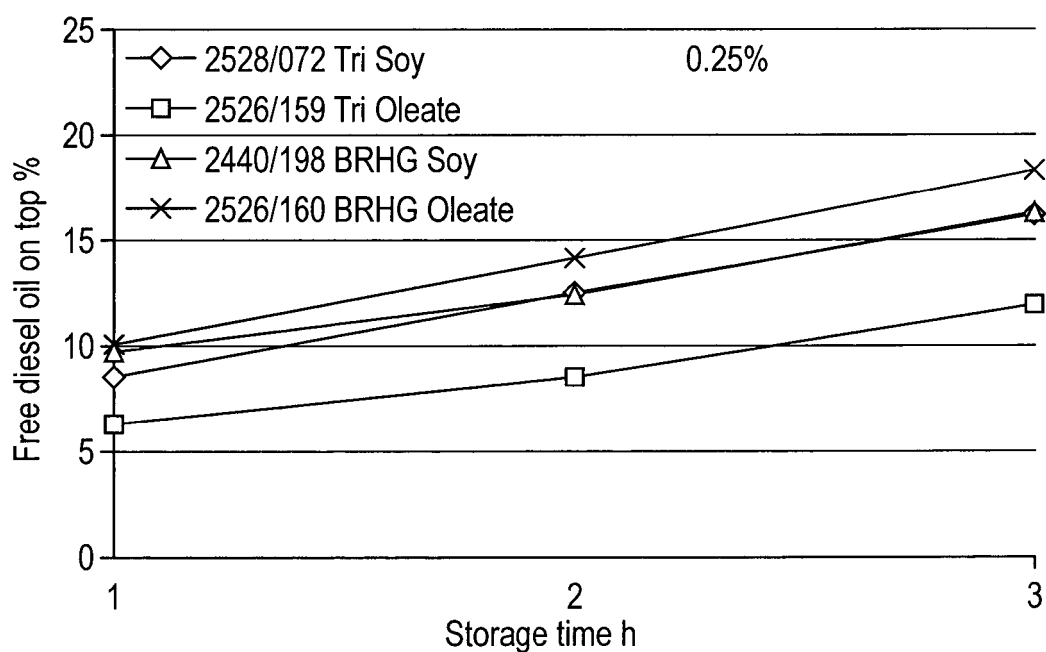


FIG. 2



Degree of sedimentation at 0.5% dosage during 3 hours storage at 55°C

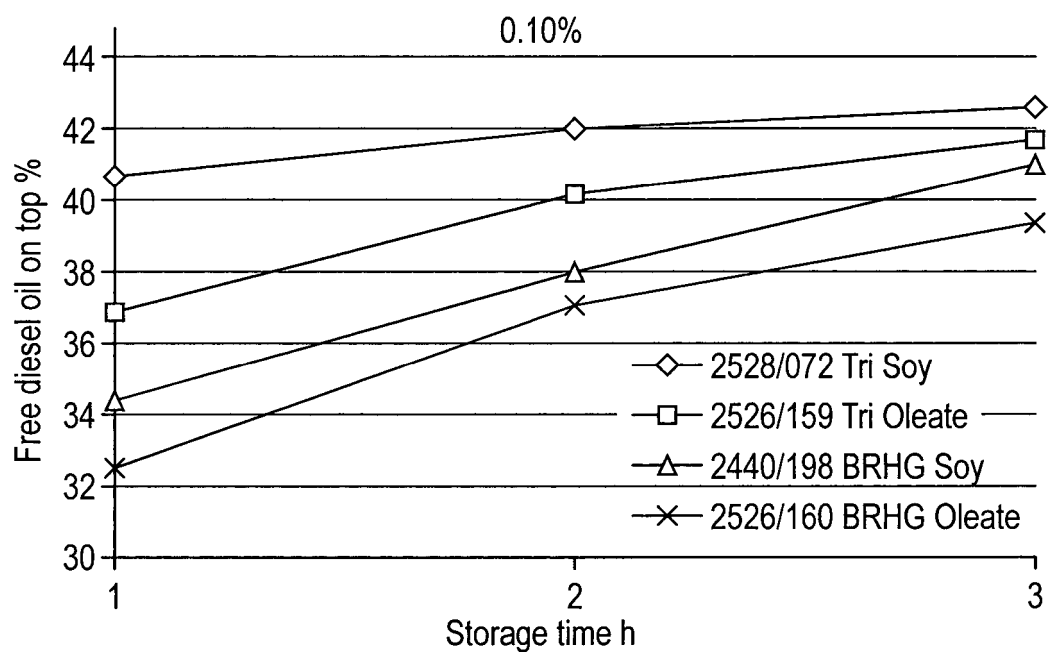
FIG. 3A



Degree of sedimentation at 0.25% dosage during 3 hours storage at 55°C

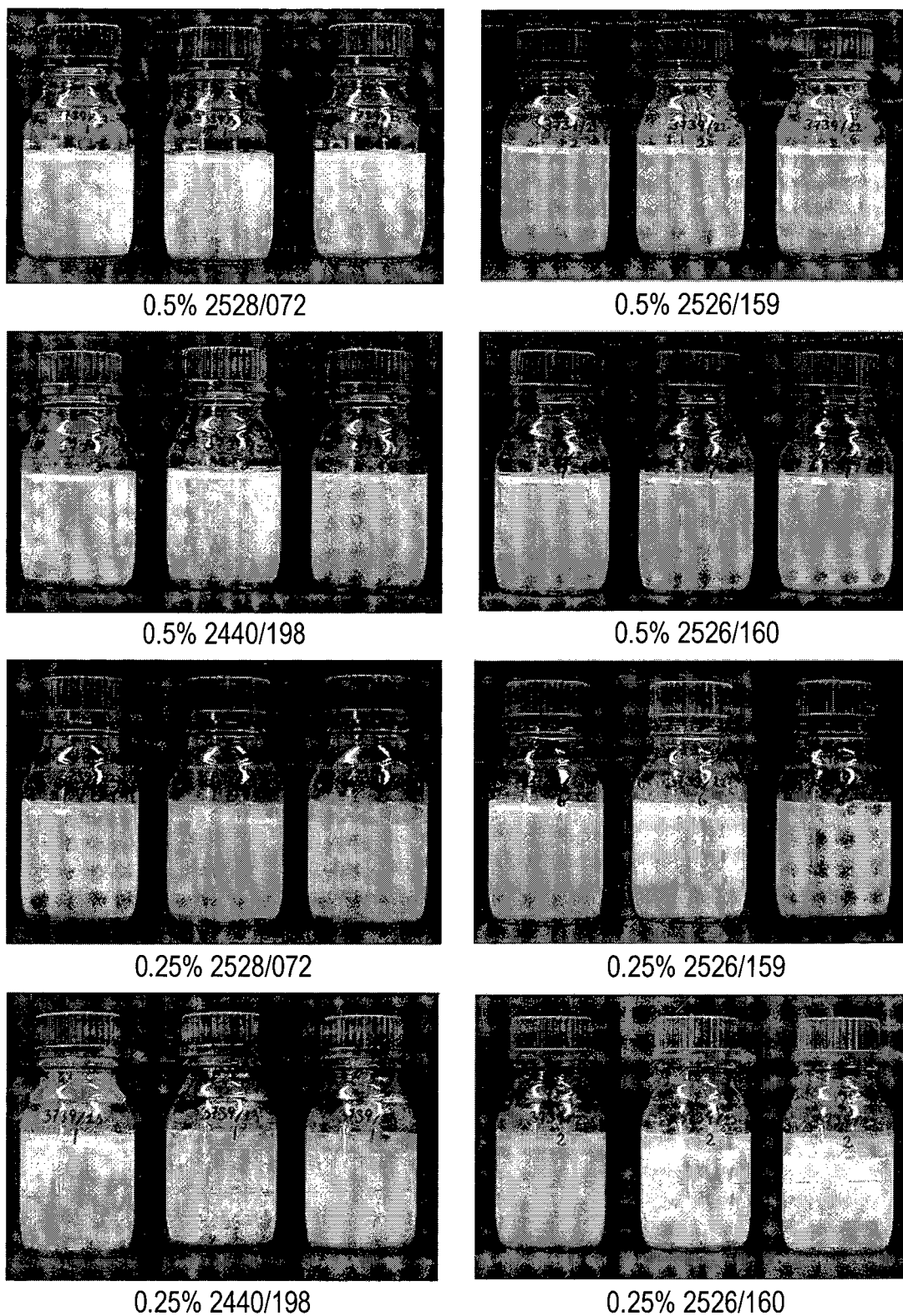
FIG. 3B





Degree of sedimentation at 0.1% dosage during 3 hours storage at 55°C

FIG. 3C



Samples during 3 hours storage at 55°C

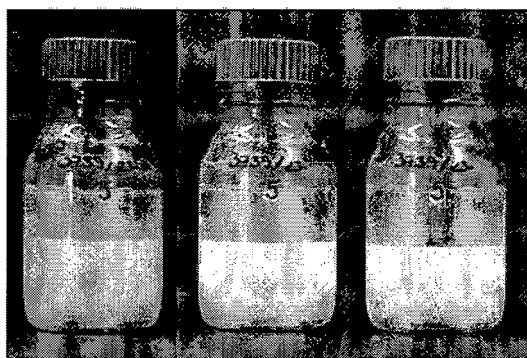
FIG. 4



0.1% 2528/072



0.1% 2526/159



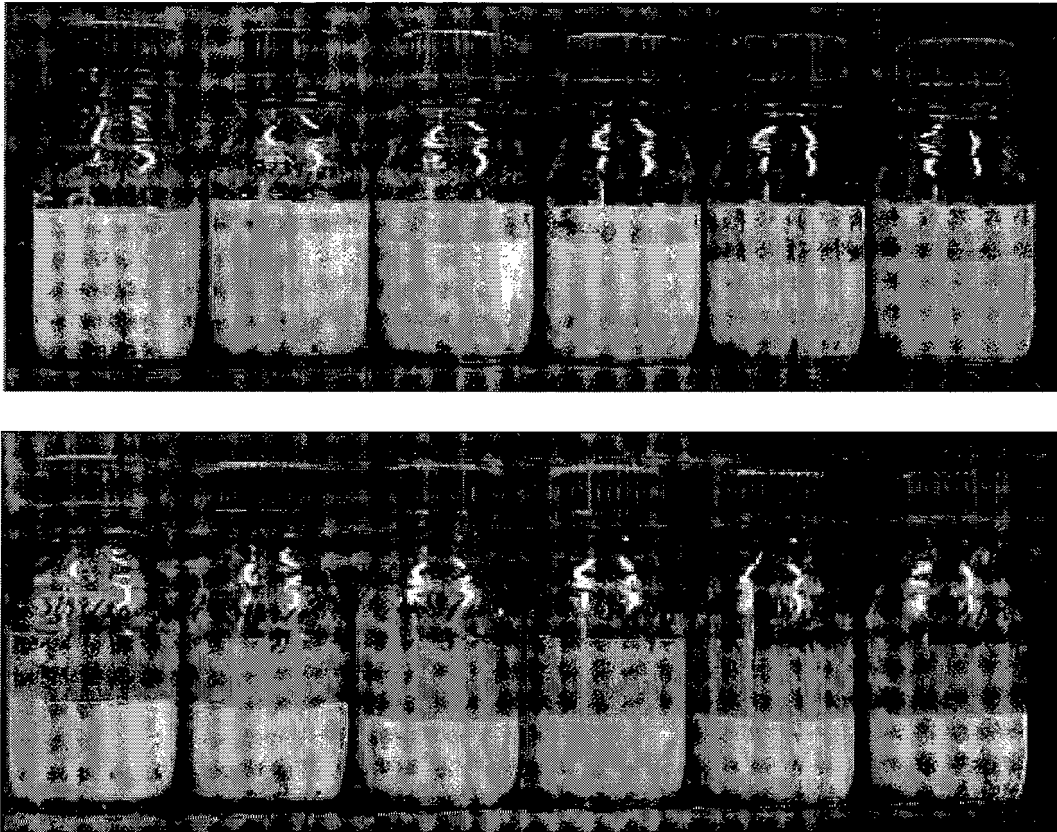
0.1% 2440/198



0.1% 2526/160

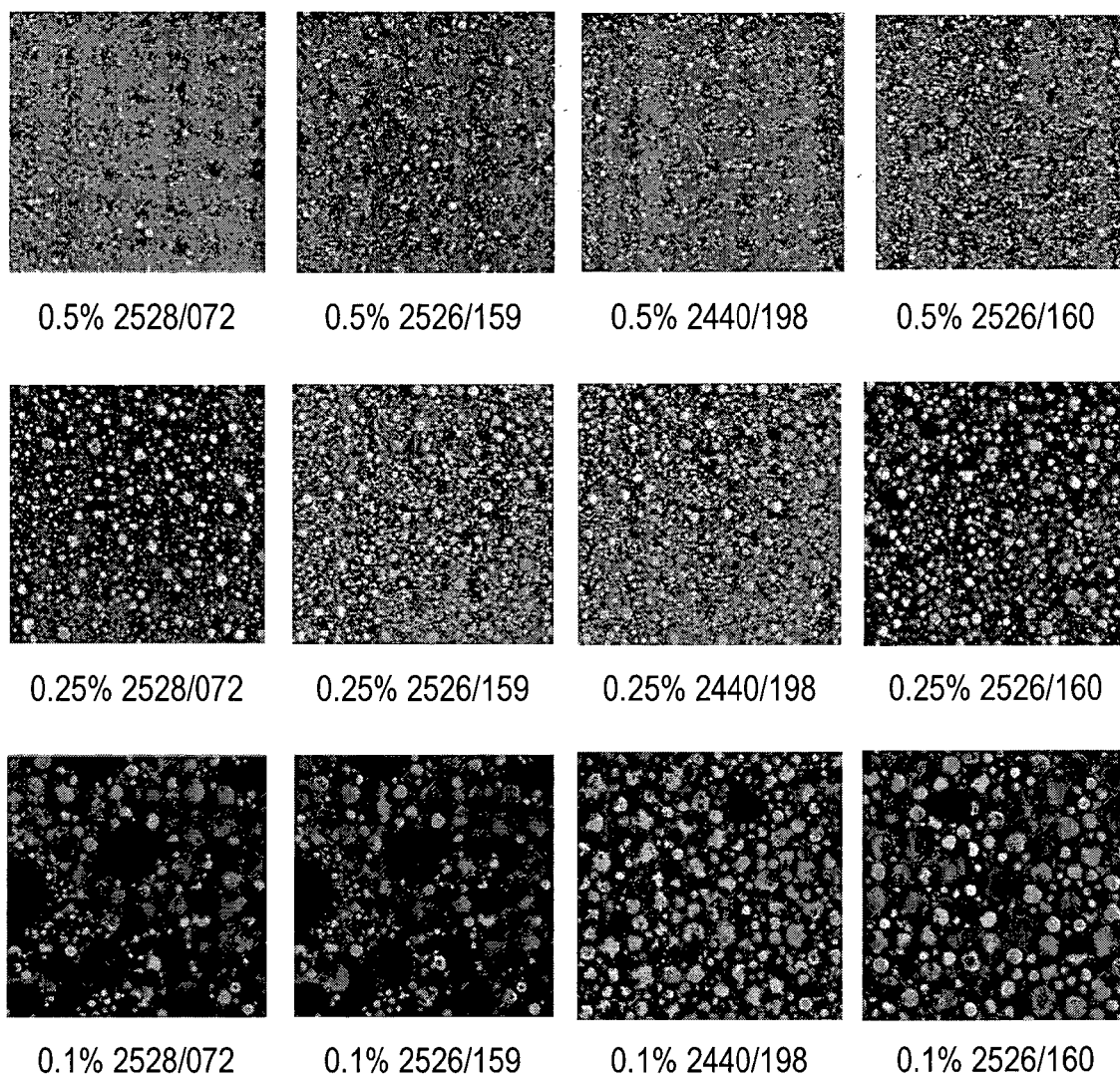
Samples during 3 hours storage at 55°C

FIG. 4 (continued)



Samples After 24 hours storage at 55°C (same sample order as above)

FIG. 5



Water droplet size by CLSM

FIG. 6

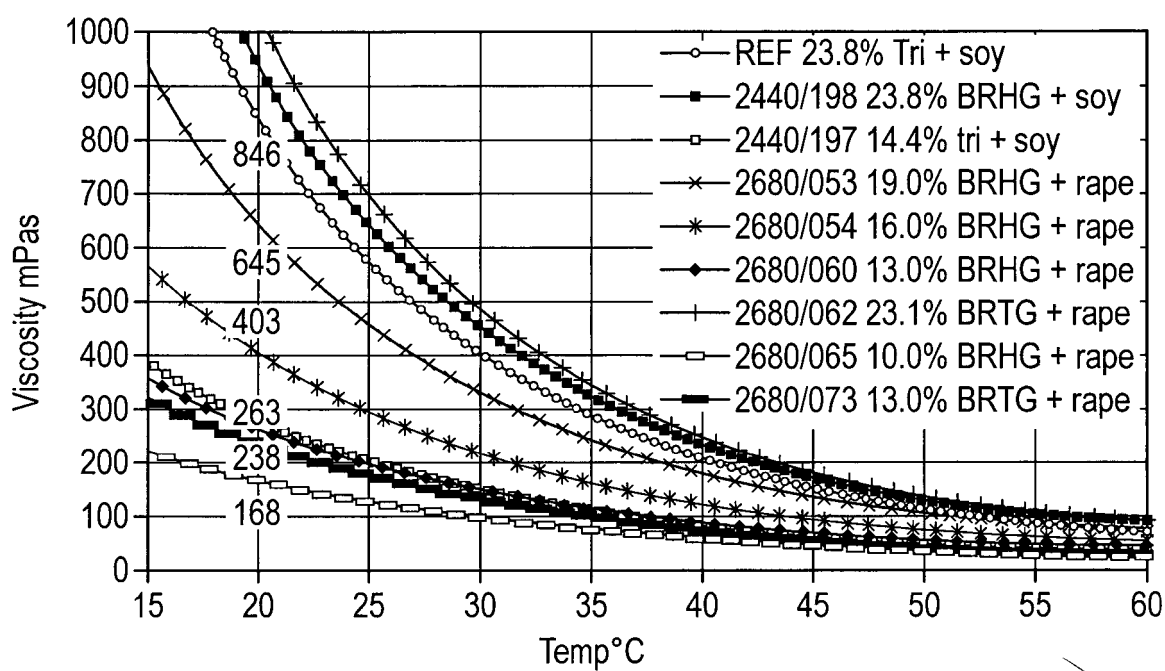


FIG. 7

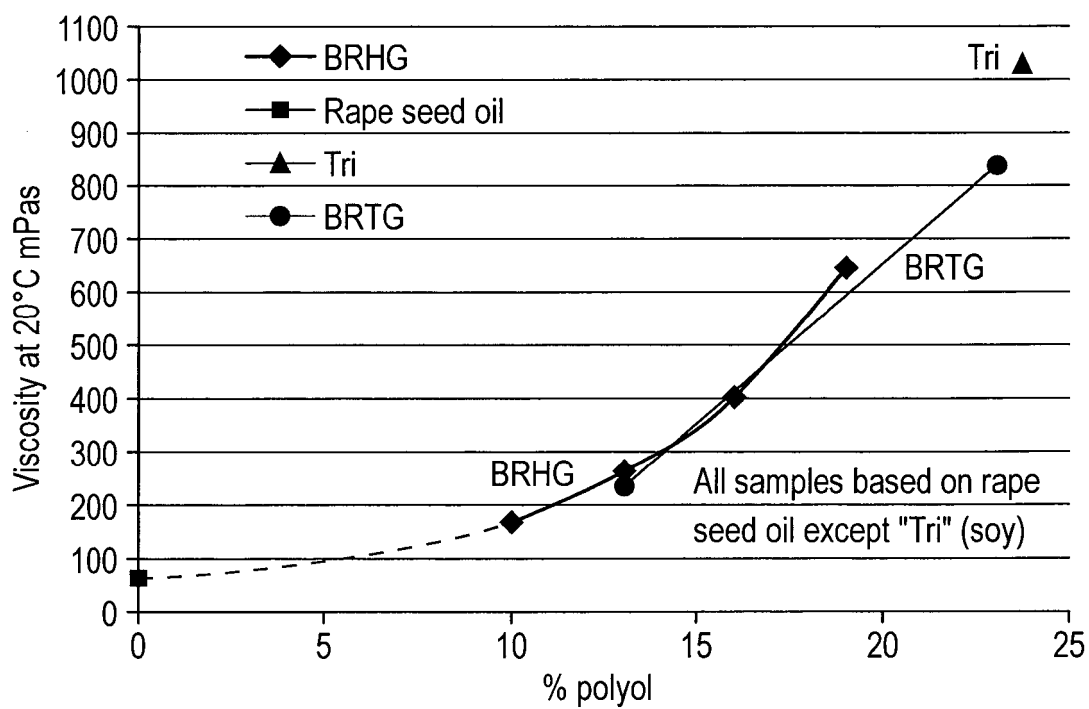
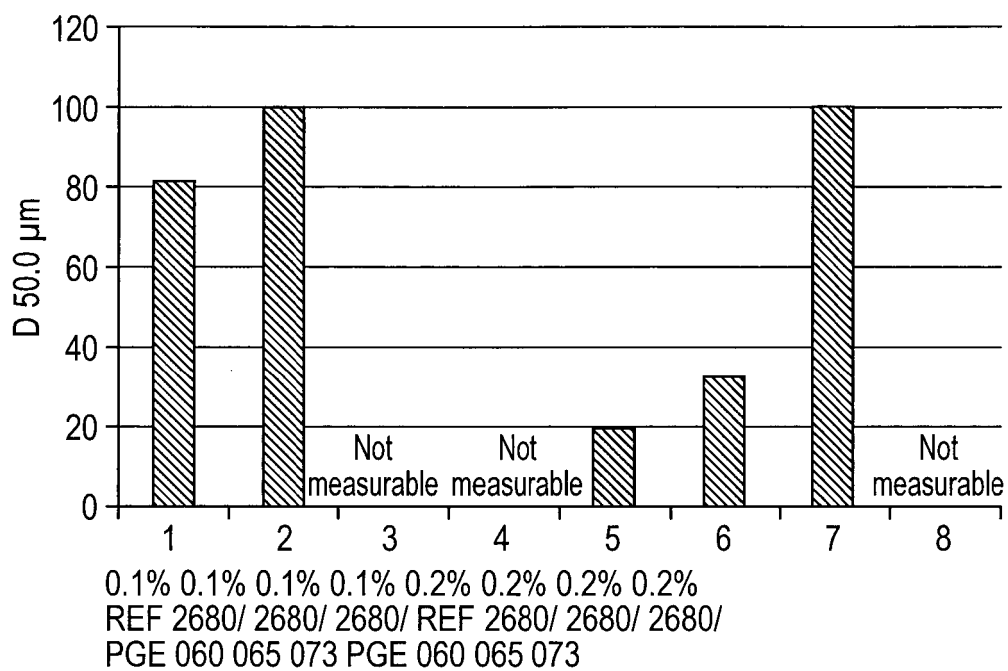


FIG. 8



D50,0 water droplet size for the WIF-emulsions

FIG. 9

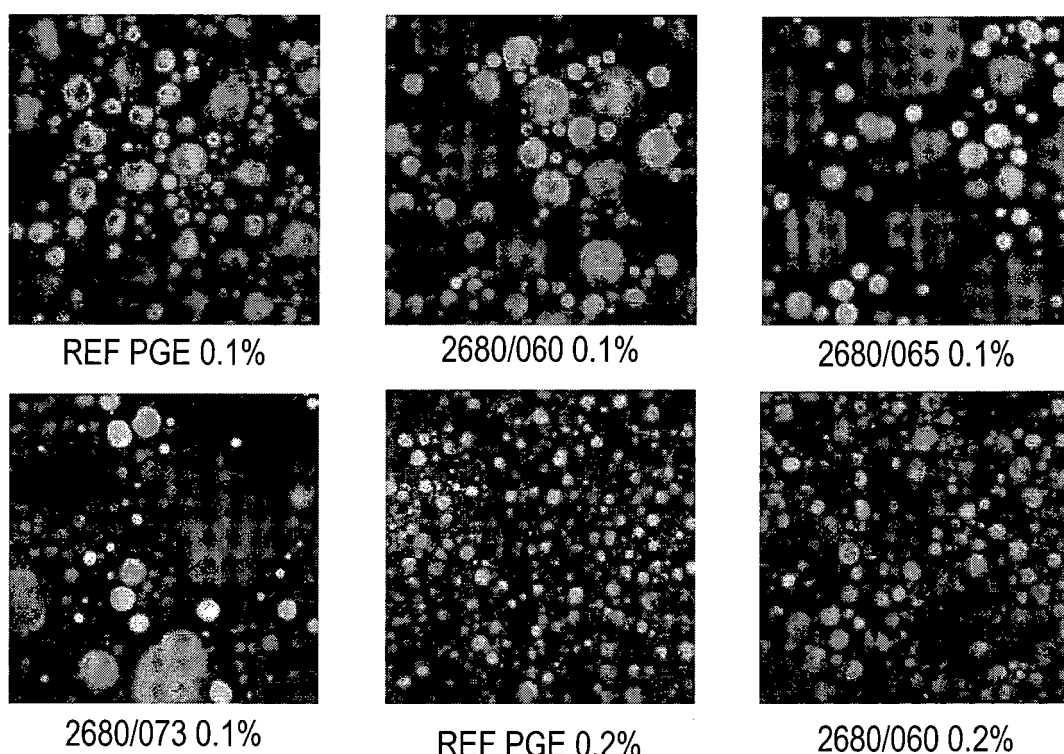


FIG. 10

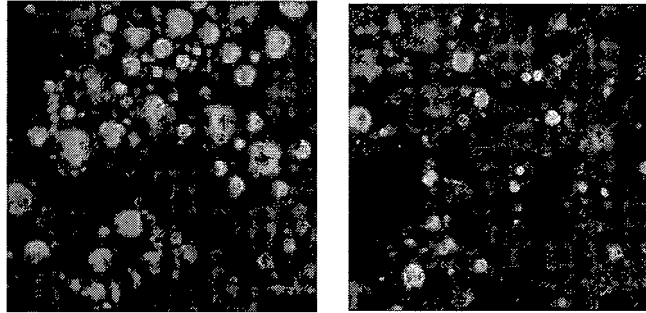


FIG. 11



FIG. 12



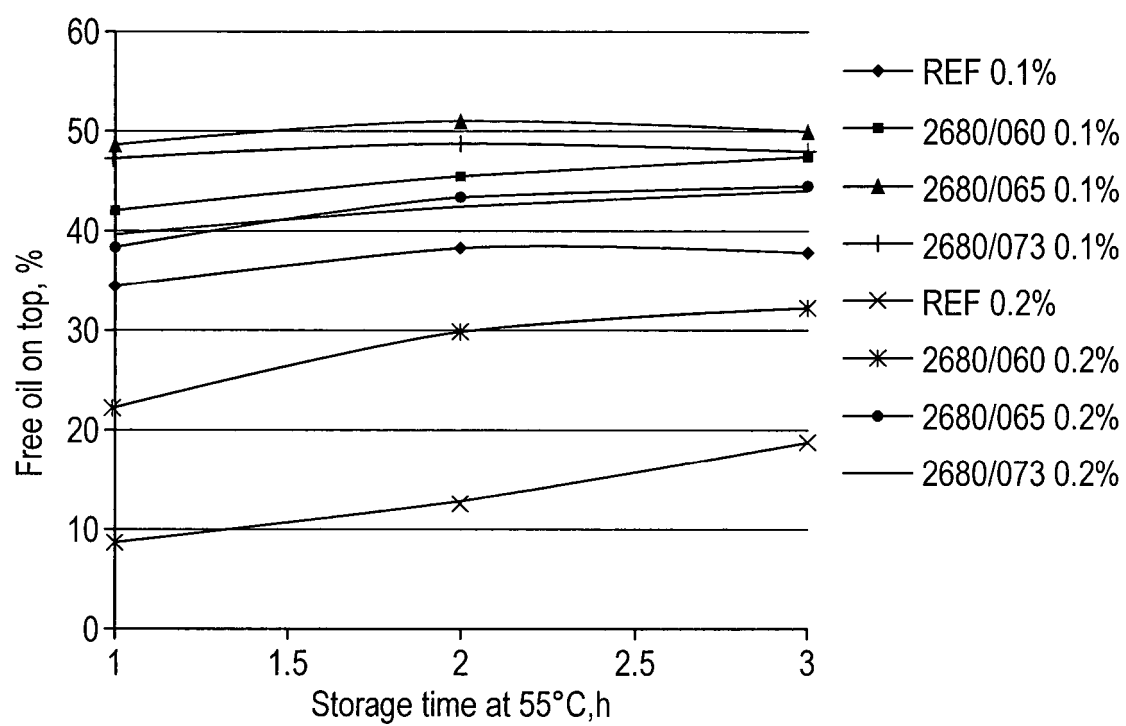


FIG. 13



REF PGE 0.1%



2680/060 0.1%



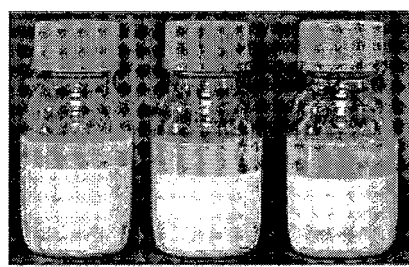
2680/065 0.1%



2680/073 0.1%



REF PGE 0.2%



2680/060 0.2%



2680/065 0.2%



2680/073 0.2%

FIG. 14

**REFERENCES CITED IN THE DESCRIPTION**

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