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- (54) Diesel fuel composition.
- Diesel fuel composition, in the form of a stable and homogeneous mixture, containing: (a) Diesel fuel; (b) a mixture of aliphatic alcohols (C1-C4 alcoholic fraction), containing more than 50% by weight of methanol, coming from the catalytic preparation processes of methanol and higher alcohols by reaction of carbon monoxide and hydrogen, and (c) an aliphatic alcohol containing from 2 to 18 carbon atoms in its molecule.

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# **DIESEL FUEL COMPOSITION**

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This invention relates to a Diesel fuel composition in the form of a stable and homogeneous mixture.

In recent years, due to the petroleum product crisis, many studies have been carried out in the field of alternative fuels and hybrid fuels.

More particularly, in the field of Diesel fuels, hybrid compositions have been proposed, which contained a fraction of alcoholic products, and especially methanol and ethanol.

The problems inhrent in such hybrid compositions stem basically from the circumstance that methanol is insoluble in Diesel fuels and that ethanol, even being soluble therein in all proportions, demixes in the presence of small quantities of water.

In order to overcome such shortcomings, there have been suggested, in the technics, compositions containing a Diesel fuel and lower alcohols, in the form of emulsions and microemulsions (obtained with the aid of one or more surface-active agents), or in the form of homogeneous mixtures (wherein homogeneousness is basically obtained with the aid of higher aliphatic alcohols).

Such known art is represented by US-A-4 451 267 and EP-AO 117 915.

The suggested approaches, however, are not completely satisfactory. As a matter of fact, high amounts of surface-active agents are generally required in order to obtain stable emulsions or microemulsions, and this is an economic liability.

On the other hand, in the compositions devoid of surface-active agents, comparatively high amounts of higher alcohols are required in order to be able to retain interesting amounts of lower alcohols. Also this fact is a liability, in view of the cost of the higher alcohols.

In the field of gasolines, there have been proposed fuel grade mixtures of methanol and higher alcohols, to be used as such as fuels, or in admixture with gasolines.

More particularly, US-A-4 481 012 discloses the preparation and the separation of a C1-C4 alcoholic fraction rich with methanol and obtained by causing carbon monoxide and hydrogen to catalytically interact.

It has now been found that such a C1-C4 alcoholic fraction, in spite of its high methanol content, is capable of giving stable and homogeneous mixtures with a Diesel fuel, in the presence of reduced amounts, and sometimes extremely reduced amounts, of an aliphatic alcohol containing at least two carbon atoms in its molecule.

By so doing, it becomes possible to solve, or

at least to undertone, the problems inherent in the hybrid Diesel fuel compositions referred to above.

Accordingly, the present invention relates to a Diesel fuel composition, in the form of a stable and homogeneous mixture, containing:

- (a) a Diesel fuel;
- (b) a mixture of aliphatic alcohols (C1-C4 alcoholic fraction) containing more than 50% by weight of methanol and coming from the catalytic methanol and higher alcohol preparation processes by reaction of carbon monoxide and hydrogen, and
- (c) an aliphatic alcohol containing from 2 to 18 carbon atoms in its molecule.

Appropriately, the composition of this invention contains the components (a) and (b) in a weight ratio of the former to the latter of from 3:1 to 7:1, whereas the component (c) is present at a concentration, on a weight basis, of from 0.1% to 6% relative to the overall composition.

Component (a) of the composition of this invention can be any petroleum cut fulfilling the ASTM-Standards for Diesel fuels. Diesel Fuel N°2 is preferred, which is the most commonly used one for commercial and agricultural vehicles. Among the several Diesel fuels, those of predominantly aromatic nature are preferred.

Component (b) of the composition of this invention is a C1-C4 alcoholic fraction as obtained in the process for preparing methanol and higher alcohols by catalytic interaction of carbon monoxide and hydrogen. More particularly, in such processes, working temperatures are usually adopted which range from 300°C to 500°C, under pressures which are equal to, or higher than 151987.75 kPa (150 abs.atm or ata), in the presence of catalysts based on copper, zinc or chromium, modified with alkali metal or alkaline earth metals. By working under such conditions, it is possibile to produce and to separate a C1-C4 alcoholic fraction, the composition of which is, on a weight basis, typically within the following ranges:

from 70% to 80% of methanol from 2% to 5% of ethanol from 5% to 10% of propanol from 12% to 15% of butanol from 0.1% to 1% of water.

Component (c) of the composition of this invention is an aliphatic alcohol which contains from 2 to 18 carbon atoms it its molecule: obviously, mixtures of such alcohols can be used.

As outlined above, the amount of component (c) in the composition can generally be varied within the range of from 0.1% to 6% on a weight basis. The accurate value of the amount of compo-

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nent (c) to be adopted in the various circumstances in order to impart both stability and homogeneousness to the composition concerned, is selected within said range, on taking into account both the nature of the component (c) concerned and that of the Diesel fuel used in said composition.

More particularly, the amount of component (c) which is necessary to achieve the purpose aforesaid is decreased as the number of carbon atoms which are present in the molecule of that component (c) is increased.

If the number of carbon atoms of component (c) is the same, the quantity of it which is required is decreased when passing from Diesel fuels of a predominantly aliphatic nature to those having a predominantly aromatic nature.

Thus, for example, using as component (a) a predominantly aromatic Diesel fuel, and with a weight ratio of component (a) to component (b) in ther order of 4:1, the quantity of component (c) is appropriately varied within a range of from about 0.5% to about 2.0% by weight when passing from a component (c) having 18 carbon atoms in its molecule, to a component (c) having two carbon atoms in its molecule.

In the case of a predominantly aliphatic Diesel fuel as the component (a) and with a weight ratio of (a) to (b), in the composition, in the order of 4:1, the quantity of the component (c) is appropriately varied within a range of from about 4% to about 6% by weight when passing from a component (c) having 16 carbon atoms in its molecule, to a component (c) having 6 carbon atoms in its molecule.

The composition according to this invention may contain, in addition to the components enumerated above, minor amounts (generally less than 1% by weight) of additives known in the art, such as improvers of the cetane number, corrosion inhibitors, metal deactivators and antioxidants.

The procedure for preparing the composition according to the present invention is not critical as itself, inasmuch as the components can be blended in any sequential order whatsoever.

In the ensuing practical examples, the component (b) which is used is a C1-C4 alcoholic fraction as obtained according to the process of US-A-4 481 012, said alcoholic fraction having the following composition, on a weight basis:

78.5% of methanol 2.4% of ethanol 5.6% of propanol 13.4% of butanol 0.1% of water.

#### **EXAMPLE 1**

A homogeneous and stable composition is prepared by using as the component (a) a predominatly aromatic Diesel fuel by AGIP PETROLI S.p.A., the component (b) being the C1-C4 alcoholic fraction referred to above, the component (c) being oleyl alcohol.

The content, on a weight basis, of the individual components of the composition is as follows:

79.60% of component (a)

19.90% of component (b)

0.50% of component (c).

#### **EXAMPLE 2**

A stable and homogeneous composition is prepared using the components (a) and (b) as in Example 1, and decyl alcohol as the component (c).

The content, on a weight basis, of the individual components of the composition is as follows:

79.45% of component (a)

19.85% of component (b)

25 0.70% of component (c).

#### **EXAMPLE 3**

A stable and homogeneous composition is prepared using the components (a) and (b) as in Example 1, hexyl alcohol being component (c).

The content, on a weight basis, of the individual components of the composition is as follows:

79.40% of component(a)

19.80% of component (b)

0.80% of component (c).

#### **EXAMPLE 4**

A homogeneous and stable composition is prepared using the components (a) and (b) of Example 1, with ethyl alcohol as the component (c).

The content, on a weight basis, of the individual components of the composition, is as follows:

78.4% of the component (a)

. 19.6% of the component (b)

2.0% of the component (c)

The compositions of Examples 1 through 4 are stored for 3 months at ambient temperature (20-25°C) and, after that period of time, they retain their stability and no demixing phenomenon is observed.

### **EXAMPLE 5**

Compositions are prepared, which contain the components (a) and (b) of Example 1 in a weight ratio of (a) to (b) equal to 4:1 and hexanol is added as the component (c).

The behaviour of such compositions is observed within a temperature range of from +25°C to -10°C: it is noted that the quantity of component (c) which is required to maintain homogeneousness and stability for the composition varies from 0.8% by weight at a temperature of +25°C to 3.5% by weight at -10°C. Even at low temperatures, storage for a long time does not originate plural-phase demixing problems, and the compositions retain their homogeneousness and transparency properties unaltered.

## **EXAMPLE** 6

A stable and homogeneous composition is prepared using, as the component (a) a predominantly aliphatic Diesel fuel, supplied by AGIP PETROLI S.p.A., the component (b) is the C1-C4 alcoholic fraction referred to above, and the component (c) is hexanol.

The content, on a weight basis, of the individual components of the composition is:

75.2% of component (a)

18.8% of component (b)

6.0% of component (c).

## **EXAMPLE 7**

A homogeneous and stable composition is prepared using the components (a) and (b) of Example 6 and decanol as the component (c).

The content, on a weight basis, of the individual components of the composition is as follows:

75.6% of component (a)

18.9% of component (b)

5.5% of component (c).

## **EXAMPLE 8**

A homogeneous and stable composition is prepared using the components (a) and (b) of Example 6, and tetradecanol as the component (c).

The content, on a weight basis, of the individual components of the composition is as follows: 75.4% of the component (a)

18.8% of the component (b) 5.8% of the component (c).

The compositions of the Examples 6 through 8 are stored for three months at the environmental temperature (20° C-25° C) and, after that period of time, they retain their stability and no demixing phenomenon is observed.

#### 10 Claims

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- 1. A Diesel fuel composition in the form of a stable and homogeneous mixture, containing:
  - (a) a Diesel fuel
- (b) a mixture of aliphatic alcohols (C1-C4 alcoholic mixture), containing more than 50% by weight of methanol, coming from catalytic processes of preparation of methanol and higher alcohols by reaction of carbon monoxide and hydrogen, and
- (c) an aliphatic alcohol containg from 2 to 18 carbon atoms in its molecule.
- 2. Composition according to claim 1, characterized in that the components (a) and (b) are present in a weight ratio of the former to the latter of from 3:1 to 7:1 and the component (c) is present at a concentration of from 0.1% to 6% by weight in said composition.
- 3. Composition according to claim 1, characterized in that the component (b) is composed, on a weight basis, of:

from 70% to 80% of methanol

from 2% to 5% of ethanol

from 5% to 10% of propanol

from 12% to 15% of butanol

from 0.1% to 1% of water.

- 4. Composition according to claim 1, characterized in that the component (a) is a predominantly aromatic Diesel fuel, the weight ratio of component (a) to component (b) is in the order of 4:1, and the component (c) is an aliphatic alcohol containing from 2 to 18 carbon atoms in its molecule and is present in an amount of from 2.0% to 0.5% by weight in the composition.
- 5. Composition according to claim 1, characterized in that the component (a) is a predominantly aliphatic Diesel fuel, the weight ratio of the component (a) to the component (b) is in the order of 4:1, and the component (c) is an aliphatic alcohol containing from 6 to 16 carbon atoms in its molecule and is present in an amount of from about 6% to about 4% by weight in the composition.
- 6. Composition according to claim 1, characterized in that it additionally contains minor amounts of one or more additives selected from among

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cetane number improvers, corrosion inhibitors, metal deactivators, and antioxidants.