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Method for the marking of oil products and of organic solvents.

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A method for the permanent marking of oil products and of organic solvents to make them easily and quickly identifiable, by the addition of an alkyl-phenyl-ketone to the oil product or organic solvent.

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METHOD FOR THE MARKING OF OIL PRODUCTS AND OF ORGANIC SOLVENTS

The present invention relates to a method for the marking of oil products and of organic solvents.

The necessity of marking oil products, such as fuel oils, petroleum fractions for motor traction and the like, e.g. gasoline, kerosene and so on, or organic solvents such as turpentine, alcohols and so on, is associated with the different selling price which the same oil product or solvent may have, because of the taxation to which it is subjected according to the final use.

In Italy, for instance, Diesel oil for agricultural or fishing purposes is taxed less than Diesel oil for motor traction.

Therefore, situations can occur such as to engender fiscal frauds by utilization of a product for purposes different from that for which it had been detaxed.

Just to avoid these frauds, some organic solvents and oil products, generally, are marked by means of a suitable substance which can allow their easy identification.

The marking substances which can be used to this purpose should be stable under the application conditions, not present in the natural products; they should be of such a type as not to affect the physico-chemical properties of the organic solvent or of the oil product, they should be sufficiently soluble and preferably their use should be allowed also in the form of concentrated solutions; they should further be eliminatable with difficulty or not quite eliminatable by physical or physico-chemical methods, usable in small amounts and moreover they should be detectable by simple, quick and sensitive analytical methods.

Numerous additives and tracing substances have been proposed and used; however, not all the substances wholly satisfy the above mentioned requirements or have certain drawbacks. Among these marking substances it is possible to mention:

- the organometallic compounds, having however poor stability to storage;
- the radioactive substances, which however require particular expedients, their handling being physiologically dangerous;
- the solvent dyestuffs, such as Solvent Red 24, 19 and the like, which however can be easily extracted from the system;
- primary, secondary and tertiary aromatic amines, which however are easily extractable by dilute acids;
- acetone, which however could be previously present in an organic solvent of the vegetable type;
- quinizarine, which has a poor solubility and therefore must be used as a powder and not in the form

of concentrated solution and can be easily removed;

- furfural, diphenylamine and naphthols which can be previously present in oil fractions and furthermore are easily removable from the system;

- cumarine (1,2-benzopyrone), which however is a lactone and is therefore easily hydrolyzed and can be removed by alkalis;

- ethylanthraquinone, which however not only has a poor solubility (and the related drawbacks), but also is difficult to detect quantitatively in the marked products.

It has now been found that it is possible to permanently mark organic solvents and oil products, avoiding the drawbacks of the known marking substances, by use of an alkyl-phenyl-ketone, containing from 1 to 4 carbon atoms in the linear or branched alkyl chain.

In particular, the use of the alkyl (C₁-C₄)-phenyl-ketone, defined according to the present invention, allows working under conditions of higher stability and sensitivity in comparison with some recent tracers which have been the subject of particular interest, such as nitro-derivatives of benzene and homologues thereof.

For instance, in comparison with meta-dinitrobenzene, the alkyl (C₁-C₄)-phenyl-ketone has the advantages of being a highly soluble liquid (possibility of preparing a liquid masterbatch), not toxic and not requiring particular expedients for handling. In comparison with nitro-xylenes, alone or in admixture, aceto-phenone, because of the absence of nitrogen in its structure, is more resistant to reducing agents and is more easily detectable and measurable, also in amounts in the order of 100 ppm, by a simpler chromatic detection text.

Therefore, the present invention provides a method for the marking of oil products and of organic solvents, characterized by the addition of a small amount of an alkyl (C₁-C₄)-phenyl-ketone as a tracing substance to said solvents or oil products.

Preferably, methyl-phenyl-ketone (acetophenone) is used.

By the above mentioned method any organic solvent can be marked, such as turpentine, acetone, alcohols, glycols, esters, aliphatic amines or any product or oil product cut, such as Diesel oil, gasoline, kerosene, benzene, toluene, xylene, aliphatic hydrocarbons and cyclohexane.

The amount of alkyl-phenyl-ketone which can be used as marking agent can vary within wide limits, the minimum amount being only dependent on the sensitivity of the detection text. Acceptable working results are obtained by weight amounts comprised from 100 to 10,000 ppm, on the marked

product.

By use of a simple and quick detection test, which will be described hereinafter, it is possible to use concentrations of 100 parts of alkylphenylketone per million parts of the organic product or of the oil product.

Generally, a much higher amount is added, so that the test is always positive if, with the intention of fraud, the marked product is diluted up to 10 times.

In practice, it is possible to use 0.1% by weight of the marking product.

By use of alkyl (C₁-C₄)-phenyl-ketones as marking substances, many advantages are obtained.

In fact, they are stable substances, which do not affect the properties of the organic solvent or of the oil product.

Because of their chemical structure, it is possible to exclude that they are naturally present in the solvents and in the oil fractions.

They can be removed with difficulty from their solutions in the oil products or in the organic solvents, for instance by treatment with acids or alkalis or by absorption with charcoal, alumina, decolourizing earths and so on.

They are practically colourless and therefore their presence in the oil products and organic solvents (for instance in solvents for lacquers, mastics and stopping) can be detected by a quite specific and sensitive test.

They are easily identifiable by a simple test, which is free from interference and has a remarkable sensitivity, even in amounts of the order of 100 ppm; furthermore it is possible to use them as tracers even in very small amounts. They are also easily prepared, have a reduced cost and are readily commercially available.

In particular, acetophenone is a known product widely used. The marking products used in the present invention can be added either as a highly concentrated solution (liquid master-batch), or as such, because they are liquids and because of their easy and complete solubility in aromatic hydrocarbons as well as in the main industrial solvents.

Suitable solvents are for instance the aromatic and/or aliphatic hydrocarbons.

The simple identification method referred to herein does not require a complicated apparatus and can be quickly performed also by a non-specialized worker.

Said method comprises bringing into contact a small volume, generally about 20 cm³, of marked oil product or of marked solvent with a certain amount of methanol, of reagent and of an aqueous-methanolic solution of potassium hydroxide, as illustrated in the examples.

The whole is agitated and, after having allowed it to stand, hexane and methyl alcohol are added, and a purple colouration appears of the aqueous layer, which reveals the presence of acetophenone.

It is possible to use chemical identification methods using a chemical detector, such as sodium nitroprussiate, 2,4-dinitrophenyl-hydrazine and so on, or physico-chemical methods, which are more sensitive, but also more complicated and less quick, for instance thin layer chromatography, gas chromatography and so on, by which methods it is possible to detect the presence of the acetophenone also if present in traces.

The invention will be further described with reference to the following illustrative Examples.

Example 1

1 g of acetophenone was dissolved in 1,000 cm³ of Diesel oil. A concentration of 1,000 ppm (w/v) was obtained without imparting any particular colouration to the oil.

20 cm³ of the marked Diesel oil were added with 10 cm³ of methanol, pure for analysis and 5 cm³ of a methanolic saturated solution of 2,4-dinitrophenylhydrazine and then stirred for 20 seconds and thereafter allowed to stand for 5 minutes. 5 cm³ of a 10% solution of sodium hydroxide in methanol-water (80-20) were added. After 1 minute 20 cm³ of ethanol and 30 cm³ of hexane were added. Two layers were obtained, the lowermost showing an intense purple colour and the uppermost one being colourless.

When the test was carried out on un-marked Diesel oil, the lower layer remained practically colourless.

Example 2

100 cm³ of the marked Diesel oil of the preceding example were mixed with 900 cm³ of un-marked Diesel oil.

1,000 cm³ were obtained of a mixture containing 100 ppm of tracer. On 20 cm³ of the marked Diesel oil the test was carried out as described in Example 1. Two layers were obtained, the lower of which was coloured purple with a much lower intensity than that of the Example 1, but nevertheless still apparent.

Example 3

1 g of acetophenone was dissolved in 1,000 cm³ of gasoline. A concentration of 1,000 ppm was obtained without any particular colouration of the

gasoline. 100 cm³ of marked gasoline were added to 900 cm³ of un-marked gasoline. 1,000 cm³ were obtained of gasoline containing 100 ppm of tracer. 20 cm³ of this mixture were handled as described in example 1 and, also in this case, after 5 minutes a purple colouration was obtained. By carrying out the test on 20 cm³ of un-marked gasoline no colouration was obtained.

Analogous results were obtained by use of the so-called "ecological" (environmental) gasolines.

Example 4

1 g of acetophenone was dissolved in 1,000 cm³ of kerosene. A concentration of 1,000 ppm (w/v) was obtained without any particular colouration of the kerosene. 100 cm³ of the marked kerosene were added to 900 cm³ of un-marked kerosene, thus obtaining 1,000 cm³ of a mixture containing 100 ppm of tracer. By proceeding as described in Example 1, on 20 cm³ of this mixture, a purple colouration was obtained. When the test was carried out on 20 cm³ of un-marked kerosene, no colouration was obtained.

Example 5

1 g of acetophenone was dissolved in 1,000 cm³ of toluene. A concentration of 1,000 ppm (w/v) was obtained, without any colouration of the toluene. 100 cm³ of marked toluene were added to 900 cm³ of un-marked toluene, thus obtaining 1,000 cm³ of toluene containing 100 ppm of the tracer. The test procedure was carried out on 20 cm³ of this mixture as described in Example 1, and after 5-10 minutes a purple colouration was obtained. When the test is carried out on 20 cm³ of un-marked toluene, no colouration was obtained.

Similar behaviour was shown by benzene, xylenes, cyclohexane, hexane, acetone and other similar products.

Example 6

1 g of acetophenone was dissolved in 1,000 cm³ of ethyl alcohol. A concentration of 1,000 ppm (w/v) was obtained without any particular colouration of the ethyl alcohol. 100 cm³ of marked ethyl alcohol were added to 900 cm³ of un-marked ethyl alcohol, thus obtaining 1,000 cm³ of mixture containing 100 ppm of the tracer. 10 cm³ of this mixture were treated as described in Example 1 and after about 10 minutes a purple colouration was obtained. By carrying out the test on un-marked ethyl alcohol, no colouration was obtained.

Similar behaviour was observed also with other alcohols and glycols, for example methyl alcohol, ethylene glycol, diethylene glycol-monobutyl ether and butyl acetate.

Claims

1. A method for the marking of oil products and of organic solvents, characterized by the addition to said oil product or solvent of a small amount of an alkyl (C₁-C₄)-phenyl-ketone.

2. A method as claimed in Claim 1, characterized in that the alkyl (C₁-C₄)-phenyl-ketone is methyl-phenyl-ketone (acetophenone).

3. A method as claimed in Claim 1 or 2, characterized in that the alkyl (C₁-C₄)-phenyl-ketone is added in an amount from 100 to 10,000 ppm.

4. Oil products and solvents, when marked with small amounts of acetophenone.