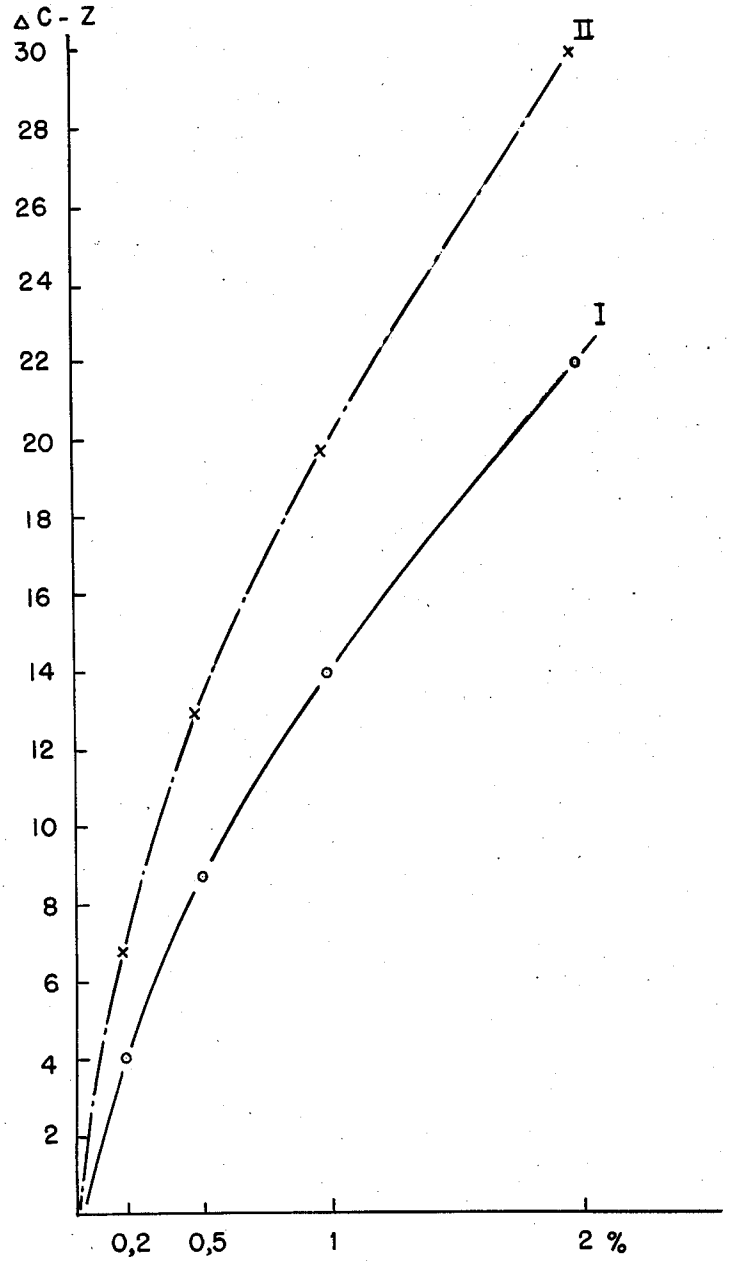
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DIFFICULTLY HYDROLYSABLE ADDITIVES FOR DIESEL FUELS

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DIFFICULTLY HYDROLYSABLE ADDITIVES FOR DIESEL FUELS

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This invention relates to the improvement of diesel fuels.

The increase in the consumption of diesel fuels has led in many countries to a scarcity of hydrogen-rich products so that it is often necessary to use diesel oils poor in hydrogen, such as are obtained for example by cracking, which have relatively low cetane numbers, and to raise the cetane number of these oils by the addition of ignition improvers. As additives for improving cetane numbers there have hitherto been proposed a large number of chemical compounds, including nitrates (see for example Marder: "Motorenkraftstoffe," page 347 et seq.).

The known nitrate-containing ignition improvers, however, have the disadvantage that in general they are relatively readily saponifiable. For example when diesel oils which contain amyl nitrate as the ignition improver most usually employed, come into contact with water, a hydrolysis of the amyl nitrate takes place and the nitric acid thereby split off causes a corrosion of the storage container. This corrosion is practically unavoidable especially when using diesel oils in shipping traffic, because the diesel oil comes into contact with seat water by filling up the tanks.

We have now found that nitric acid esters of hydroaromatic or cycloaliphatic alcohols are especially well suited as additives to diesel fuels. They not only increase the ignition quality of the diesel fuels but are also products which are hydrolysable only with difficulty.

As nitric acid esters of hydroaromatic or cycloaliphatic alcohols there come into question especially: cyclopentanol nitrate, cyclohexanol nitrate, the different isomers of methylcyclohexanol nitrate, the different isomers of dimethylcyclohexanol nitrate, ethylcyclohexanol nitrate, diethylcyclohexanol nitrate, cyclooctanol nitrate and decahydronaphthol nitrate.

The fact that the nitric acid esters of the foregoing saturated cycloaliphatic alcohols are difficulty saponifiable may be seen from the following table in which the saponification numbers of amyl nitrate and cyclohexanol nitrate in an excess of half-normal methanolic caustic potash solution are given. Whereas after boiling for 6 hours at the boiling point of the methanolic caustic potash solution about 20% by volume of the amyl nitrate has been saponified, scarcely any saponification has taken place in the case of the cyclohexanol nitrate.

TABLE

Product	Saponification number				
	½ hour	1 hour	2 hours	3 hours	6 hours
amyl nitrate	16	32	45	56	85
cyclohexanol nitrate	1	2	5	6	6

As a rule the diesel fuel should contain between about 0.1% and 3 or more percent by weight of the nitric acid esters of hydroaromatic or cycloaliphatic alcohols.

The following examples will further illustrate this invention but the invention is not restricted to these examples.

Example 1

The increase in the cetane number as compared with the fundamental cetane number of a gas oil without the addition of additive (ΔC–Z) is shown in the accompanying drawing for amyl nitrate according to the amount of amyl nitrate added in the case of a cracking diesel oil in curve I. It will be clearly seen that the effect of an equal amount of cyclohexanol nitrate in raising the cetane number according to curve II is far greater than in the case of amyl nitrate.

Example 2

The increase in the saponification number in a diesel oil to which 2% by volume of amyl nitrate have been added as compared with the same diesel oil to which 2% by volume of cyclohexanol nitrate have been added may be seen from the next table.

The diesel oil is boiled for 3 hours under reflux with an excess of half-normal methanolic caustic potash solution. The cyclohexanol nitrate in the diesel oil is practically unattacked, while the amyl nitrate in the diesel oil has reacted substantially after a few hours.

TABLE GIVING SAPONIFICATION NUMBERS OF DIESEL OIL CONTAINING 2% BY VOLUME OF AN AGENT FOR IMPROVING THE CETANE NUMBER

Material treated	Saponification number after boiling for 3 hours
Diesel oil without addition	0
Diesel oil+amyl nitrate	16.7
Diesel oil+cyclohexanol nitrate	0

Example 3

Samples of gas oil which contain 1% by volume of cyclohexanol nitrate are rolled at room temperature for an hour with seat water in rolling flasks. Strips of clean sheet iron of the same size and the same weight are previously laid in the flasks.

Further samples which contain 1% by volume of amyl nitrate and samples which contain no additives for increasing cetane number (blank value) are treated under the same conditions.

In the flasks containing gas oil to which amyl nitrate has been added, there is surface attack clearly visible on the sheet iron even after one hour, whereas the sheet iron in the gas oil to which 1% by volume of cyclohexanol nitrate has been added, and in the blank sample, is practically unattacked.

Example 4

The good effect of the ignition improvers according to this invention may be seen from the following table, the additions having been made in each case to a diesel fuel having a cetane value (C.Z.) of 50:

Addition	C.Z.	Increase in C.Z.
0.2% of cyclopentanol nitrate	57.0	7.0
0.5% of cyclopentanol nitrate	64.5	14.5
1.0% of cyclopentanol nitrate	72.0	22.0
0.2% of cyclohexanol nitrate	56.5	6.5
0.5% of cyclohexanol nitrate	64.0	14.0
1.0% of cyclohexanol nitrate	70.0	20.0
2.0% of cyclohexanol nitrate	81.0	31.0
0.2% of methylcyclohexanol nitrate	56.0	6.0
0.5% of methylcyclohexanol nitrate	60.0	10.0
1.0% of methylcyclohexanol nitrate	68.0	18.0
0.2% of dimethylcyclohexanol nitrate	56.0	6.0
0.5% of dimethylcyclohexanol nitrare	61.0	11.0
1.0% of dimethylcyclohexanol nitrate	67.0	17.0

Example 5

0.5% by weight of decahydronaphthol nitrate (i.e. the nitric acid ester of decahydro-β-naphthol) is added to a gas oil having a fundamental cetane number of 50. The cetane number is increased by this addition to 62.

If decahydronaphthol nitrate is boiled for three hours with a large excess of half-normal methyl alcoholic caustic potash solution, a saponification number of only 2.8 is obtained. Decahydronaphthol nitrate is thus far more stable to hydrolysis than amyl nitrate.

Example 6

0.5% by weight of cyclo-octanol nitrate is added to a diesel oil having a fundamental cetane number of 50. The cetane number is increased to 60 by this addition.

What we claim is:

1. As a new composition of matter, a diesel fuel containing the nitric acid ester of a cycloalkyl alcohol in an amount sufficient to increase the cetane number of said fuel.

2. As a new composition of matter, a diesel fuel containing the nitric acid ester of cyclopentanol in an amount sufficient to increase the cetane number of said fuel.

3. As a new composition of matter, a diesel fuel containing the nitric acid ester of cyclohexanol in an amount sufficient to increase the cetane number of said fuel.

4. As a new composition of matter, a diesel fuel containing the nitric acid ester of a methylcyclohexanol in an amount sufficient to increase the cetane number of said fuel.

5. As a new composition of matter, a diesel fuel containing the nitric acid ester of a dimethylcyclohexanol in an amount sufficient to increase the cetane number of said fuel.

6. As a new composition of matter, a diesel fuel containing the nitric acid ester of cyclooctanol in an amount sufficient to increase the cetane number of said fuel.

7. As a new composition of matter, a diesel fuel containing the nitric acid ester of decahydronaphthol in an amount sufficient to increase the cetane number of said fuel.

8. As a new composition of matter, a diesel fuel containing the nitric acid ester of an ethylcyclohexanol in an amount sufficient to increase the cetane number of said fuel.

9. As a new composition of matter, a diesel fuel containing about 0.1% to 3% by weight of the nitric acid ester of a cycloalkyl alcohol.

10. As a new composition of matter, a diesel fuel containing about 0.1% to 3% by weight of the nitric acid ester of an alkylcyclohexanol.

11. As a new composition of matter, a diesel fuel containing about 0.1% to 3% by weight of the nitric acid ester of cyclohexanol.

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