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REFINING USED LUBRICATING OILS WITH SULFURIC ACID AND HYDROGENATION

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This invention relates to a process for re-refining used engine lubricating oils or used industrial lubricating oils containing also engine-lubricating oils.

The expression "used lubricating oil" relates to engine and industrial lubricating oils which, due to their use, do not comply with their original composition.

It is known that the collection and re-refining of the used lubricating oils is realized throughout the world and mainly in the countries having no suitable home petroleum basis.

The known processes serving for the re-refining (regeneration) of used lubricating oils employ a regeneration process using a treatment with sulphuric-acid and bleaching earth or with a solvent or both. The object of these processes is to extract from the used lubricating oil the changed lubricating-oil components and the impurities, and thereby to recover in pure form the unchanged part of the primary lubricant. The disadvantage of these processes is that they are not economic because they work with high losses, especially if the engine-lubricating oil component of the starting material, i.e., used lubricating oil has to be recovered in a quality corresponding to that of the primary lubricant. In such cases, the losses often attain even 60%.

The object of the invention is to eliminate the above-described disadvantages and to provide a regenerating process which makes it possible to utilize the changed components, as well as to recover in practically unchanged quantity the engine-lubricating and other lubricating components of the used lubricating oil.

With the aid of the process according to the invention it is possible to recover from used lubricating oils products of better quality than that of the primary lubricants. Accordingly, the prior art view, according to which the properties of the re-refined lubricant cannot be better than those of the primary lubricant, is not applicable to the product obtained in accordance with the present invention.

The invention resides in a process for re-refining used engine-lubricating oils or used industrial lubricating oils containing also engine-lubricating oils, comprising the steps of prepurifying the used lubricating oil with a coagulating agent and/or by vacuum distillation and subjecting the prepurified used lubricating oil to catalytic hydrogenation under a pressure of 15 to 50, preferably 20 to 40 atm., at a temperature of 280 to 380° C., preferably 320 to 360° C., with a space velocity of 0.5 to 2.0, preferably 0.5 to 1.0 liter/liter/hour and with a gas-liquid ratio of 10 to 120 Nm³/m³, preferably 20 to 80 Nm³/m³, in the presence of a hydrotreating catalyst and, if desired, fractionating the obtained re-refined lubricant.

As the pressure of the hydrogenation according to the invention can be varied between 20 and 40 atm., in the practice the hydrogen-rich products of the catalytic refining process can be very advantageously used under their own pressure of about 20 to 40 atm. Pure hydrogen or synthesis gas can be also advantageously employed. Used engine lubricating oils containing gas oil may also be processed according to the invention.

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A great advantage of the invention consists in the fact that, as contrasted with the conventional regeneration processes consisting of several steps, it consists but of two steps, namely, of pre-cleaning and hydrogenation. Moreover, it ensures, at considerably lower costs, a high yield, especially of the most valuable engine lubricating oils.

Nickel oxide and molybdenum trioxide on an aluminum-oxide carrier, preferably on gamma-aluminum-oxide, can be advantageously used as catalyst. The catalyst may contain other metal oxides, such as ferric oxide and silica as well. The nickel and molybdenum oxides can be preferably used with a NiO:MoO₃ ratio of 4-12:6-20. The following composition of the catalyst has been found very advantageous:

NiO, 4-5 parts
MoO₃, 15-17 parts
SiO₂, 0-5 parts, preferably 0-2 parts
Fe₂O₃, 0-15 parts, preferably 5-10 parts.

It is advantageous to sulphidize the catalyst before use, which, according to our experiments, is very favourable from the point of view of ensuring a durable activity. Moreover, it has been established that the activity of the catalyst is advantageously influenced by activating it before use in the hydrogenating reactor itself. The essence of the activating treatment is to pass over the catalyst a gas or an oil, preferably gas oil, containing hydrogen and at least 0.1% by weight of bound sulphur, under atmospheric or higher pressures, at temperatures exceeding 200° C., for 4 to 12 hours.

Other known activating treatments can be employed as well.

The process according to the invention gives a product of suitable viscosity, viscosity index, pour point and flash point, colour and odour. The oxidation stability of the product is better than that of the primary lubricants obtained by conventional methods. A further advantage of the invention is that it can be employed in the existing oil-hydrogenating or desulphurizing works, without requiring new installations. Moreover, used lubricating oils originating from mixed collection can be also employed as the basic material for the re-refining process.

The process according to the invention is further illustrated by the following examples.

EXAMPLE 1

A used lubricating oil consisting of used engine-oils and used industrial lubricating oils and containing 7% by weight of water is treated with 5% by weight of concentrated sulphuric acid. In this way, with a loss of 17.5% by weight, 82.5% by weight of prepurified used oil are obtained. This oil is hydrogenated at a pressure of 40 atm., a temperature of 360° C., with a space velocity of 0.5 liter/liter/hour and with a gas-liquid ratio of 0.1 Nm³/liter, with a synthesis gas containing 75% by volume of hydrogen and 25% by volume of nitrogen, using a catalyst consisting of 4.5% by weight of nickel oxide, 16% by weight of molybdenum trioxide, 2% by weight of silica and 7% by weight of iron oxide, on a carrier of gamma aluminum oxide. Before use, the catalyst was heat-treated in the hydrogenation reactor in a stream of synthesis gas at 200° C., whereafter the catalyst was sulphided under a pressure of 40 atm., at a temperature of 350° C., with a space velocity of 1.0 liter/liter/hour, with a gas-liquid ratio of 0.5 Nm³/liter, with a gas oil containing 2% by weight of bound sulphur.

The hydrogenated product leaving the reactor is fractionated under vacuum. In this way, the following prod-

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ucts are obtained, in percent by weight with reference to the used oil forming the starting material:

	Percent by weight
Re-refined engine oil	48.2
Re-refined gas oil and industrial lubricating oil distillates	32.5
Prepurification losses	17.5
Hydrogenation and distillation losses	1.8
Total	100.0

Properties of the re-refined engine oil:

Conradson residue, percent by weight	0.09
Viscosity at 50° C. cst.	66.8
Viscosity ratio (V_2/V_1)	1.35
Conradson difference (C_2-C_1)	1.04

The same used lubricating oil is prepurified by the same method and the 82.5% by weight of prepurified used oil obtained is processed by the conventional re-refining technology, that is by distilling the prepurified used oil under vacuum, extracting the fraction containing the engine oils with furfural and treating the thus-obtained solvent raffinate as well as the distillates containing lubricating oils with sulphuric acid and bleaching earth. In this way the following products are obtained:

	Percent by weight
Gas oil and industrial use oils	38.9
Re-refined engine oil	26.4
Heating oil	8.5
Prepurification losses	17.5
Regeneration losses	8.7
Total	100.0

The thus-obtained re-refined engine oil has the following properties:

Viscosity index	79
Conradson residue, percent by weight	0.15
Viscosity at 50° C., cst.	59.8
Viscosity ratio (V_2/V_1)	1.5
Conradson difference (C_2-C_1)	1.4

By the above data it is shown that by following the process of the present invention re-refined engine oils are obtained in a considerably higher yield and better quality, and the other products of lower boiling point are of better quality too.

EXAMPLE 2

One proceeds as described in Example 1, with the difference that the hydrogenation is carried out at 320° C., with a space velocity of 0.5 liter/liter/hour, with a gas-liquid ratio of 0.05 Nm.³/liter, under a pressure of 35 atm. with reforming gas containing 90% by volume of hydrogen and 10% by volume of light hydrocarbons. The composition of the catalyst is the same as described in Example 1 but before use, the catalyst was pretreated in the hydrogenating reactor at 210° C. with synthesis gas and then it was sulphided under a pressure of 20 atm. at 360° C. with synthesis gas containing 2% by weight of CS₂.

In this manner the following products are obtained:

	Percent by weight
Re-refined engine oil	54.1
Re-refined gas oil and industrial lubricating oil distillates	26.9
Prepurification losses	17.5
Hydrogen and distillation losses	1.5
Total:	100.0

Properties of the re-refined engine oil:

Viscosity index	75
Conradson residue, percent by weight	0.19
Viscosity at 50° C., cst.	72.6
Viscosity ratio (V_2/V_1)	1.38
Conradson difference (C_2-C_1)	1.08

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EXAMPLE 3

One proceeds as described in Example 1 but after prepurification with sulphuric acid, the prepurified used oil is subjected to distillation under vacuum and thereby the components boiling under 420° C. are distilled off and the distillation residue containing the used engine oil is processed as in Example 1. In this way the following products are obtained:

	Percent by weight
Re-refined engine oil	58.2
Gas oil and industrial lubricating oil distillates	22.8
Prepurification losses	17.5
Hydrogenation and distillation losses	1.5
Total	100.0

Properties of the re-refined engine oil obtained:

Viscosity index	80
Conradson residue, percent by weight	0.15
Viscosity at 50° C., cst.	53.66
Viscosity ratio (V_2/V_1)	1.54
Conradson difference (C_2-C_1)	0.86

EXAMPLE 4

One proceeds as described in Example 3, with the difference that the distillation residue is hydrogenated at a temperature of 355° C., with a space velocity of 0.25 liter/liter/hour, with a gas-liquid ratio of 0.12 Nm.³/liter, under a pressure of 20 atm. with synthesis gas containing 75% by volume of hydrogen and 25% by volume of nitrogen. In this way the following products are obtained:

	Percent by weight
Re-refined engine oil	57.8
Gas oil and industrial lubricating oil distillates	22.8
Prepurification losses	17.5
Hydrogenation and distillation losses	1.9
Total	100.0

Properties of the thus-obtained re-refined engine oil:

Viscosity index	85
Conradson residue, percent by weight	0.18
Viscosity at 50° C., cst.	46.24
Viscosity ratio (V_2/V_1)	1.69
Conradson difference (C_2-C_1)	1.08

EXAMPLE 5

One proceeds as described in Example 1, with the difference that the hydrogenation is carried out at 350° C. with a space velocity of 0.8 liter/liter/hour, with a gas-liquid ratio of 0.1 Nm.³/liter, under a pressure of 50 atm., with synthesis gas containing 75% by volume of hydrogen and 25% by volume of nitrogen.

In this way the following products are obtained:

	Percent by weight
Re-refined engine oil	53.6
Re-refined gas oil and industrial lubricating oil distillates	26.8
Prepurification losses	17.5
Hydrogenation and distillation losses	2.1
Total	100.0

The thus-obtained re-refined engine oil has the following properties:

Viscosity index	81
Conradson residue, percent by weight	0.10
Viscosity at 50° C., cst.	68.31
Viscosity ratio (V_2/V_1)	1.28
Conradson difference (C_2-C_1)	1.06

What we claim is:

1. A process for re-refining used engine lubricating oils and used industrial lubricating oils containing such engine

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lubricating oils, said process comprising the step of pre-purifying the used lubricating oil by treatment with sulphuric acid; then subjecting the oil to catalytic hydrogenation at a pressure between 20 and 40 atmospheres, at a temperature between 280 and 380° C., at a space velocity of 0.5 to 2.0 liters per liter-hour and at a gas-to-liquid ratio of 10 to 120 Nm.³/m.³ in the presence of a preactivated, sulphided hydro-refining catalyst.

2. The process of claim 1, wherein the hydro-refining catalyst consists of 4 to 5% by weight of NiO, 15 to 17% by weight of MoO₃, 0 to 5% by weight of SiO₂ and 0 to 15% by weight of Fe₂O₃, the said catalyst being deposited on an alumina carrier and being activated, before use, at

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a temperature exceeding 200° C., in a hydrogen stream containing at least 0.1% by weight of bound sulphur.

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