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(54) **Process for reducing the amount of metal contaminants in a hydrocarbon oil.**

(57) Process for reducing the amount of metal(s)-containing solid contaminants present in a hydrocarbon oil containing such contaminants, which process comprises contacting the hydrocarbon oil with porous solid material having a pore volume of at least 0.05 ml/g in pores having a diameter of at least 15 microns, which process is carried out without adding hydrogen.

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The present invention relates to a process for reducing the amount of metal(s)-containing solid contaminants present in a hydrocarbon oil containing such contaminants.

It is well known that various metallic elements are found in hydrocarbon oils. These metals, particularly iron, nickel and vanadium, are harmful when included in feedstocks used for further refining operations in that they limit the life of catalyst used in such further refining operations. Such metals tend to deposit on the outer surface of the catalyst and in this way cause plugging of the catalyst bed. In particular the interstitial voids become blocked. This limits catalyst life since unacceptable pressure drops develop. Additionally, the deposits deactivate (poison) the catalyst requiring premature shutdown of the reactor and replacement of the catalyst.

For the removal of metals like nickel and vanadium, hydrogen needs to be present, preferably together with a catalytically active metal. Surprisingly, it has now been found that the metal content of some other metals, such as certain metals from Group 1a, 2a, 3a, 4a, 6b and/or 8 of the Periodic Table of the Elements such as given in the CRC Handbook of Chemistry and Physics, 63rd edition, e.g. sodium, calcium, iron and/or molybdenum, can be brought down to an acceptable level by removing solids containing such contaminating metals. Such process can be carried out without adding hydrogen to the process and at ambient temperature and atmospheric pressure. Solid contaminants having a relatively large diameter can be removed in a conventional desalting step. However, contaminants having a smaller diameter must be removed in another way. It has now been found that such metal(s)-containing solid contaminants can be removed without adding hydrogen by the use of certain porous solid material having a substantial pore volume in pores having a diameter which is larger than the diameter of solid contaminants generally present in hydrocarbon oils. It is thought that thus metal containing solid contaminants are taken up inside the porous material by a combination of convection and diffusion such that the contaminants are removed from the hydrocarbon oil while the interstitial voids remain substantially open.

Therefore, the present invention relates to a process for reducing the amount of metal(s)-containing solid contaminants present in a hydrocarbon oil containing such contaminants, which process comprises contacting the hydrocarbon oil with porous solid material having a pore volume of at least 0.05 ml/g in pores having a diameter of at least 15 microns, which process is carried out without adding hydrogen.

The pore diameter in which a substantial amount of pore volume is preferred to be present depends on the diameter of the solid contaminants which are to be removed. Generally a pore volume of at least 0.05 ml/g in pores having a diameter of at least 15 microns is suitable. Preferably, a substantial pore volume, e.g. 0.03 ml/g, is present in pores having a diameter of at least 100 microns. Very suitable porous material to be used has a pore volume of at least 0.02 ml/g in pores having a diameter of at least 200 micons.

The pore size distribution and pore volume of the material employed can be readily measured by the mercury intrusion method.

The shape of the material is not critical and may take the form of spheres, hollow tubes, wheels, trilobes, quadrulobes, etc.

Preferably, the diameter of the porous solid material particles is between 0.50 and 60 mm, more preferably between 1 and 40 mm.

The surface area of the porous solid material is not critical. However, due to the requirements on the pore diameter and pore volume, the porous material to be employed in the process according to the present invention will generally have a surface area of less than 2 m^2/gram.

Porous solid material to be used comprises e.g. silica, alumina and silica/alumina. Preferred materials comprise pumice stone and some commercially available catalyst carriers, e.g. as used in the preparation of ethylene oxyde catalysts. Suitable materials are mentioned in European patent specification 399.592, in which a hydrotreating process for the removal of suspended and dissolved (organo)metallic compounds has been described.

The process can be carried out at ambient temperature and atmospheric pressure. If desired, the process can be carried out at a temperature up to 500 °C and a pressure up to 200 bar. The operating conditions which are preferred depend on the hydrocarbon oil which is subjected to the process. If for example a short residue, i.e. a residual hydrocarbon oil boiling above 520 °C, is to be subjected to the process of the present invention, the temperature and optionally pressure will be elevated due to the viscosity of such residue; suitable process conditions would comprise a temperature of between 200 and 350 °C and a pressure up to 80 bar. A long residue, containing hydrocarbons boiling above 270 °C, is preferably processed at a temperature of between 150 and 350 °C and a pressure up to 80 bar.

The amount of metal(s)-containing solid contaminants which is to be removed from the hydrocarbon oil by the present process can vary. Suitably, a substantial amount of the metal(s)-containing solid contaminants is removed.

Claims

1. Process for reducing the amount of metal(s)-containing solid contaminants present in a hydrocarbon oil containing such contaminants, which process comprises contacting the hydrocarbon oil with porous solid material having a pore volume of at least 0.05 ml/g in pores having a diameter of at least 15 microns, which process is carried out without adding hydrogen.

2. Process according to claim 1, in which process the porous solid material has a pore volume of at least 0.03 ml/g in pores having a diameter of at least 100 microns.

3. Process according to claim 1 or 2, in which process the porous solid material has a pore volume of at least 0.02 ml/g in pores having a diameter of at least 200 microns.

4. Process according to any one of claims 1-3, in which process the porous solid material has a diameter of between 0.5 and 60 mm.

5. Process according to any one of claims 1-4, in which process the solid contaminants contain metal(s) from Group 1a, 2a, 3a, 4a, 6b and/or 8 of the Periodic Table of the Elements.

6. Process according to claim 5, in which process the solid contaminants comprise sodium, calcium, iron and/or molybdenum.

7. Process according to any one of claims 1-6, which process is carried out at a temperature up to 500 °C and a pressure up to 200 bar.

8. Process according to any one of claims 1-7, in which process use is made of porous solid material comprising pumice stone.

9. Hydrocarbon oil comprising a reduced amount of metal(s)-containing solid contaminant(s) obtained in a process as described in any one of claims 1-8.

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EUROPEAN SEARCH REPORT

Application Number

EP 90 20 3247

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-4 414 098 (ZANDONA et al.)		C 10 G 25/00 C 10 G 29/16
A	BE-A- 508 479 (ANGLO-IRANIAN OIL)		
A	EP-A-0 175 799 (ASHLAND OIL)		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 10 G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	25-04-1991	MICHIELS P.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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