

PROCESS TO PREPARE A PROCESS OIL

The invention relates to a process to continuously prepare a process oil with an aromatic content of more than 50 wt% (according to ASTM D 2007) and a polycyclic aromatics (PCA) less than 3 wt% (according to IP346).

5 Process oils having the above properties are used in the preparation of rubber tires. For environmental and health reasons it becomes increasingly important to reduce the content of polycyclic aromatics in rubber tire products and therefore also in the process oils which are
10 used for their preparation.

 EP-A-950703 describes a process to prepare a process oil as described above. The process oil is prepared by contacting a mixture of a base oil and an aromatic rich extract with furfural as the polar solvent. The base oil
15 is either obtained by hydrotreating or solvent refining. The aromatic rich extract is obtained by solvent extraction of a distillate fraction. This distillate fraction is obtained in a vacuum distillation of the residue of an atmospheric distillation of a crude oil. A
20 disadvantage of this process is that the starting base oil is relatively expensive, when reviewing the numerous solvent or hydrotreating process steps to prepare the base oil.

 Another process for preparing such a process oil is
25 known from EP-A-417980. This publication describes a process in which first a petroleum fraction boiling in the lubricating oil range is extracted with a solvent, typically furfural or NMP. The extract mixture obtained is subsequently extracted with the same solvent in a
30 second extraction step in which the process oil is obtained as the raffinate product.

The process of EP-A-417980 is either carried out in two extraction columns or in a so-called blocked-out operation in which the process oil is prepared in one and the same extraction column. In a blocked out operation the feed for the second extraction is first prepared and stored. The extraction column is subsequently prepared to perform the extraction of the stored extract mixture to obtain the process oil. Both schemes are disadvantageous. The first one because it requires an extra extraction column. The second option is disadvantageous because it requires significantly different operating conditions than those used for normal operation. Normal operation being the extraction of waxy distillate (fractions of the vacuum distillation) to make petroleum fractions poor in aromatics which are suitable for subsequent processing to make base oils. It would be desirable to use an existing solvent extraction unit to prepare the process oil. With the process according to this publication however switching between the two operating modes will be time consuming and laborious. Furthermore switching between the two production modes is likely to produce products that are unsuitable for subsequent processing to produce either base oils or the process oils, as described in EP-A-417980, that fall within the specifications of these products. It is therefore likely that these intermediate materials will have to be disposed of in other, less economical refinery streams, for example as the feedstock to a catalytic cracker.

An alternative route to the manufacture of process oils suitable for the application in rubber tires involves the extraction of a petroleum fraction boiling in the lubricating oil range which is extracted with furfural under "medium" severity processing conditions as described in Tire Technology International 1998. The disadvantage of this process route is that the "medium"

severity operation differs from those normally used for the production of base oils. Thus when such a medium severity process would be used in an existing solvent extraction process problems will occur with regard to for example the throughput of heat exchangers resulting in clogging and other obvious problems.

US-A-5840175 and US-A-5853569 describe processes to prepare a process oil which can be used as rubber extender oils from naphthenic crude oils. A disadvantage of the processes as disclosed in these publications is that the content of aromatics in the process oil is low while the content of polycyclic aromatic compounds is relatively high. A further disadvantage is that the process comprises both hydrotreating steps and solvent refining steps. The present process aims at providing a process wherein additional hydrotreatment steps are not necessary.

Applicants have now found that with the following process the above disadvantages can be overcome. Process to prepare a process oil with an aromatic content of more than 50 wt% (according to ASTM D 2007) and a polycyclic aromatics (PCA) less than 3 wt% (according to IP346) by (a) contacting a feed mixture of a petroleum fraction boiling in the lubricating oil range and an aromatic rich hydrocarbon fraction with a polar solvent in a counter-current liquid-liquid extraction column, wherein the process oil is obtained by removing the polar solvent from the top product and an extract is obtained by removing the polar solvent.

With the process according to the invention it has been found possible to prepare a process oil directly using the distillate fractions obtained in the vacuum distillation. Moreover, additional hydrotreatment steps are not necessary. Another advantage is that the process according the invention can be performed in an existing

solvent extraction column of a lubricating base oil process, while minimising the transition period between the lubricating base oil mode of operation and the mode of operation of the present invention. A further
5 advantage is that the existing heat exchangers and settlers of the existing process equipment can be used under throughput conditions which are similar to the base oil mode of operation. This is advantageous because this eliminates the necessity to install dedicated equipment
10 for the production of the process oil. It has furthermore been found that the process oil obtained by the process according to the invention gives the same properties to the tire when compared to the process oil as obtained by the method as described in EP-A-417980.

15 The aromatic rich hydrocarbon fraction can be any hydrocarbon mixture containing aromatic compounds. Examples of refinery fractions which could be used in the present process are the heavy and light cycle oils obtained in a fluid catalytic cracking process. In order
20 to meet a specific requirement of the tire industry with respect to viscosity of the process oil the aromatic rich fraction preferably has a kinematic viscosity at 100 °C of between 13 and 30 cSt, and more preferably between 14 and 20 cSt. The aromatic content of the aromatic rich
25 fraction is preferably between 50 and 90 wt%. A suitable aromatic hydrocarbon fraction comprises the extract fraction obtained by removing the polar solvent from the bottom product of the present process. By recycling the extract fraction to the extraction column no intermediate
30 storage of extract is needed.

A most preferred aromatic rich hydrocarbon fraction comprises the extract fraction obtained when removing aromatics by means of solvent extraction from a petroleum
35 fraction boiling in the lubricating oil range in a process to prepare a lubricating base oil. In this

preferred embodiment extract, preferably obtained when the same extraction column is used in the base oil mode of operation, is collected, stored and used when preparing the process oil according to the present invention. Although storage is needed a more robust process is nevertheless obtained. The aromatic rich fraction may also be a mixture of two or more of the above referred to examples of aromatic rich hydrocarbon fractions.

The petroleum fraction boiling in the lubricating base oil range is suitably obtained by first distilling a crude petroleum feedstock at atmospheric pressure and subsequently performing a vacuum distillation on the residue of the atmospheric distillation. The distillate products obtained in the vacuum distillation, also referred to as vacuum distillates, are the petroleum fractions boiling in the lubricating base oil range. The crude petroleum feedstock is preferably not a naphthenic crude. More preferably a crude feedstock is used comprising more paraffinic compounds, comprising preferably more than 15 wt%, most preferably more than 20 wt% of paraffins. Because of the more paraffinic character of the feedstock an additional dewaxing step will suitably be required. The fractions boiling in the lubricating base oil range have not been subjected to a solvent refining or hydrorefining. Solvent refining and hydrorefining are process steps to prepare a base oil product starting from the petroleum fractions boiling in the lubricating base oil range as for example described in Lubricant base oil and wax processing, Avilino Sequeira, Jr., Marcel Dekker Inc., New York, 1994, pages 2-4. The boiling range of the vacuum distillates are suitably between 300 and 620 °C and preferably between 350 and 580 °C. Deasphalted residues of the above mentioned vacuum distillation are also considered to be

the petroleum fractions boiling in the lubricating base oil range according to this invention.

5 The feed mixture which is contacted with the polar solvent does not necessarily be mixed before being fed to the extraction column in order to obtain the desired process oil. However when using an existing solvent extraction column it is preferred to mix the two fractions beforehand and use the existing single feed inlet. Preferably the mass ratio of the petroleum
10 fraction boiling in the lubricating base oil range and the aromatic rich fraction is between 3:1 and 1:3. More preferably the mass ratio is between 3:1 and 1:1.

The mass ratio of the polar solvent to the feed mixture is preferably between 3:1 and 1:1. High polar
15 solvent to feed mixture ratios are used when the content of the aromatic rich fraction in the feed mixture is relatively high. When operating in the more preferred range of the feed mixture composition the polar solvent to the feed mixture is preferably between 2.5:1 and
20 1.5:1.

The temperature in the extraction column is an important operation condition in order to obtain the desired properties of the process oil. The temperature will be dependent on the composition of the feed, i.e.
25 the content of aromatics, polyaromatics, and the choice of polar solvent. The temperature of the top product is preferably between 50 and 90 °C and the temperature of the bottom product is preferably between 60 and 80 °C. These temperatures can be easily controlled by adjusting
30 the temperature of the polar solvent and of the feed mixture.

When using an existing solvent extraction column as described above the polar solvent is typically removed from the bottom product by means of phase separation in a
35 settler. Preferably the temperature in this settler is

between 40 and 80 °C. It will be understood that the temperature in the settler is equal or below the bottom product temperature and that the bottom product temperature is lower than the top product temperature.

5 The polar solvent can be any solvent which is capable of selectively removing aromatic compounds from a hydrocarbon fraction boiling in the lubricating oil range. Examples of these polar solvents are phenol, N-methylpyrrolidone and furfural, of which furfural is
10 preferred.

 The counter-current liquid-liquid extraction column may be any suitable liquid-liquid extraction vessel, for example a rotating disk contactor.

15 More preferably the process of the present invention is carried out in an existing solvent extraction process which is normally used to remove aromatic compounds from a hydrocarbon fraction boiling in the lubricating oil range. By making use of an existing solvent extraction unit considerable investment in a new unit will not have
20 to be made. More preferably the existing process makes use of furfural as the polar solvent and the extraction column is of the rotating disk type. Examples of such existing solvent, furfural, extraction processes are described in general literature on base oil
25 manufacturing, for example on pages 86-95 of Lubricant base oil and wax processing, Avilino Sequeira, Jr., Marcel Dekker Inc., New York, 1994. In a preferred embodiment the production of the process oil according to the present invention is performed alternatively with a
30 process to prepare a lubricating base oil in the same extraction column in a so-called blocked out mode of operation. Preferably the aromatic rich extract obtained in the lubricating base oil mode of operation is stored and used as aromatic rich fraction in the process mode to
35 prepare the process oil.

The process oil as obtained by the process according to the invention is preferably dewaxed, especially when the feedstock to the present process is obtained from a more paraffinic crude petroleum feedstock. Suitable dewaxing processes are solvent dewaxing and catalytic dewaxing as for example described in "Lubricating base oil and wax processing", by Avilino Sequeira, Jr., 1994, Marcel Dekker Inc. New York, pages 153-224. Existing solvent dewaxing units are suitably used in combination with existing solvent extraction steps. An example of a suitable solvent dewaxing process is to cool the process oil together with a suitable solvent, for example methylisobutyl ketone/toluene or methyl ethyl ketone to a temperature of between -10 and -40 °C and subsequently filtering off the precipitated wax. Catalytic dewaxing can be performed by contacting the process oil in the presence of hydrogen with a suitable catalyst, preferably comprising SAPO-11, SAPO-31, SAPO-41, ZSM-5, ZSM-8, ZSM-11, ZSM-22, ZSM-23 and/or ZSM-35 and a Group VIII metal, preferably Pt, Pd, Ni or Co.

The invention shall be illustrated by the following non-limiting examples.

Example 1; preparation of the aromatic rich fraction

In a counter current extraction column a hydrocarbon petroleum fraction boiling in the lubricating base oil range having the properties as listed in Table 1 was contacted with furfural. The hydrocarbon feed was fed to the bottom and the furfural was fed to the top of the column. The operating conditions are listed in Table 2, 1st column together with the most relevant results. The extract obtained after removing furfural from the bottom product is the so-called "aromatic rich fraction" to be used in the below examples according to the invention. After removing furfural from the top product, the hydrocarbon fraction so obtained product poor in aromatics, had the

properties to be further processed, i.e. by means of a dewaxing step, to a lubricating base oil.

Table 1

Density (d70/4)	0.908
Refractive Index, 70 °C	1.5092
Viscosity at 100 °C (mm ² /s)	14.14
Viscosity at 120 °C (mm ² /s)	8.391
Aromatics, %wt	62.7

Example 2; preparation of the process oil

5 An aromatic rich fraction was prepared in a commercial Furfural Extraction Unit, according to the process described in Example 1. Main characteristics of this extract are given in Table 3:

Table 3

Aromatic-rich fraction:	
Density (d70/4)	0.957
Refractive Index, 70 °C	1.5420
Viscosity at 100 °C (cSt)	21.3
Aromatics (wt%) ASTM D2007)	83.6
PCA content (wt%; IP 346)	15.8

10 A feed mixture of the petroleum fraction as used in Example 1 and of the above-described extract in a wt:wt ratio of 2:1 was contacted with furfural (in a mass ratio to the feed mixture of 1.50:1) in the same column as used in Example 1. The process conditions, temperatures used and properties of the thus obtained process oil are listed in Table 2.

15 Example 3; preparation of the process oil

Example 2 was repeated except that the mass ratio of the polar solvent to the feed mixture was increased from

1.5:1.0 to 2.0:1.0. The process conditions and properties of the thus obtained process oil are listed in Table 2.

Example 4; preparation of the process oil

5 Example 2 was repeated with a feed mixture of the petroleum fraction as used in Example 1 and the commercial extract described in Example 2 in a wt:wt ratio of 1:1. The process conditions and properties of the thus obtained process oil are listed in Table 2.

Example 5; preparation of the process oil

10 Example 4 was repeated except that the temperature of the settler was lowered to 50 °C. The process conditions and properties of the thus obtained process oil are listed in Table 2.

Table 2

Example	Example 1	Example 2	Example 3	Example 4	Example 5
mass flow petroleum fraction (kg/h)	1.00	0.67	0.67	0.50	0.50
mass flow aromatic rich extract (kg/h)	0.00	0.33	0.33	0.50	0.50
mass flow furfural (kg/h)	3.00	1.50	2.00	1.50	1.50
top product temperature (°C)	113	80	80	80	79
bottom product temperature (°C)	98	70	70	70	70
temperature settler (°C)	80	70	70	70	50
product properties of:	extract example 1	process oil example 2	process oil example 3	process oil example 4	process oil example 5
WAXY PRODUCT:					
Yield (kg/h)	0.50	0.66	0.60	0.67	0.72
Density (d70/4)	0.978	0.875	0.865	0.876	0.879
Refractive Index, 70 °C	1.5550	1.4845	1.4790	1.4850	1.4860

Table 2 (cont'd)

product properties of:	extract example 1	process oil example 2	process oil example 3	process oil example 4	process oil example 5
DEWAXED (@-20 °C)PRODUCT:					
Viscosity at 100 °C (cSt) (1)	14.1	13.14	12.43	13.28	13.38
Viscosity Gravity Constant (ASTM D2501)		0.895	0.843	0.855	0.859
Aromatics (wt%) (ASTM D2007)	> 90 (*) (*) : 91.7%, as calc. from mass balance	50.7	53.0	59.0	62.0
PCA content (wt%; IP 346)		1.6	<3	1.0	<3

(1) Solvent dewaxing at -20 °C.

C L A I M S

1. Process to prepare a process oil with an aromatic content of more than 50 wt% (according to ASTM D 2007) and a polycyclic aromatics (PCA) less than 3 wt% (according to IP 346) by (a) contacting a feed mixture of a petroleum fraction boiling in the lubricating oil range and an aromatic rich hydrocarbon fraction with a polar solvent in a counter-current liquid-liquid extraction column, wherein the process oil is obtained by removing the polar solvent from the top product and an extract is obtained by removing the polar solvent from the bottom product.

2. Process according to claim 1, wherein the aromatic rich hydrocarbon fraction has a kinematic viscosity at 100 °C of between 12 and 30 cSt and an aromatic content of between 50 and 90 wt%.

3. Process according to claim 2, wherein the aromatic rich hydrocarbon fraction comprises the extract fraction obtained when removing aromatics by means of solvent extraction from a petroleum fraction boiling in the lubricating oil range in a process to prepare a lubricating base oil.

4. Process according to claim 2, wherein the aromatic rich hydrocarbon fraction comprises the extract fraction obtained by removing the polar solvent from the bottom product of the present process.

5. Process according to any one of claims 1-4, wherein the mass ratio of the petroleum fraction boiling in the lubricating base oil range and the aromatic rich fraction is between 3:1 and 1:3.

6. Process according to claim 5, wherein the mass ratio is between 3:1 and 1:1.

7. Process according to any one of claim 1-6, wherein the mass ratio of the polar solvent to the feed mixture is between 3:1 and 1:1.

5 8. Process according to claim 7, wherein the mass ratio is between 2.5:1 and 1.5:1.

9. Process according to any one of claims 1-8, wherein the temperature of the top product is between 50 and 90 °C, the temperature of the bottom product is between 60 and 80 °C and wherein the polar solvent is removed
10 from the bottom product by means of phase separation in a settler at a temperature of between 40 and 80 °C, provided that the temperature in the settler is equal or below the bottom product temperature and that the bottom product temperature is below the top product temperature.

15 10. Process according to any one of claims 1-9, wherein the polar solvent is furfural.

11. Process according to any one of claims 1-10, wherein the production of the process oil is performed alternatively with a process to prepare a lubricating
20 base oil in the same extraction column in a so-called blocked out mode of operation.

12. Process according to any one of claims 1-11, wherein the process oil is furthermore dewaxed.

25 13. Use of a process oil obtained by a process according to any one of claims 1-11 in a process to make a tire.