(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 260 569 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
27.11.2002 Bulletin 2002/48

(51) Int Cl.[7]: **C10G 45/00**

(21) Application number: **02076964.2**

(22) Date of filing: **21.05.2002**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **21.05.2001 US 862794**

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(54) Process for making non-carcinogenic, high aromatic process oil

(57) An atmospheric distillate or a vacuum distillate stream is combined with a calculated amount of lubricant extract stream. This well-mixed stream is then hydrotreated to yield a non-carcinogenic, high aromatic process oil. A desired level of high aromatic lubricant product streams and having the desired solvency properties is achieved by varying the feed stream ratio and hydrotreating conditions.

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Description

[0001] The invention is related to a process for obtaining non-carcinogenic aromatic oils from a mixed distillate and an extract feed obtained in the manufacture of lubricant base oils. A simple feed blending and hydrotreating process is shown for producing aromatic process oil, which shows a mutogenicity index of less than one by a Modified Ames Test.

[0002] Repsol Petroleo patent EP-839891 discloses a process for obtaining aromatic oils with a polycyclic aromatic compounds content of less than 3% (IP-346) from the mixed extract flow obtained in the manufacture of lubricant base oils, a flow which contains a polar solvent, preferably phenol, furfural or N-methyl-2-pyrrolidone (NMP), especially furfural, comprises: (a) cooling the flow of mixed extract to render non-polyaromatic components insoluble; (b) settling to bring about separation of the phases; (c) total or partial redissolution in solvent of the light phase obtained from the settling in (b); (d) cooling to effect separation of the non-polyaromatic components; and (e) settling to recover the light phase having a low polyaromatic compounds (PCA) content.

[0003] The yield loss by this process is expected to be larger than in the process of the instant invention. Only extraction is used, which removes material from the product. In the instant invention, a blending and hydrogenation steps are used, yield is close to 100% (typically 95-105%).

[0004] In EP-A-417980 process oils with more than 50 weight percent aromatics content (ASTM D 2007) and less than 3% of polycyclic aromatic compounds (IP 346) are obtained by extracting a primary extract (obtained by treatment of a lubricating oil distillate originating from a mineral oil) in a countercurrent extraction column with a polar solvent, using a ratio by volume of primary extract feed: polar solvent of 1:(1-1.8); the top temperature in the extraction column is 50-90 °C, the bottom temperature is 20-60 °C and the top temperature is higher than the bottom temperature. This process of making process oils with a low content of polycyclic aromatic compounds uses a countercurrent extraction process. Extract from the lubes extraction unit is re-extracted by another column (via countercurrent extraction methodology) at low temperatures. The major advantage for this process seems to be that it is a single step process. However, investment costs for a separate countercurrent extractor devoted to a high polycyclic stream is expensive. Using an existing lube extractor for this process might lead to other product contamination with PCA.

[0005] WO-A-9844075 discloses a process for reducing the polycyclic aromatic content of a lubricating oil extract which comprises: (a) extracting vacuum distillates or vacuum residuals with a first extraction solvent to form a primary raffinate and a primary extract mix; and (b) recovering the lubricating oil from the primary extract mix by (c) reextracting the lubricating oil extract with a second extraction solvent, different from the first solvent, to form a secondary raffinate and secondary extract mix; (d) separating the secondary raffinate from the secondary extract mix; and (e) separating the secondary raffinate and the secondary extract from the second extraction solvent. In this process PCA is removed by re-extracting the lube oil. The second solvent during extraction is different from the first solvent.
Applicants' process uses a hydrotreating step as part of the invention.

[0006] US-A-3619414 is different from Applicants' process. The feed of this process is a "petroleum distillate" and the process is used for improving electrical properties or for obtaining a lighter color. The process describes approximately 30% aromatics in the product.

[0007] US-A-3462358 discloses hydrorefining of the distillates and the product is used for electrical applications. The art of hydrorefining of the distillates is different from hydrotreating.

[0008] FR-A-2685705 discloses and claims compositions useful as process oils that are made from mixtures of 'conventionally' processed oils (i.e., distillation, extraction, dewaxing). Hydroprocessing is not mentioned. The resulting process oils are relatively low in aromatics (40-50%).

[0009] An atmospheric distillate or a vacuum distillate stream is combined with a lubricant extract stream. A known quantity, i.e., ratio, of distillate and lubricant extract streams are blended in a mixer/feed tank. This well-mixed stream is then hydrotreated to obtain a product having a desired aromatic content, i.e., non-carcinogenic, high aromatic process oil. This process has more operating flexibility, yield and better efficiency than the processes reported in the prior literature. For example, desired levels of high aromatic lubricant streams and the desired solvency properties can be achieved by varying the ratio of the feed stream components and hydrotreating conditions.

[0010] FIGURE 1 is a schematic drawing of the process according to a preferred embodiment.

[0011] High aromatic content in process oil is desired for many applications. For example, process oil with high aromatic content has been used in ink, pole treating, rubber extenders and in the tire industry. The extracts from lube units typically have high aromatic content (>70%). However, these extracts contain carcinogens. The present invention process removes undesired carcinogens from the feed streams, while maintaining a desired aromatic content, thus making it a desirable product for the above applications.

[0012] In the pole treating industry, pole oil is used as a carrier for pentachlorophenol (an insecticide) to treat wood (as a preservative). Development of a non-carcinogenic pole treating oil is a challenging area due to the properties required (a high aromatic, low viscosity stream with a flash point above 150 °F). Using a combination of distillate and extract feed streams and a new process, we have successfully produced pole oil that meets all the specifications of the American Wood Preservative Association (AWPA).

[0013] The distillate streams referred to in this invention mean either (i) an atmospheric distillate stream from an atmospheric distillation unit or (ii) a vacuum distillate stream from a vacuum distillation unit. These distillate streams may include for example, atmospheric gas oil, gas oil, naphtha, light lube distillate and heavy lube distillate. Processes of making such streams are for example described in Lubricant base oil and wax processing, Avilino Sequeira, Jr., Marcel Dekker Inc., New York, 1994, pages 42-52.

[0014] The lube extract stream is the fraction as obtained when removing aromatics by means of solvent extraction from a petroleum fraction boiling in the lubricating oil range. Such extraction processes are known to be used in a process to prepare a lubricating base oil. 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. 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.

[0015] Referring now to Figure 1, a distillate stream, having known properties (such as those shown in Table 1) is fed into a mixer as is well known to those skilled in the art. A lube extract stream, also having known properties (such as those also shown in Table 1) is also fed into the mixer. The two streams are fed in known quantities and in selected ratios, e.g., those shown in Table 1. Preferably the content of total aromatics in the mixture is between 30 and 100 wt% and the content of poly cyclic aromatics (PCA) is between 3 and 80 wt%. The two streams are well-mixed in the tank by mixing/stirring e.g., for one hour at 50 °C. The objective of this step is to have a homogeneous mixture for the hydrotreating step. Thus, one skilled in the art is free vary mixing time and temperature as long as a homogeneous blend mixture is obtained.

[0016] After the two streams are well mixed, the resulting mixture is fed into a hydrotreater where it is processed under predetermined conditions, as is also well known to those skilled in the art as for example described in Lubricant base oil and wax processing, Avilino Sequeira, Jr., Marcel Dekker Inc., New York, 1994, pages 138-147. Examples of suitable hydrotreating catalyst could be selected from the group of Nickel-Molybdenum and Nickel-Cobalt catalysts. Typical operating conditions of the hydrotreating process are pressures in the range of 2.72-20.4 Mpa (400-3000 psi), preferably between 6.12 and 8.16 Mpa (900 and 1200 psi) and temperatures in the range of 204-427 °C (400-800 °F) and preferably between 265 and 321 °C (510 and 610 °F).

[0017] The resulting process oil exits the hydrotreater having the desired characteristics of high aromaticity and being non-carcinogenic.

[0018] The invention will now be illustrated with the following non-limiting examples.

[0019] In the examples use was made of an atmospheric distillate having the properties as listed in Table 1.

Table 1

	Atmospheric distillate	Lubricant extract
Sulphur content (ppm)	3230	13100
Nitrogen content (ppm)	129	11400
Total aromatics (*)	70.4	211.5
Diplus aromatics	1.46	137.22
Benzenes	68.94	74.25
Naphthalenes	1.09	41.66
Phenanthrenes	0.23	45.2
Chrysenes	0.12	33.07
Tetraphenes	0.02	17.29

(*) as determined by UV (in mmol/100g)

Example 1

[0020] (Feed 1 in Table 2): Distillate extracts (25 wt%) and a distillate (75 wt%) were mixed well by stirring at 50 °C for one hour. The sample was drawn out and its properties were measured: Density 0.9120 g/cc at 15.5 °C (60 °F)

and the other feed properties are listed in Table 2 for Feed 1.

Example 2

[0021] (Feed 2 in Table 2): Distillate extracts (20 wt%) and a distillate (80 wt%) were mixed well by stirring at 50 °C for one hour. The sample was drawn out and its properties were measured: Density 0.9046 g/cc at 15.5 °C (60 °F); D2887E Distillation 5% 411, 50% 509, 95% 939 °F; and the other feed properties are listed in Table 2 for Feed 2.

Example 3

[0022] (Feed 3 in Table 2): Distillate extracts (15 wt%) and a distillate (85 wt%) were mixed well by stirring at 50 °C for one hour. The sample was drawn out and its properties were measured: Density 0.8989 g/cc at 15.5 °C (60 °F) and the other feed properties are listed in Table 2 for Feed 3.

Table 2

	Feed 1	Feed 2	Feed 3
Sulphur content (ppm)	5800	5420	4550
Nitrogen content (ppm)	2810	2270	1610
Total aromatics (*)	102.6	109.8	95.3
Diplus aromatics	35.2	30.72	22.71
Benzenes	67.35	79.09	72.58
Naphthalenes	11.73	10.62	8.13
Phenanthrenes	11.38	9.7	7.04
Chrysenes	8.02	6.89	5.02
Tetraphenes	4.07	3.51	2.52

Example 4

[0023] The feed (as detailed in Example 1 above) was used. The feed was hydrotreated in a hydrotreating unit using a typical Ni-Mo lube oil hydrotreating catalyst at a liquid hourly space velocity (LHSV) of 0.5, at 288 °C (550 °F) and at 6.8 Mpa (1000 psi) hydrogen pressure. The unit was allowed to line-out for several hours before collecting the sample. The product has density 0.9215 g/cc at 15.5 °C (60 °F); D2887E Distillation 5% 224 °C (436), 50% 289 °C (552), 95% 514 °C (957 °F); Kinematic viscosity 13.31 cSt at 40 °C, 2.8 cSt at 100 °C; Minimum of 10% pentachlorophenol solubility. The other properties of the product are listed in Table 3.

Example 5

[0024] The feed (as detailed in Example 2 above) was used. The feed was hydrotreated in a hydrotreating unit using a typical Ni-Mo lube oil hydrotreating catalyst at a liquid hourly space velocity (LHSV) of 0.5, at 288 °C (550 °F) and at 6.8 Mpa (1000 psi) hydrogen pressure. The unit was allowed to line-out for several hours before collecting the product. The product has density 0.91 g/cc at 15.5 °C (60 °F); D2887E Distillation 5% 228 °C (443), 50% 283 °C (542), 95% 505 °C (942 °F); Kinematic viscosity 10.3 cSt at 40 °C, 2.43 cSt at 100 °C; Minimum of 10% pentachlorophenol solubility; Pour Point -57 °C (-70 °C); Color L4.5; D2549: Saturates 62.84%, Aromatics 36.32%, Polars 0.84%. The other properties of the product are listed in Table 3.

Example 6

[0025] Example 5 was repeated except that the reaction temperature during the hydrotreatment was different. See Table 3 for results.

Table 3

	Example 4	Example 5	Example 6
Space velocity	0.5	0.5	0.5
Temperature (°C)	288	288	316
H_2 pressure (Mpa)	6.8	6.8	6.8
Sulphur content (ppm)	2340	2040	818
Nitrogen content (ppm)	3670	2890	2790
Total aromatics(*)	129.5	126.9	121.6
Diplus aromatics	41.39	35.20	27.16
Benzenes	88.14	91.74	94.41
Naphthalenes	16.73	14.60	10.88
Phenanthrenes	12.72	10.65	8.21
Chrysenes	7.94	6.65	5.69
Tetraphenes	4.0	3.30	2.38
Mutogenicity Index (MI) as measured by Modified Ames Test**	0.77	0.80	Not measured

** MI < 1 is considered non-carcinogen

Example 7

[0026] Example 4 was repeated using Feed 3. The results are in Table 4.

Example 8

[0027] Example 7 was repeated under the hydrotreatment conditions as mentioned in Table 4. The results are in Table 4.

Example 9

[0028] Example 7 was repeated under the hydrotreatment conditions as mentioned in Table 4. The results are in Table 4.

Table 4

	Example 7	Example 8	Example 9
Space velocity	0.5	1	1.5
Temperature (°C)	288	288	288
H_2 pressure (Mpa)	6.8	6.8	6.8
Sulphur content (ppm)	1520	2150	3420
Nitrogen content (ppm)	2160	1990	1820
Total aromatics (*)	111.5	104.3	98.2
Diplus aromatics	25.03	23.24	21.29
Benzenes	86.46	81.06	76.86
Naphthalenes	10.44	9.67	8.58
Phenanthrenes	7.49	6.87	6.43
Chrysenes	4.74	4.39	4.13

Table 4 (continued)

	Example 7	Example 8	Example 9
Tetraphenes	2.36	2.31	2.15
Mutogenicity Index (MI) as measured by Modified Ames Test	Not measured	0.68	0.67

[0029] A significant reduction in Sulfur content was achieved by hydrotreating, while keeping almost the same level of aromaticity as shown by comparison of the UV Aromatics data in the tables 3 and 4. UV Aromatics is a standard UV spectrophotometric method wherein an aromatic type in lubricant base oils is measured. Using this method one could measure the amount of benzenes (mono-aromatics), naphthalenes (diaromatic), phenanthrenes (triaromatics), chrysenes, tetraphenes, and polyaromatics in mmol/100 gram of oil sample. A slight increase in the aromaticity relative to feed could be due to a change in molecular weight.

[0030] The Modified Ames test result shows that the MI of the product obtained in Example 4 is less than 1 indicating it to be non-carcinogen. Similar results were observed in the case of runs using Feed 2 and Feed 3. ASTM D2887 is a simulated distillation method using an automated gas chromatograph. A lower level of total aromatic content was observed in Example 5 than in Example 4 due to the lesser quantity of extract stream in Feed 2 than in Feed 1. This was further illustrated in Examples 7-9. Thus, aromatic content may be tailored for desired results by varying the quantity of extract in the feed stream in addition to the standard variations used during the hydrotreating step (e.g., pressure, temperature, catalyst, rate, etc.).

Claims

1. A process for producing a non-toxic aromatic oil having less than one mutogenicity index comprising the steps of:

pre-blending an extract from a lube plant and a distillate in a feed tank; and
hydrotreating said pre-blend feed in the next stage.

2. A process for producing a non-toxic aromatic oil having a mutogenicity index of less than one comprising the steps of:

mixing a suitable grade, calculated amount of an extract stream to a distillate stream of desired properties; and
treating said pre-blend feed in a hydrotreator.

3. The process of claim 1 wherein said extract is selected from the group consisting of different cuts of extracts of a lube plant.

4. The process of claim 1 wherein said distillate is selected from the group consisting of different cuts of distillates of a vacuum distillation unit.

5. The process of claim 1 wherein the proportion of said extract component to said distillate in said pre-blend is in the range of 1-99%.

6. The process of claim 5 wherein the proportion of said extract component in said pre-blend is in the range of 1-50%.

7. The process of claim 1 wherein said hydrogenation of said feed uses an appropriate hydrotreating catalyst selected for example from the group consisting of Nickel-Molybdenum and Nickel-Cobalt.

8. The process of claim 1 wherein said hydrotreating process is performed at a pressure in the range of 2.72-20.4 MPa, and at a temperature in the range of 204-427 °C.

9. The process of claim 8 wherein said hydrotreating process is performed at a pressure in the range of 6.12-8.16 MPa, and at a temperature in the range of 204-427 °C.

10. The process of claim 8 wherein said hydrotreating process is performed at a pressure in the range of 2.72-20.4 MPa, and at a temperature in the range of 265-321 °C.

11. The process of claim 1 wherein said hydrotreating process is performed at a pressure in the range of 6.12-8.16 MPa, and at a temperature in the range of 265-321 °C.