

(19)



Europäisches Patentamt

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Office européen des brevets



(11)

**EP 1 106 673 B1**

(12)

**EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the grant of the patent:

**06.10.2004 Bulletin 2004/41**

(51) Int Cl.7: **C10G 67/04**

(21) Application number: **00204357.8**

(22) Date of filing: **06.12.2000**

**(54) Removal of polycyclic aromatic compounds from extracts**

Entfernung von polycyclischen aromatischen Verbindungen aus Extrakten

Enlèvement de composés aromatiques polycycliques à partir d'extraits

(84) Designated Contracting States:  
**DE FR GB IT NL SE**

(30) Priority: **06.12.1999 US 455069**

(43) Date of publication of application:  
**13.06.2001 Bulletin 2001/24**

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**EP 1 106 673 B1**

**Description**

**[0001]** The invention is related to a process for obtaining aromatic oils having a polycyclic aromatic (PCA) compounds content of less than three percent from a mixed extract flow obtained in the manufacture of lubricant base oils. A two-stage process is shown for producing aromatic process oil containing less than three weight percent polycyclic aromatics.

**[0002]** Process oils having a suitable high aromatic content, preferably greater than 40%, is desired for many applications. For example, process oils with high aromatic hydrocarbon content have been used in ink production, in wood preservatives such as those used in pole treating, and as rubber extenders for products such as tires. The extracts from lube units typically have a high aromatic content, suitably greater than 70%. However, these extracts contain a high concentration of polycyclic aromatics, for example between 10-40% as well. Polycyclic aromatics (PCA's) are considered to be carcinogens and products containing these extracts require adherence to additional requirements for proper use. It is required to have less than three weight percent PCA's in the product in order to have an unlabeled product. That is, not labelled as a class 2 carcinogen in the European Community or potentially hazardous under current U.S. OSHA regulations. Processes are known to reduce the polycyclic aromatic content of a mix extract to less than three weight percent while keeping a desired aromatic content, preferably greater than 40%.

**[0003]** EP-A-839891 discloses such 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 a furfural extraction of a vacuum distillate fraction. Such a furfural extraction step is a typical process step when manufacturing lubricant base oils. In the disclosed process the mixed extract consisting of furfural and an aromatic rich hydrocarbon mixture is first (a) cooled 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 content.

**[0004]** A disadvantage of this two stage extraction process is that not all extracts from a lube extraction process step can be used to yield a product having less than three weight percent PCA. Further, the yield loss by this process is expected to be high.

**[0005]** GB-A-1518162 discloses a process to prepare an aromatic product by solvent extraction an extract and a distillate stream followed by a hydrofining treatment to improve color. The solvent used in this publication is phenol.

**[0006]** The object of the present invention is to provide a process wherein a high yield of aromatic process oils is obtained having the desired PCA specification.

**[0007]** This object is achieved with the following process. A process for producing a non-toxic aromatic oil having a PCA content of below 3 wt% comprising the steps of precleaning a mix extract from a lube plant comprising an aromatic rich fraction in a first stage by adding appropriate amounts of N-methyl pyrrolidinone (NMP) and water to said mix extract and separating a precleaned extract; and hydrotreating said precleaned-extract in a second stage at a pressure in range of 68-204 bar.

**[0008]** Applicants found that the disclosed combination of extraction and hydrotreating provides a process wherein the desired process oil can be obtained in a high yield.

**[0009]** The invention comprises a two stage process of producing aromatic process oil containing less than three weight percent polycyclic aromatics: A single step extraction of extract from a lube extraction unit is carried out in the first stage. In this feed preparation step, sulphur, nitrogen, and polycyclic aromatics are significantly reduced. This precleaned extract is then used for the second stage, wherein a hydrogenation process is adopted to reduce polycyclic aromatics to less than three weight percent. In this process, the starting material has a high polycyclic aromatics content and a final product with less than three weight percent polycyclic aromatics is obtained.

**[0010]** This approach has more operating flexibility than the processes reported in the literature. In the first step, most of the PCA's may be removed. Sulphur and Nitrogen-containing molecules are removed selectively. In addition, by the variation of solvent/water/extract ratio and temperature, one can tailor it to a particular lube plant. The second step, a hydrotreating step, is then used to reduce the PCA level to less than three weight percent. The large reduction in sulphur and nitrogen that occurs in the precleaning step allows the hydrotreating step to be carried out under economical conditions.

**[0011]** The mix extract which can be used in the present invention is obtained in a process to prepare lubricant base oils. In such a process aromatics are removed from a suitable base stock by means of solvent extraction. Examples of suitable solvent extraction processes are described in Lubricant Base Oil and Wax Processing, Avilino Sequeira, Jr, Marcel Dekker Inc, New York, 1994, pages 81-91. In these processes aromatic compounds are separated from the hydrocarbon mixture by means of solvent extraction, thereby obtaining a hydrocarbon product containing less aromatics than the feed, also referred to as a mix raffinate, and a mix extract rich in aromatics. The mix extract which is used in the present process is preferably the mixture of solvent and the aromatic rich hydrocarbon fraction directly obtained in the above described solvent extraction process. Optionally the mix extract may also be an oily fraction wherein the solvent has been separated from. The hydrocarbon fraction alone will further be referred to as oil. Suitable extraction

solvents are furfural, N-methyl pyrrolidone (NMP) and phenol. The mix extract is preferably obtained in a process wherein a hydrocarbon base oil feed is contacted with N-methyl pyrrolidone (NMP) as described on page 88-90 of the reference cited above.

**[0012]** According to the process of the present invention a solvent and water is added to the mix extract. The solvent is N-methyl pyrrolidinone (NMP) The weight ratio of total solvent-to-oil after addition is preferably in the range of 0.25-10 and more preferably between 1-8. The water content as calculated on the water/solvent fraction after addition is preferably above 2 wt%, preferably above 4 wt% and preferably below 12 wt% and more preferably below 8 wt%.

**[0013]** The separation in the first step of the process according to the present invention is preferably performed by

cooling said mixture of the mix extract, solvent and water;  
 mixing said mixture of said extract stream and said solvent/water stream in a mixer;  
 settling said mixture of said cooled extract stream and said solvent/water stream in a settler thereby producing a first stream having a high PCA and a second stream comprising a precleaned extract and solvent;  
 sending said first high PCA stream to a solvent recovery system;  
 recovering said solvent from said precleaned extract.

**[0014]** The temperature after said cooling is preferably such that the PCA is reduced to 5-25 wt% and more preferably to 8-19 wt%. Preferably the temperature is between -1 and 93 °C (30-200 °F) and more preferably between 38 and 66 °C (100-150 °F).

**[0015]** The hydrogenation of said precleaned extract can be performed by any hydrogenation process known to one skilled in the art. Examples are described in the above referred to general textbook of Sequeira. Preferably a process is used wherein the hydrotreating catalyst is selected from the group comprising Nickel-Molybdenum and Nickel-Cobalt. The hydrotreating process is preferably performed at a pressure in the range of 34-204 bar (500-3000 psi), more preferably between 68-136 bar (1000-2000 psi), and at a temperature in the range of 260-426 °C (500-800 °F), more preferably between 343-371 °C (650-700 °F).

**[0016]** Figure 1 is a schematic drawing of the process according to a preferred embodiment. Mix extract stream 1, extract without solvent/water stream 2, and solvent/water stream 3 are brought together in appropriate quantities. It is then cooled in cooler 14 before sending it to mixer 4, followed by settler 5. Cooling could be effectively carried out by pre-chilling solvent/water stream 2. Depending on the lubricant plants, mixer 4 and settler 5 could be combined without sacrificing the desired precleaned extract properties. The high PCA stream 5a from the settler 5 would then be sent to solvent recovery system 6. Stream 8 is a recovered solvent. Stream 7 contains high PCA compounds. Solvent of precleaned-extract 5b from settler 5 is also recovered as stream 10. The precleaned extract 11 from solvent recovery system 9 would then be sent to a hydrotreater 12. It is then appropriately treated to obtain the product, aromatic process oil 13.

**[0017]** The invention shall be illustrated with the following non-limiting examples.

**[0018]** Properties of an extract obtained during the production of a 250 SUS base oil are shown in Table-1. The analysis results of this extract stream clearly shows a high PCA content (29.1%), coupled with high sulphur and nitrogen. Both clay gel analysis and gas chromatography-mass spectrometry (GC-MS) analysis shows an aromatic content of nearly 80%. This extract was precleaned by single stage extraction. The extraction conditions and properties of the precleaned extract are shown in Table-2. The precleaning experiments were designed statistically so as to predict the results for various solvent (NMP), oil and water-in-solvent compositions. It is clear from Table-2 that the effect of solvent/oil ratio, water in the solvent, and extraction temperature are factors in maximizing the yield of the precleaned extract with low PCA (as measured by IP 346 method), low sulphur, and low nitrogen content. As higher yield reduces the cost of the process, it is important to optimize the yield for a particular extract. However, it is also critical that such precleaned extract when used in the hydrotreating step should result in less than three weight percent PCA. Thus, the optimization of the precleaning step depends on plant hydrotreating capability and the extract source. The preferred NMP-to-oil weight ratio was found to be 0.5 to 5 with preferred water in NMP between 6-12% by weight. In this step, experiments were designed to achieve a reduction of 50% PCA in the stream, with a preferred yield of 50-60%. Additionally, significant amounts of sulphur and nitrogen were also removed.

Table-1

Middle Distillate Extract analysis	
(solvent-free basis)	
Viscosity	
cSt@40 °C (Calc)	658

## EP 1 106 673 B1

Table-1 (continued)

Middle Distillate Extract analysis	
(solvent-free basis)	
Viscosity	
cSt@60 °C	136
cSt@100 °C	17.8
Nitrogen, PPM	2820
Sulphur, PPM	37600
Density @ 16°C (60 °F), g/ml	1.02
Pour Point, °C (°F)	23 (73)
COC Flash Point, °C (°F)	257 (495)
Clay Gel Analysis, %	
ASTM D2007, POLARS	9.1
AROMS	76.6
SATS	14.3
PCA by IP346, wt%	
Aniline Cloud Point, °C (°F)	29 (84)
D2887 Distillation	
5% off Temp, °C (°F)	403 (757)
50% off Temp, °C (°F)	449 (841)
95% off Temp, °C (°F)	483 (902)
GC-MS: ASTM D3239	
Saturates, wt%	17.4
Aromatics, wt%	79.4
Polars, wt%	4.26

**[0019]** In the second step, precleaned extracts were hydrotreated. The hydrotreating conditions and the resulting products for two samples [(a) Expt. No. 10 & (b) Expt. No. 11 from Table 2] are tabulated in Table-3. Each precleaned extract was hydrotreated at 138 bar (2,000 psi), at 360°C (680 °F) (duplicate experiments) and also (in Run # 3) at 34 bar (500 psi), 360°C (680 °F). In the first set, the precleaned starting material has a PCA of 9.6 weight percent and was reduced to 1.2, 1.4 and 6.1 respectively. This illustrates that starting from an extract having high PCA (29.1 weight percent, Table-1), a product with less than three weight percent is obtained by precleaning and hydrotreating at 138 bar (2,000 psi) hydrogen pressure. However, hydrotreating at 34 bar (500 psi) with a liquid hourly space velocity (LHSV) of 0.5 is not sufficient to bring the PCA level down to the desired level. In the second set of hydrotreating experiments, it is clear that the PCA level of 16.55 weight percent in the precleaned extract is not sufficient to obtain a product with less than three weight percent PCA under given conditions (see Table-3). Table-3 also illustrates high (greater than 40%) aromatics in the product. Results show that by varying hydrogen pressure and the reaction temperature coupled with precleaning conditions, less than three weight percent PCA could be achieved. Thus, in this new process, a product with high aromaticity and less than three weight percent PCA from extracts is demonstrated. Hydrogenation can be done under feasible conditions because the extraction step has removed the species (sulphur, nitrogen) that are typically most detrimental to a hydrogenation catalyst.

# EP 1 106 673 B1

Table-2

Laboratory Single Stage Extraction							
of Middle Distillate Extract							
Expt. No.	NMP/ Oil ratio wt./ wt.	Water in NMP wt%	Extraction Temp, °C (°F)	Raffinate Yield, %	IP346 wt%	Sulphur PPM	Nitrogen PPM
1	0.5	4	60 (140)	86.1	26.5	37300	3290
2	0.5	6	60 (140)	89.4	25.1	36000	2720
3	0.8	5	60 (140)	71.8	22.3	34400	1980
4	0.8	5	60 (140)	72.9	21.9	34200	2110
5	1	4	60 (140)	60.7	18.8	34600	1870
6	1	6	60 (140)	76.1	20.3	26200	1790
7	3.7	6	60 (140)	24.8	6.8	18000	6
8	4.2	6	60 (140)	21.7	6.7	17800	6
9	3.8	8	49 (120)	52	11.3	27200	1040
10	3.8	8	49 (120)	53.8	9.6	24600	3560
11	1	4	49 (120)	59.9	16.6	28800	5820

Table-3									
Results from Hydrotreating Experiments of Precleaned Middle Distillate Extract*									
Analysis	First Set of Hydrotreating Expts.			Second Set of Hydrotreating Expts.					
	Pre-cleaned Starting Material	Run # 1	Run # 2	Run # 3	Pre-cleaned Starting Material	Run # 4	Run # 5	Run # 6	
H <sub>2</sub> Pressure, bar (psi)		138 (2000)	138 (2000)	34 (500)		138 (2000)	138 (2000)	34 (500)	
Temperature, °C (°F)		360 (680)	360 (680)	360 (680)		360 (680)	360 (680)	360 (680)	
Viscosity, cSt@40 °C	159.4	74.64	78.05	98.08	187.2	100.2	117.1	128.5	
Viscosity, cSt@100 °C	11	7.84	7.99	8.88	11.32	8.7	9.34	9.66	
Sulphur, ppm	24600	413	339	2680	28800	1780	3770	5220	
Nitrogen, ppm	3560	14	23	489	5820	133	297	1000	

Table-3 (cont'd)									
Results from Hydrotreating Experiments of Precleaned Middle Distillate									
Extract*									
Analysis	First Set of Hydrotreating Expts.			Second Set of Hydrotreating Expts.					
	Pre-cleaned Starting Material	Run # 1	Run # 2	Run # 3	Pre-cleaned Starting Material	Run # 4	Run # 5	Run # 6	
Clay Gel Analysis									
Polars %	4.5	0.3	0.3	2.4	7.8	0.8	1.1	2.6	
Aromatics %	69.5	43.7	44.6	62.9	70.7	60.7	64.9	68.8	
Saturates %	26	56	55.1	34.7	21.3	38.5	34	28.6	
PCA by IP346	9.6	1.2	1.4	6.1	16.55	3.4	4.4	10.2	
*Space velocity 0.5 LHSV									

[0020] The general procedure followed for precleaning the extract and hydrotreating is as follows:

(a) Example 1

[0021] (Expt. No. 1 in Table-2): Preheated Middle Distillate extract (150 g)(Table-1), N-methyl pyrrolidinone (75 g),

and water (3.0 g) at 60°C (140 °F) were mixed in a separatory funnel. The separatory funnel was kept in a constant-temperature oven maintained at 60°C (140 °F). The mixture was physically agitated for one-two minutes every hour for four hours. The extraction set-up was left in the oven overnight without agitation. The raffinate part was collected and the solvent was removed. Product yield 129.15 g; PCA by IP 346 method, 26.5; sulphur, 3.73%; N 0.329%.

#### (b) Example 2

**[0022]** (Expt. No. 10 in Table-2): Preheated Middle Distillate extract (2,001 g)(Table-1), N-methyl pyrrolidinone (7,001 g), and water (560 g) were mixed at 49°C (120 °F) in a 4-neck, 12 l round bottom glass flask, equipped with a drainage stopper in the bottom. The mixture was maintained at a constant temperature at 49°C (120 °F) via a heating mantle. The mixture was mechanically stirred for a duration of ten minutes every two hours for eight hours. The extraction set-up was left overnight without stirring. The raffinate part was collected and the solvent was removed. This experiment was repeated to get sufficient quantity for the next hydrotreating step. Product yield 53.8%; PCA by IP 346 method, 9.6; S, 2.46%; N 0.356%.

#### (c) Example 3

**[0023]** (Typical hydrotreating procedure, Run # 1, Table-3): The precleaned extract (as detailed in Example 2 above) was used as a feed. The feed was hydrotreated in a pilot scale hydrotreating unit using a typical lube oil hydrotreating catalyst (Ni-Mo or Ni-Mo-Co) at an LHSV of 0.5, at 360°C (680 °F) and at 138 bar (2000 psi) hydrogen pressure. The unit was allowed to line-out for nine hours before collecting the sample. The properties of the product are listed in Table-3.

### Claims

1. A process for producing a non-toxic aromatic oil having a polycyclic aromatic content of below 3 wt% comprising the steps of:

an extraction performed in a single extraction step by precleaning a mix extract from a lube plant comprising an aromatic rich fraction in a first stage by adding appropriate amounts of N-methyl pyrrolidinone (NMP) and water to said mix extract and separating a precleaned - extract and

hydrotreating said precleaned-extract in a second stage at a pressure in range of 68-204 bar.

2. Process according to claim 1, wherein the separation is performed by:

cooling said mixture of the mix extract, NMP and water;  
mixing said mixture of said extract stream and said NMP and water stream in a mixer;  
settling said mixture of said cooled extract stream and said NMP and water stream in a settler thereby producing a first stream having a high PCA and a second stream comprising a precleaned extract and NMP;  
sending said first high PCA stream to a NMP recovery system;  
recovering said NMP from said precleaned extract.

3. Process according to any one of claims 1-2, wherein the weight ratio of total NMP-to-oil after addition is in the range of 0.25-10.

4. Process according to claim 3, wherein said ratio is between 1-8.

5. Process according to any one of claims 1-4 wherein the water content as calculated on the water and NMP fraction after addition is in the range of 2-12 wt%.

6. Process according to claim 5, wherein said water content is between 4-8 wt%.

7. Process according to any one of claims 1-6, wherein said precleaning of said extraction is performed at a temperature between 38 and 66 °C.



## Patentansprüche

1. Verfahren zur Herstellung eines nichttoxischen aromatischen Öls mit einem Gehalt an polycyclischen Aromaten von unter 3 Gew.-%, das die folgenden Schritte umfaßt:

eine in einem einzigen Extraktionsschritt ausgeführte Extraktion durch Vorreinigen eines eine aromatenreiche Fraktion umfassenden Mischextraktes aus einer Schmiermittelanlage in einer ersten Stufe durch Zusetzen geeigneter Mengen an N-Methylpyrrolidinon (NMP) und Wasser zu dem Mischextrakt und Abtrennen eines vorgereinigten Extraktes; und  
Hydrotreating dieses vorgereinigten Extraktes in einer zweiten Stufe bei einem Druck im Bereich von 68 bis 204 bar.

2. Verfahren nach Anspruch 1, worin die Abtrennung vorgenommen wird durch  
Kühlen des Gemisches aus dem Mischextrakt, NMP und Wasser;  
Vermischen des Gemisches aus dem Extraktstrom, dem NMP- und Wasserstrom in einem Mischer;  
Absetzenlassen dieses Gemisches aus dem gekühlten Extraktstrom und dem NMP- und Wasserstrom in einer Absetzvorrichtung, unter Ausbildung eines ersten Stroms mit einem hohen Gehalt an polycyclischen Aromaten und eines zweiten, einen vorgereinigten Extrakt und NMP umfassenden Stroms;  
Zuführen dieses ersten Stroms mit hohem Gehalt an polycyclischen Aromaten zu einem NMP-Rückgewinnungssystem;  
Rückgewinnen des NMP aus dem vorgereinigten Extrakt.

3. Verfahren nach einem der Ansprüche 1 bis 2, worin das Gewichtsverhältnis von Gesamt-NMP zu Öl nach der Zugabe im Bereich von 0,25 bis 10 liegt.

4. Verfahren nach Anspruch 3, worin das Verhältnis zwischen 1 und 8 liegt.

5. Verfahren nach einem der Ansprüche 1 bis 4, worin der Wassergehalt, berechnet auf die Wasser- und NMP-Fraktion, nach der Zugabe im Bereich von 2 bis 12 Gew.-% liegt.

6. Verfahren nach Anspruch 5, worin der Wassergehalt zwischen 4 und 8 Gew.-% beträgt.

7. Verfahren nach einem der Ansprüche 1 bis 6, worin die Vorreinigung dieser Extraktion bei einer Temperatur zwischen 38 und 66°C vorgenommen wird.

## Revendications

1. Procédé de production d'une huile aromatique non toxique ayant une teneur en aromatiques polycycliques inférieure à 3% en poids, comprenant les étapes suivantes :

une extraction effectuée au cours d'une seule étape d'extraction en pré-épurant un extrait mixte d'une usine de fabrication de lubrifiants comprenant une fraction riche en aromatiques dans un premier stade en ajoutant des quantités appropriées de N-méthyl pyrrolidinone (NMP) et de l'eau audit extrait mixte et en séparant un extrait pré-épuré; et  
un hydrotraitement dudit extrait pré-épuré dans un second stade sous une pression dans la plage de 68 à 204 bars.

2. Procédé selon la revendication 1, dans lequel la séparation est effectuée par les étapes suivantes :

on refroidit ledit mélange de l'extrait mixte, de la NMP et de l'eau;  
on malaxe ledit mélange dudit courant d'extrait et dudit courant de NMP et d'eau dans un mélangeur;  
on laisse ledit mélange dudit courant d'extrait refroidi et dudit courant de NMP et d'eau se déposer dans un dispositif de dépôt de manière à produire un premier courant ayant une teneur élevée en PCA et un second courant comprenant un extrait pré-épuré et de la NMP;  
on envoie ledit premier courant à haute teneur en PCA à un système de récupération de NMP; et  
on récupère ladite NMP dudit extrait pré-épuré.

## EP 1 106 673 B1

3. Procédé selon l'une quelconque des revendications 1 et 2, dans lequel le rapport pondéral de la NMP totale à l'huile après addition se situe dans la plage de 0,25 à 10.
4. Procédé selon la revendication 3, dans lequel ledit rapport se situe entre 1 et 8.
5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel la teneur en eau, telle que calculée sur la fraction d'eau et de NMP après addition, se situe dans la plage de 2 à 12% en poids.
6. Procédé selon la revendication 5, dans lequel ladite teneur en eau se situe entre 4 et 8% en poids.
7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel ladite pré-épuration de ladite extraction est effectuée à une température comprise entre 38 et 66°C.

Figure 1

