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(54) **Process for the preparation of bitumen for road use**

(57) Process for the preparation of bitumens for road use, characterized in that it comprises the oxidation of a composition consisting of (a) a bituminous component (I) having a content of asphaltenes of between 10 and 50%, a content of aromatics of between 10 and 50% by weight, and a penetration at 25°C of from 1 to 50

dmm, and (b) an aromatic component (II) essentially without asphaltenes and having a content of aromatics of from 80 to 95%, and a viscosity at 60°C of from 100 to 1000 cSt; the weight ratio between the aromatic component (II) and the bituminous component (I) being from 10:90 to 50:50.

EP 0 863 196 A1

Description

The present invention relates to a process for the preparation of bitumens for road use, particularly with high performance characteristics.

There are three main characteristics which are required for a bitumen to be used for road paving, i.e. good consistency when hot, excellent flexibility when cold, high resistance to oxidation.

The above characteristics are measured according to the following methods:

- "Ring & Ball softening point" (Method ASTM D36) and "Dynamic Viscosity" (method CEN TC19 143) for evaluating the consistency when hot;
- "Fraass Breakingpoint" (method IP 80) for the flexibility when cold;
- "Accelerated Thin Layer Aging RTFOT" (method ASTM D2872) with subsequent evaluation of the "Penetration at 25°C" (method ASTM D5) and "Ring & Ball Softening Point" (method ASTM D36) characteristics, compared to those of the initial product.

With respect to bitumens for road use, the main specifications applied at present in Italy (CNR BU N.68) and the corresponding specifications which will be introduced in the near future on a European scale (doc. CEN TC19 SC1 WG1 N112) are shown in table 1.

TABLE 1

	Method	Unit	CNR	CEN
Penetration at 25°C	ASTM D5	dmm	80/100	70/100
Ring & Ball	ASTMD36	°C	44/49	43/51
Fraass Breakingpoint	IP 80	°C	≤-10	≤-10
Penetration at 25°C after T.L.	ASTM D5	init %	--	≥46
Increase in Ring & Ball after T.L.	ASTM D36	°C	--	≤9
Viscosity at 60°C	CEN TC19	Pa.sec	--	≥90

At present, bitumens for road use can be obtained from fractions coming from different refinery processes such as distillation (atmospheric and vacuum), visbreaking and thermal cracking, reconstruction (for example with LUBE cycle aromatic components).

Regardless of the type of crude oil used, which may more or less influence the final characteristics of the bitumen, a particular bitumen derives from each of these processes, generally having the following particular aspects:

- bitumens from distillation, having good consistency when hot, fair flexibility when cold and good resistance to oxidation;
- bitumens from thermal cracking, having poor consistency when hot, good flexibility when cold and very poor resistance to oxidation;
- bitumens from reconstruction, having fair consistency when hot, poor flexibility when cold and excellent resistance to oxidation.

Bitumens for road use from distillation, thermal cracking (visbreaking) and reconstruction, indicatively have the characteristics shown in table 2.

TABLE 2

	Unit	Dist.	Visbr.	Recon.
Penetration at 25°C	dmm	80/100	80/100	80/100
Ring & Ball	°C	44/48	44/48	42/46
Fraass Breakingpoint	°C	-12/-16	-14/-18	-10/-14
Pen. at 25°C after T.L. init	%	50/60	35/45	60/70
Increase in Ring & Ball after T.L.	°C	5/10	8/15	3/5
Viscosity at 60°C	Pa.sec	100/200	70/120	110/150

As can be seen, generally refinery processes do not always enable the production of a bitumen having all excellent characteristics from the point of view of performance.

As a result the necessity is even more strongly felt for having bitumens for road use which satisfy all the requisites established by present specifications and those to be applied in the near future.

A process has now been found which overcomes the above disadvantages as it allows the production of bitumens for road use with excellent characteristics.

In accordance with this, the present invention relates to a process for the preparation of bitumens for road use, characterized in that it comprises the oxidation of a composition consisting of:

- (a) a bituminous component (I) having a content of asphaltenes of between 10 and 50%, preferably from 20 to 40% by weight, a content of aromatics of between 10 and 50% by weight, preferably from 15 to 35%, and a penetration at 25°C of from 1 to 50 dmm, preferably from 15 to 45 dmm, and
- (b) an aromatic component (II) essentially without asphaltenes and having a content of aromatics of from 80 to 95%, preferably from 82 to 93%, and a viscosity at 60°C of from 100 to 1000 cSt, preferably from 150 to 800 cSt;

the weight ratio between the aromatic component (II) and the bituminous component (I) being from 10:90 to 50:50, preferably from 15:85 to 45:55, even more preferably from 20:80 to 40:60.

In the preferred embodiment the oxidation takes place at a temperature of between 150°C and 270°C, more preferably from 160°C to 250°C, even more preferably from 170°C to 190°C.

Lower temperature would in fact cause an excessive duration of the process, which is unacceptable from an industrial point of view. Higher temperatures would cause a degradation of the bitumen and would be dangerous for the running of the plant.

The above oxidation is carried out with oxygen diluted with an inert gas, preferably with air.

According to an embodiment of the present invention, the oxidation is carried out on compositions of (I) and (II) previously prepared. According to another embodiment, the oxidation is carried out contemporaneously with the mixing of the two components (I) and (II).

In other words, it is possible to operate by initially mixing the two components, and subsequently proceeding with the oxidation of the mixture thus prepared. Alternatively the oxidation can be carried out during the mixing of the two components.

A typical example of bituminous component (I) is the vacuum residue obtained by distillation at reduced pressure of the effluent of the visbreaking plant.

Table A shows the characteristics of some of these samples (which for the sake of simplicity we shall call RVB) coming from different processings of visbreaking plants.

TABLE A

	RVB1	RVB2	RVB3
Penetration 25°C (dmm)	37	24	42
Ring & Ball (°C)	57	65	52.5
Content asphaltenes (w %)	25.8	36.2	30
Content satur.prod. (w %)	6.5	5.3	3.7
Content resins (w %)	35.5	42	38.3
Content aromatics (w %)	32.2	16.5	28

A typical example of aromatic compound (II) is the aromatic fraction, extracted by a solvent extraction process, of the vacuum distillate or deasphalted vacuum residue, in an operating cycle for the production of lubricating bases. These fractions shall hereafter be abbreviated with the initials CA. Table B shows the characteristics of some of these fractions.

The above table B also indicates the characteristics of some samples of vacuum gas oils obtained by vacuum distillation of the effluent of a visbreaking plant. These samples (called GVB) cannot be used in the process of the present invention as they do not have the required characteristics of the bituminous component (I) or the aromatic component (II). They are specified here because they shall be used further on in the comparative examples.

TABLE B

	GVB 1-3	CA 1-2
Viscosity at 60°C (cSt)	34.5-31.9-36.4	305-257
Asphaltenes (w %)	0-0-0	0-0
Saturated products (w %)	48.5-41.8-50.6	2.7-0.9

TABLE B (continued)

	GVB 1-3	CA 1-2
Resins (w %)	14.5-7.3-8.3	12.2-12.5
Aromatics (w %)	37.0-50.9-41.1	85.1-86.6

With respect to the optimum ratio between bituminous component (I) and aromatic component (II), this depends on the characteristics of the two components and of the bitumen to be obtained. In any case it must be within the range indicated above.

The duration of the process of the present invention depends on the various parameters, for example temperature, stirring rate, viscosity of the components. The duration is usually from a few tens of minutes to several hours.

The process of the present invention allows the production of a road bitumen capable of satisfying the specifications indicated above which will be shortly introduced in Europe. In particular, the bitumen for road use obtained with the process of the present invention has a good consistency when hot, an excellent flexibility when cold and a high resistance to oxidation.

The following examples are provided for a better understanding of the present invention.

EXAMPLES

COMPARATIVE EXAMPLE 1

According to what is normally carried out in a refinery, in this example a road visbreaking bitumen is prepared, by simple mixing (consequently without oxidation) of RVB1 and GVB1.

The mixing is carried out at 130/150°C by stirring for 20/30 minutes with a slanting blade stirrer at a rate of about 400 revs/minute.

The characteristics of these fractions (RVB1 and GVB1) have been specified above.

The bitumen (which we shall call 1C) has the properties indicated in table 1C, which also give the CNR and CEN specification values.

TABLE 1C

		Specifications	
RVB1 content	90% w	CNR	CEN
GVB1 content	10% w		
Penetration at 25°C	90 dmm	80/100	70/100
Ring & Ball	47°C	44/49	43/51
Fraass breakingpoint	-18°C	≤-10°C	≤-10°C
Penetr. after T.L.	41%	--	≥46%
Increase Ring & Ball after T.L.	14.5°C	--	≤9°C
Viscosity at 60°C	80 Pa.sec	--	≥90

As can be seen, this bitumen proves to have a poor consistency when hot (viscosity value outside the limit) and a low resistance to oxidation (the values after the thin layer accelerated aging test are outside the limit).

COMPARATIVE EXAMPLE 2

According to the procedure of example 1, a road bitumen is prepared by the simple mixing of the bituminous component RVB1 and the aromatic component CA1. The bitumen (which we shall call 2C) has the properties indicated in table 2C, which also indicates the CNR and CEN specification values.

TABLE 2C

		Specifications	
RVB1 content	88.5%	CNR	CEN
CA1 content	11.5%		
Penetration at 25°C	88 dmm	80/100	70/100

TABLE 2C (continued)

		Specifications	
Ring & Ball	48°C	44/49	43/51
Fraass breakingpoint	-17°C	≤-10°C	≤-10°C
Penetr. after T.L.	45%	--	≥46%
Increase Ring & Ball after T.L.	11°C	--	≤9°C
Viscosity at 60°C	69 Pa.sec	--	≥90

As can be seen, the bitumen 2C, although indicating (with respect to the bitumen 1C) a good improvement in the characteristics after the thin layer accelerated aging test, is still outside the specification values, particularly with respect to the high temperature characteristics (viscosity at 60°C).

COMPARATIVE EXAMPLE 2 bis

Again according to the procedure of example 1 and starting from RVB1 and CA1, the percentage of aromatic component is increased in an attempt to further improve the characteristics of the end-product.

For this purpose a bitumen consisting of 60% by weight of RVB1 and 40% by weight of CA1 is prepared.

The bitumen thus obtained has a penetration at 25°C of about 800 dmm, against a CNR specification of 80/100 and CEN specification of 70/100. The bitumen thus obtained is therefore clearly outside the regulation values as an initial penetration value.

COMPARATIVE EXAMPLE 3

This example describes the preparation of a road bitumen obtained by the mixing of two components from vis-breaking (RVB1 and GVB1) and subsequent blowing with air at 250°C.

The two components are mixed in a metal container heated to 130/150°C by stirring for 20/30 minutes with a blade stirrer (about 600 revs/minute). During this period the temperature is increased to about 250°C. Air is blown into the mixture thus heated and stirred at a flow-rate of about 90 litres/hour per kg of mixture.

The characteristics of this bitumen (which we shall call 3C) are shown in table 3C.

TABLE 3C

		Specifications	
RVB1 content	81.0%	CNR	CEN
GVB1 content	19.0%		
Penetration at 25°C	89 dmm	80/100	70/100
Ring & Ball	48.5°C	44/49	43/51
Fraass breakingpoint	-25°C	≤-10°C	≤-10°C
Penetr. after T.L.	46%	--	≥46%
Increase Ring & Ball after T.L.	15.5°C	--	≤9°C
Viscosity at 60°C	77 Pa.sec	--	≥90

As can be seen, the bitumen 3C is still outside the specification values with respect to resistance to oxidation (in particular the value of increase in Ring & Ball after the thin layer accelerated aging test), and as consistency at high temperature (viscosity value).

EXAMPLE 4

According to the process of the present invention, a road bitumen is prepared by the air blowing of a composition consisting of a component from visbreaking (RVB1) and an aromatic component (CA1). The two components are mixed in a metal container heated to 130/150°C by stirring for 20/30 minutes with a blade stirrer (about 600 revs/minute). During this period the temperature is increased to about 250°C. Air is blown into the mixture thus heated and stirred at a flow-rate of about 90 litres/hour per kg of mixture.

The characteristics of this bitumen called bitumen 4, are shown in table 4.

TABLE 4

		Specifications	
RVB1 content	60.0%	CNR	CEN
CA1 content	40.0%		
Penetration at 25°C	90 dmm	80/100	70/100
Ring & Ball	47°C	44/49	43/51
Fraass breakingpoint	-23°C	≤-10°C	≤-10°C
Penetr. after T.L.	56%	--	≥46%
Increase Ring & Ball after T.L.	8°C	--	≤9°C
Viscosity at 60°C	121 Pa.sec	--	≥90

Unlike the previous comparative bitumens, the bitumen of example 4 is perfectly in accordance with all the specifications, with distinctly improved overall characteristics compared to the comparative bitumens described above.

In fact bitumen 4, prepared according to the process of the present invention, has a good consistency when hot, an excellent flexibility when cold and a high resistance to oxidation.

COMPARATIVE EXAMPLE 5

The formulation is provided of a road bitumen from visbreaking obtained by the simple mixing of two components from visbreaking (RVB2 and GVB2), in accordance with the normal refinery procedure. The process is the same as that previously described in example 1.

The properties of the bitumen thus obtained are indicated in table 5C.

TABLE 5C

		Specifications	
RVB1 content	86.0%	CNR	CEN
GVB1 content	14.0%		
Penetration at 25°C	90 dmm	80/100	70/100
Ring & Ball	48°C	44/49	43/51
Fraass breakingpoint	-19°C	≤-10°C	≤-10°C
Penetr. after T.L.	42%	--	≥46%
Increase Ring & Ball after T.L.	21.5°C	--	≤9°C
Viscosity at 60°C	108 Pa.sec	--	≥90

As can be seen, the bitumen has a very poor resistance to oxidation with values after the thin layer accelerated aging test which are clearly outside the regulation values.

COMPARATIVE EXAMPLE 6

According to the procedure described in example 1, a road bitumen is prepared by the simple mixing of a component from visbreaking (RVB2) and an aromatic component (CA1).

The properties of the bitumen thus obtained are indicated in table 6C.

TABLE 6C

		Specifications	
RVB2 content	85.0%	CNR	CEN
CA1 content	15.0%		
Penetration at 25°C	89 dmm	80/100	70/100
Ring & Ball	48°C	44/49	43/51
Fraass breakingpoint	-17°C	≤-10°C	≤-10°C
Penetr. after T.L.	43%	--	>46%
Increase Ring & Ball after T.L.	13°C	--	≤9°C

TABLE 6C (continued)

		Specifications	
Viscosity at 60°C	93 Pa.sec	--	≥90

As can be seen, the bitumen obtained, although showing a clear improvement in the characteristics after the thin layer accelerated aging test, is still outside the regulation values.

COMPARATIVE EXAMPLE 6bis

In this example the quantity of aromatic component is increased, in an attempt to further improve the characteristics of the end-product. A composition of bitumen is prepared starting from the same components as comparative example 6, but in a different ratio.

For this purpose, a bitumen is prepared, according to the procedure described in example 1, consisting of 60% by weight of RVB2 and 40% by weight of CA1. The bitumen thus obtained has a penetration at 25°C of about 700 dmm, against a CNR specification of 80/100 and CEN specification of 70/100. This bitumen is therefore clearly outside the regulation value as initial penetration value.

COMPARATIVE EXAMPLE 7

This example describes the formulation of a road bitumen from visbreaking obtained by the mixing of two components from visbreaking (RVB2 and GVB2), with subsequent blowing with air at 250°C, according to the procedure of example 4.

The properties of the bitumen 7C thus prepared are indicated in table 7C.

TABLE 7C

		Specifications	
RVB2 content	78%	CNR	CEN
GVB2 content	22%		
Penetration at 25°C	88 dmm	80/100	70/100
Ring & Ball	52°C	44/49	43/51
Fraass breakingpoint	-26°C	≤-10°C	≤-10°C
Penetr. after T.L.	47%	--	≥46%
Increase Ring & Ball after T.L.	21.5°C	--	≤9°C
Viscosity at 60°C	131 Pa.sec	--	≥90

As can be seen, the bitumen still has a very poor resistance to oxidation (in particular as an increase in the Ring & Ball softening point value after the thin layer accelerated aging test)

EXAMPLE 8

In this example, according to the process claimed, the formulation is provided of a road bitumen obtained by the mixing of a component from visbreaking (RVB2) and an aromatic component (CA1), with subsequent blowing with air at 170°C. The process is that described in example 4.

The characteristics of bitumen 8 thus obtained are indicated in table 8.

TABLE 8

		Specifications	
RVB2 content	70%	CNR	CEN
CA1 content	30%		
Penetration at 25°C	82 dmm	80/100	70/100
Ring & Ball	49°C	44/49	43/51
Fraass breakingpoint	-25°C	≤-10°C	≤-10°C
Penetr. after T.L.	67%	--	≥46%

EP 0 863 196 A1

TABLE 8 (continued)

		Specifications	
Increase Ring & Ball after T.L.	5.5°C	--	≤9°C
Viscosity at 60°C	153 Pa.sec	--	≥90

As can be observed, bitumen 8 thus prepared is perfectly in line with the above specifications, with clearly improved overall characteristics with respect to those of the bitumens described in the previous comparative examples.

Using the procedure described in this example, a bitumen was obtained with a good consistency when hot, an excellent flexibility when cold and a high resistance to oxidation.

EXAMPLE 9

According to the procedure of example 4, a road bitumen is prepared by mixing and subsequently subjecting to blowing with air at 180°C a composition of bituminous component (RVB3) and an aromatic component (CA2). The characteristics of this bitumen are indicated in table 9.

TABLE 9

		Specifications	
RVB3 content	70.0%	CNR	CEN
CA2 content	30.0%		
Penetration at 25°C	89 dmm	80/100	70/100
Ring & Ball	47.5°C	44/49	43/51
Fraass breakingpoint	-21°C	≤-10°C	≤-10°C
Penetr. after T.L.	63%	--	≥46%
Increase Ring & Ball after T.L.	4.5°C	--	≤9°C
Viscosity at 60°C	102 Pa.sec	--	≥90

As can be observed, the bitumen is perfectly in line with the specification values indicated above.

With the process of the present invention it is possible to obtain a bitumen having a good consistency when hot, excellent flexibility when cold and a high resistance to oxidation.

EXAMPLE 10

In this example the formulation is provided of a road bitumen obtained, according to the procedure of example 4, by mixing RVB3 and CA2 and subsequently blowing with air at 190°C.

The characteristics of this bitumen (bitumen 10) are indicated in table 10.

TABLE 10

		Specifications	
RVB3 content	80.0%	CNR	CEN
CA2 content	20.0%		
Penetration at 25°C	83 dmm	80/100	70/100
Ring & Ball	48°C	44/49	43/51
Fraass breakingpoint	-19°C	≤-10°C	≤-10°C
Penetr. after T.L.	54%	--	≥46%
Increase Ring & Ball after T.L.	7°C	--	≤9°C
Viscosity at 60°C	130 Pa.sec	--	≥90

Like the bitumen of the previous example, also this one has a good consistency when hot, an excellent flexibility when cold and a high resistance to oxidation.

Claims

1. A process for the preparation of bitumens for road use, characterized in that it comprises the oxidation of a composition consisting of:

(a) a bituminous component (I) having a content of asphaltenes of between 10 and 50%, a content of aromatics of between 10 and 50% by weight and a penetration at 25°C of from 1 to 50 dmm, and
 (b) an aromatic component (II) essentially without asphaltenes and having a content of aromatics of from 80 to 95%, and a viscosity at 60°C of from 100 to 1000 cSt;

the weight ratio between the aromatic component (II) and the bituminous component (I) being from 10:90 to 50:50.

2. The process according to claim 1, characterized in that the weight ratio between the aromatic component (II) and bituminous component (I) is from 15:85 to 45:55.

3. The process according to claim 2, characterized in that the weight ratio between aromatic component (II) and bituminous component (I) is from 20:80 to 40:60.

4. The process according to claim 1, characterized in that the bituminous component (I) has a content of asphaltenes of from 20 to 40% by weight, a content of aromatics of from 15 to 35%, and a penetration at 25°C of from 15 to 45 dmm.

5. The process according to claim 1, characterized in that the aromatic component (II) has a content of aromatics of from 82 to 93% and a viscosity at 60°C of from 150 to 800 cSt.

6. The process according to claim 1, characterized in that the oxidation is carried out at a temperature of from 150°C to 270°C.

7. The process according to claim 6, characterized in that the oxidation is carried out at a temperature of between 160°C and 250°C.

8. The process according to claim 7, characterized in that the oxidation is carried out at a temperature of between 170°C and 190°C.

9. The process according to claim 1, characterized in that the oxidation is carried out with air.

10. The process according to claim 1, characterized in that the bituminous component (I) is the vacuum residue obtained by the distillation at reduced pressure of the effluent of a visbreaking plant.

11. The process according to claim 1, characterized in that the aromatic component (II) is the aromatic fraction, extracted with a solvent extraction process, of the vacuum distillate or deasphalted vacuum residue, in an operating cycle for the production of lubricating bases.



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EUROPEAN SEARCH REPORT

Application Number
EP 98 20 0671

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.6)
A	US 3 440 074 A (R.STERN) 22 April 1969 * column 1, line 48 - column 2, line 46 *	1-11	C10C3/04
A	GB 1 064 792 A (BP) * claim 1 *	1	
A	DATABASE WPI Section Ch, Week 9618 Derwent Publications Ltd., London, GB; Class H08, AN 96-178423 XP002035823 & RU 2 041 915 C (OIL PROCESSING PETROCHEM IND CONS INST) , 20 August 1995 * abstract *	1-11	
A	DATABASE WPI Section Ch, Week 8810 Derwent Publications Ltd., London, GB; Class H08, AN 88-069594 XP002035824 & SU 1 326 603 A (UFA PETROLEUM INST) , 30 July 1987 * abstract *	1-11	
A	US 4 631 088 A (M.A.POIRIER) 23 December 1986 * claim 1 *	1	
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		5 June 1998	Rotsaert, L
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 L : document cited for other reasons & : member of the same patent family, corresponding document			

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