

Description

The present invention relates to a process for the preparation of bitumen, bitumen thus prepared and bituminous compositions comprising bitumen thus prepared.

Bitumens are widely used for purposes such as road construction, roofing, the coating of pipelines, as binders for briquettes, etc. In many applications the bitumen is mixed with aggregates and/or filler materials which render the resulting mixture strength. For example in road construction bitumen is mixed with sand and stones and the mixture is used as road asphalt. It is evident that the road asphalt should be sufficiently resistant to abrasion and fretting. So, it would be advantageous to prepare bitumens which when mixed with filler material and/or aggregates, show an increased resistance to fretting.

Another important feature of bitumen is its resistance to water ingress. This is especially the case when bitumen mixes are used in applications to protect structures from water, such as roofing, pipeline coating and road construction applications.

It has now been found that bitumen originating from a thermally cracked hydrocarbon feedstock or bituminous compositions containing such bitumen show excellent resistances to fretting and water ingress.

US-A 2 305 440 discloses hard unoxidised bituminous materials, particularly asphalts of high softening point, and a process for preparing such materials which comprises cracking a paraffin-free asphaltic base West Venezuela crude oil to a residual bottoms oil having a gravity viscosity relationship of 8° A.P.I. to 9° A.P.I. gravity and Furl viscosity of between 1000 seconds and 1400 seconds to between 600 seconds and 850 seconds at 122°F (50°C) respectively, distilling the residual oil under vacuum to obtain a residue of bituminous material having a softening point in the range between 320°F and 420°F (160°C and 215.5°C) and susceptibility factor of 27 to 35. In a typical example (Column 2 line 28 to Column 3 line 13), bottoms consisting of a fuel oil are passed through a heating coil, with or without steam, and flashed into a vacuum tower where an absolute pressure of 25 to 100 mm (3.33 to 13.33 kPa) is maintained. The maximum temperature used in the heating coil to heat and fuel oil is not above 800°F (427°C), preferably from 750° to 790°F (399°C to 421°C).

However, it is known that bitumens obtained from thermally cracked feedstocks have unsatisfactory ageing and stability properties as is described in Fuel, 60 (1981) 401-404 and Fuel, 63 (1984) 1515-1517. Therefore, such bitumens are considered to be unsuitable for use in e.g. road asphalt.

It has now been found that a specific process for handling a thermally cracked feedstock yields bitumen having excellent resistances against fretting and water ingress and showing satisfactory stability and ageing properties.

The invention therefore provides a process for the preparation of bitumen in which a residual fraction of a thermally cracked hydrocarbon feedstock is distilled under subatmospheric pressure between 2 to 120 mm Hg (0.27 to 16.0 kPa) at a distillation temperature between 310 and 370°C and that corresponds with the boiling point at the subatmospheric pressure of hydrocarbons having an atmospheric boiling point ranging from 455 to 540°C, and at least part of the distillation residue is recovered as bitumen.

The reference to the hydrocarbons boiling point at atmospheric pressure is made after conversion of a subatmospheric boiling point in accordance with (the Maxwell-Bonnett relation described in Ind. Eng. Chem., 49 (1957) 1187-1196). In practice a boiling point of a hydrocarbon is determined under subatmospheric pressure. Since at many subatmospheric pressures many different boiling points can be determined the person skilled in the art prefers to refer to an unambiguous converted atmospheric boiling point.

The distillation temperature should not be below the boiling point of hydrocarbons with an atmospheric boiling point of 455°C (455°C/bar-hydrocarbons), since otherwise an unsatisfactory removal of relatively light hydrocarbons would be obtained, which would result in relatively unstable and rapidly ageing bitumen, just as described in the above articles from Fuel. On the other hand, if the temperature would exceed the 540°C/bar-hydrocarbons boiling point the resulting residue would be too hard to be suitable for use in e.g. road asphalt and may give rise to incompatibility problems when used in bitumen blends.

The residual fraction subjected to the subatmospheric distillation can be almost any fraction from the thermal cracking unit. It is advisable to send the thermally cracked product to an atmospheric distillation unit to separate distillate products such as gases, gasoline, kerosene and gas oils from the atmospheric residue. Conveniently this atmospheric residue is sent to the subatmospheric distillation. The atmospheric distillation is suitably carried out at a bottom temperature of from 300 to 370°C. Hence, the residual fraction sent to the subatmospheric distillation suitably has at least 80%w of components having an atmospheric boiling point of at least 300°C.

Thermal cracking is a rather simple cracking process. At a temperature level of about 400 to 500°C the longer hydrocarbons become unstable and tend to break into smaller molecules of all possible sizes and types. The feedstock for thermal cracking is generally a mixture of complex heavy hydrocarbons left over from an atmospheric or vacuum distillation of a crude oil. Visbreaking, i.e. reducing viscosity by breaking of molecules, is an important application of thermal cracking because it reduces the viscosity of the residue obtained after the thermal cracking considerably. Visbreaking is carried out by sending a feed after appropriate preheat to a furnace for heating the feed to the cracking temperature. From there the feed is fed into a soaker downstream of the furnace where most of the cracking takes place. The soaker has suitably internal baffles to prevent too much back-mixing. The products are gas, distil-

lates and residue. This residue has a lower viscosity than the feed. Preferably such a residue, i.e. the residue of a visbroken hydrocarbon feed, is used as the residual fraction in the process according to the present invention. The visbreaking conditions are suitably a pressure of from 2 to 30 bar, a temperature of 400 to 500°C and a residence time of from 5 to 60 min.

The residual fraction is distilled under subatmospheric pressure. This includes that it is subjected to a conventional vacuum distillation, provided that the requirement as to the distillation temperature is met. It is, however, preferred to subject the residual fraction to flash distillation. In flash distillation the residual fraction is heated to a temperature within the boiling range at a lower pressure of the liquid and introduced into a subatmospheric flash zone to yield distillate and residue. The residue is at least partly recovered as bitumen.

Many subatmospheric pressures can be used in the process according to the invention. Each pressure applied determines the temperature limits within which the distillation has to be carried out.

As stated hereinbefore, the distillation temperature is selected such that on the one hand a satisfactory removal of relatively light hydrocarbons is obtained but on the other hand the formation of an unacceptably hard bitumen is avoided. Preferably, the maximum distillation temperature corresponds with the boiling point of 460-510°C/bar-hydrocarbons.

The bitumen prepared according to the invention has satisfactory ageing and stability properties. To even improve the oxidation stability the bottom fraction of the distillation is preferably at least partly subjected to blowing before being recovered as the desired bitumen. The blowing process is generally carried out continuously in a blowing column, into which liquid bitumen is fed and wherein the liquid level is kept approximately constant by withdrawing bitumen near the bottom. Air is blown through the liquid mass via an air distributor at the bottom of the column. Suitable blowing temperatures are 170-320°C, in particular 220-275°C.

It is known in the art to blend various types of bitumen to obtain a bitumen composition having the desired properties. The present invention further provides bituminous compositions comprising bitumen prepared in a process according to the present invention. It should, however, be avoided that such a bituminous composition contains an overbalance of asphaltenes since in such compositions heterogeneity may occur. There is a chance of creating an overbalance of asphaltenes when a thermally cracked residue is used as blending component, since it is known, e.g. from the above-mentioned articles in Fuel, that the asphaltene content in thermally cracked residue is rather high. For, though during the thermal cracking the heavy hydrocarbon oils are converted to lower-boiling compounds, the asphaltenes are concentrated in the residue. Moreover, new asphaltenes are formed during the cracking operation. The possibility of creating an asphaltenes overbalance is substantially excluded if the maximum distillation temperature in the process according to the invention is below the boiling point of 540°C/bar-hydrocarbons, preferably of 510°C/bar-hydrocarbons. Suitably, the bituminous composition contains from 5 to 60%w of the bitumen prepared according to the invention and 95 to 40%w of at least one other bitumen component. A person skilled in the art will be able to select the proper other bitumen component(s) in accordance with his desires. Suitable other bitumen components include straight-run bitumen, propane bitumen, bright stock extracts such as furfural extracts. The components may be blown or unblown and may or may not contain flux oils. Criteria on which the other bitumen components are selected comprise the volatility, density, penetration, softening point, etc, as can be determined by the person skilled in the art.

It is evident that the bituminous compositions according to the present invention may contain other additives such as diluents and/or polymers, in particular styrene-butadiene or styrene-isoprene block copolymers or atactic polypropylene.

The invention will be further elucidated by means of the following examples.

EXAMPLE I

In this Example some characteristics of thermally cracked residues were determined. Residue I was a thermally cracked residue which has not been subjected to a flashing step. Residue II is obtained after flashing Residue I at 364°C/30 mmHg (4.0kPa), corresponding to 496°C/bar. Residue III is obtained after flashing Residue I at 330°C/30 mmHg (4.0 kPa) corresponding to 460°C/bar and a blowing step at an air consumption of 20-30 Nl/kg residue and at 280-300°C. In a thin film oven test (TFOT, ASTM D1754) the residues were subjected to heat (163°C) and air, and their ageing behaviour was determined. After the test the penetration was measured and compared with the original penetration, yielding a retained-penetration value (in %). The higher the retained penetration, the better is the residue able to stand up against heat and air. The loss of weight during the test was determined as well; and also the change in the softening point, determined by the Ring and Ball method was measured (R & B). The results are indicated in Table I.

TABLE I

Residue		I	II	III
Penetration/25°C	mm	7.1	8.1	8.5
	(dmm)	71	81	85
Softening point R & B, °C	52	46	48	
Flash point, °C	210	320	316	
TFOT (163°C)				
Loss on heating, % m/m	1.8	-0.08	0.06	
Retained penetration	%	46	62	57
R & B, °C	14	5	6	

From comparison of the results of Residues I and II it is apparent that bitumen prepared according to the invention has improved ageing behaviour as shown by the higher retained penetration, no loss on heating and a smaller change in the softening point. Comparison between the results of Residues II and III teaches that the similar characteristics can be obtained by some milder flashing followed by blowing.

Example II

For a number of compositions their suitability for use in asphalt mixes was tested. Therefore asphalt mixes were subjected to the Marshall test, extended for retained Marshall values upon storage of the mixes for two weeks in water at 60°C, to obtain information on the sensitivity of the stability of the mix towards water.

The mixes contained 6.0% m/m of bituminous composition, based on 100% m/m of mineral aggregate, with a typical void content of 2% v/v.

The bituminous composition consists of a Middle East, short residue and vacuum-flashed thermally cracked residue, flashed at conditions corresponding to 495°C/bar. The results are indicated in Table II.

TABLE II

Composition No.	cracked residue %w	Short residue %w	Retained Marshall value, %
1	34	66	91
2	40	60	83
3	46	54	98
4	50	50	92

Similar tests were carried out with bituminous compositions in asphalt mixes, which compositions consisted of propane bitumen (PB), bright stock furfural extract (BFE) and vacuum-flashed thermally cracked residue (VFCR) flashed at conditions corresponding to 500°C/bar. The retained Marshall values for the compositions are indicated in Table III.

TABLE III

No.	Bituminous composition			Retained Marshall Value, %
	VFCR %w	PB %w	BFE %w	
5	0	58	42	62
6	21	42	37	81
7	43	37	20	87
8	55	18	27	89
9	60	23	17	92

From the above results it is apparent that the bituminous compositions according to the invention have excellent water resistance.

5 Example III

Compositions 6 and 7 of Example II were subjected to a fretting test in which the percentage of abraded material was determined after storage in water for 240 hours at 40°C. The test is described in "Proceedings of AAPT, 463, vol. 32, pp. 380-411.

10 The smaller the loss of material, the better was the resistance to abrasion and fretting. The results are indicated in Table IV.

TABLE IV

No.	Bituminous composition			Loss of surface material, g
	VFCR %w	PB %w	BFE %w	
6	21	42	37	29.2
7	43	37	20	25.1

From these results it is apparent that the composition with the higher VFCR content has even improved fretting and abrasion resistance.

Claims

1. Process for the preparation of bitumen in which a residual fraction of a thermally cracked hydrocarbon feedstock is distilled under subatmospheric pressure between 2 to 120 mmHg (0.27 to 16.0 kPa) at a distillation temperature that is between 310 and 370°C, and that corresponds with the boiling point at the subatmospheric pressure of hydrocarbons having an atmospheric boiling point of 455-540°C, and at least a part of the distillation residue is recovered as bitumen.

2. Process according to claim 1 in which the residual fraction is the residue of a visbroken hydrocarbon feed.

3. Process according to claim 2 in which the hydrocarbon feed has been visbroken at a pressure of from 2 to 30 bar, a temperature of from 400 to 500°C and at a residence time of from 5 to 60 minutes.

4. Process according to any one of claims 1-3, in which the residual fraction is subjected to flash distillation.

5. Process according to any one of claims 1-4 in which the distillation temperature corresponds with the boiling point at the subatmospheric pressure of hydrocarbons having an atmospheric boiling point of 460 to 510°C.

6. Process according to any one of claims 1-5, in which the bottom fraction of the distillation is subjected to blowing before being recovered as bitumen.

7. Bitumen, whenever prepared with the process according to any one of claims 1-6.

8. Bituminous composition comprising bitumen according to claim 7.

9. Bituminous composition according to claim 8 which comprises 5 to 60%w of the bitumen according to claim 7 and 95 to 40%w of at the least one other bitumen component.

Revendications

1. Procédé pour la préparation de bitume, dans lequel une fraction résiduelle d'une charge de départ hydrocarbonée ayant subi un craquage thermique est distillée sous pression réduite entre 2 et 120 mm de Hg (0,27 et 16,0 kPa) à une température de distillation comprise entre 310 et 370°C et qui correspond au point d'ébullition sous la pression réduite d'hydrocarbures ayant un point d'ébullition sous la pression atmosphérique de 455-540°C, et au moins une partie du résidu de distillation est recueillie comme bitume.

2. Procédé selon la revendication 1, dans lequel la fraction résiduelle est le résidu d'une charge hydrocarbonée ayant subi une viscoréduction.

3. Procédé selon la revendication 2, dans lequel la charge hydrocarbonée a été soumise à une viscoréduction à une pression de 2 à 30 bars, une température de 400 à 500°C et avec un temps de séjour de 5 à 60 minutes.

4. Procédé selon l'une quelconque des revendications 1-3, dans lequel la fraction résiduelle est soumise à une distillation éclair.

From the above results it is apparent that the bituminous compositions according to the invention have excellent water resistance.

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6. Process according to any one of claims 1-5, in which the bottom fraction of the distillation is subjected to blowing before being recovered as bitumen.

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4. Procédé selon l'une quelconque des revendications 1-3, dans lequel la fraction résiduelle est soumise à une distillation éclair.



5. Procédé selon l'une quelconque des revendications 1-4, dans lequel la température de distillation correspond au point d'ébullition sous la pression réduite d'hydrocarbures ayant un point d'ébullition sous la pression atmosphérique de 460 à 510°C.

6. Procédé selon l'une quelconque des revendications 1-5, dans lequel la fraction de queue de la distillation est soumise à un soufflage avant d'être recueillie comme bitume.

7. Bitume, chaque fois que préparé par un procédé selon l'une quelconque des revendications 1-6.

8. Composition bitumineuse comprenant du bitume selon la revendication 7.

9. Composition bitumineuse selon la revendication 8, qui comprend de 5 à 60% en poids du bitume selon la revendication 7 et de 95 à 40% en poids d'au moins un autre constituant bitume.

Patentansprüche

1. Verfahren zur Herstellung von Bitumen, in welchem eine Rückstandsfraktion eines thermisch ge crackten Kohlenwasserstoffeinsatzmaterials bei unteratmosphärischem Druck zwischen 2 und 120 mmHg (0,27 bis 16,0 kPa) und bei einer Destillationstemperatur zwischen 310 und 370°C destilliert wird, welche dem Siedepunkt von Kohlenwasserstoffen bei dem unteratmosphärischen Druck entspricht, die bei atmosphärischem Druck einen Siedepunkt von 455 bis 540°C aufweisen, und in welchem mindestens ein Teil des Destillationsrückstandes als Bitumen gewonnen wird.

2. Verfahren nach Anspruch 1, in welchem die Rückstandsfraktion der Rückstand einer einer Visbreaking-Behandlung (leichter Crackprozeß zur Ausbeute von Crackprodukten mittlerer Siedelage) unterworfenen Kohlenwasserstoffzuspeisung ist.

3. Verfahren nach Anspruch 2, in welchem die Kohlenwasserstoffzuspeisung bei einem Druck von 2 bis 30 bar, einer Temperatur von 400 bis 500°C und einer Verweilzeit von 5 bis 60 Minuten einer Visbreaking-Behandlung unterworfen worden ist.

4. Verfahren nach einem der Ansprüche 1 bis 3, in welchem die Rückstandsfraktion einer Kurzwegdestillation unterworfen wird (flash distillation).

5. Verfahren nach einem der Ansprüche 1 bis 4, in welchem die Destillationstemperatur dem Siedepunkt von Kohlenwasserstoffen bei dem unteratmosphärischen Druck entspricht, welche einen Siedepunkt von 460 bis 510°C bei atmosphärischem Druck aufweisen.

6. Verfahren nach einem der Ansprüche 1 bis 5, in welchem die Bodenfraktion der Destillation einer Blasbehandlung unterworfen wird, bevor sie als Bitumen gewonnen wird.

7. Bitumen, hergestellt durch das Verfahren nach einem der Ansprüche 1 bis 6.

8. Bituminöse Zusammensetzung, umfassend Bitumen nach Anspruch 7.

9. Bituminöse Zusammensetzung nach Anspruch 8, welche 5 bis 60 Gewichtsprozent des Bitumens nach Anspruch 7 und 95 bis 40 Gewichtsprozent mindestens einer anderen Bitumenkomponente enthält.

