

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

**0 240 090
A2**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **87200630.9**

(51) Int. Cl.4: **C10C 3/06**

(22) Date of filing: **03.04.87**

(30) Priority: **04.04.86 GB 8608302**

(43) Date of publication of application:
07.10.87 Bulletin 87/41

(84) Designated Contracting States:
BE CH DE ES FR GB IT LI NL SE

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(54) **Process for the preparation of bitumen.**

(57) Process for the preparation of bitumen in which a residual fraction of a thermally cracked hydrocarbon feedstock is distilled under subatmospheric pressure at a maximum distillation temperature 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.

EP 0 240 090 A2

PROCESS FOR THE PREPARATION OF BITUMEN

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.

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 at a maximum distillation temperature 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 maximum 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 maximum 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, distillates 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.

5 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 maximum 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
10 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. Preferably, the actual temperature in the distillation does not exceed 400°C. Below this temperature reactions between or of the hydrocarbons in the residue, e.g. cracking reactions, are substantially excluded. Since at relatively
15 long residence times cracking reactions can take place at high temperatures up to 400°C it is even more preferred to have somewhat lower actual distillation temperatures, in particular between 310 and 370°C. To comply with the requirement as to the boiling point of the hydrocarbons, the pressure in the subatmospheric distillation is preferably between 2 and 120 mmHg (0.27 to 16.0 kPa).

As stated hereinbefore, the maximum distillation temperature is selected such that on the one hand a
20 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
25 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.

30 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
35 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
40 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
45 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
50 copolymers or atactic polypropene.

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°/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 NI/hg 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 Bell method was measured (R & B). The results are indicated in Table I.

TABLE I

Residue		I	II	III
Penetration/25°C,	dnm	71	81	85
Softening point R & B,	°C	52	46	48
Flash point,	°C	210	320	316
<u>TFOT</u> (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.

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.

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

TABLE IV

5	No.	Bituminous composition			Loss of surface material, g
		VFCR	PB	BFE	
		%w	%w	%w	
10	6	21	42	37	29.2
	7	43	37	20	25.1

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

20 Claims

1. Process for the preparation of bitumen in which a residual fraction of a thermally cracked hydrocarbon feedstock is distilled under subatmospheric pressure at a maximum distillation temperature 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 subatmospheric pressure is between 2 to 120 mmHg (0.27 to 16.0 kPa) and the maximum distillation temperature is between 310 and 370°C.

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

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

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

9. Bituminous composition comprising bitumen according to claim 8.

10. Bituminous composition according to claim 9 which comprises 5 to 60%w of the bitumen according to claim 10 and 95 to 40%w of at least one another bitumen component.

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