PATENT SPECIFICATION (11) 1 582 489

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(21) Application No. 37927/77 (22) Filed 12 Sep. 1977 (19)

(31) Convention Application No. 7629004 (32) Filed 27 Sep. 1976 in

(33) France (FR)

(44) Complete Specification Published 7 Jan. 1981

(51) INT. CL.[3] C10C 3/04

(52) Index at Acceptance
C5E ED

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(54) PROCESS FOR MANUFACTURING BITUMEN

(71) We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Moor Lane, London, EC2Y 9BU, a British Company, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:-

The present invention relates to a process for the accelerated manufacture of bitumens possessing an improved resistance to combustion.

Petroleum bitumens possess physico-chemical characteristics such as a relatively high softening point, a good power of adhesivity, a low density, an excellent impermeability and a good ductility which allow them to be used widely, especially in the building industry, for example for roofing coverings, sealing joints, glues and mastics, and coverings for sound or themal insulation. Furthermore, their comparatively low cost and their easy handling give them advantages over equivalent chemical polymers.

Nevertheless, experience shows that these bitumens, when used in the abovementioned applications, do not always possess a satisfactory behaviour in the presence of a flame, since their hydrocarbon structure renders them combustible. Furthermore, their rheological properties make them subject to flow phenomena when they are at elevated temperatures.

Attempts have, therefore been made to remedy these drawbacks by incorporating in the raw materials or in the final bitumens mineral agents which are known for their fireproofing properties and containing for example atoms of chlorine ($FeCl_3$) or phosphorus (P_2O_5, phosphates) or boron (borates). However, these agents have the drawback of remaining in the solid state inside the bitumen, and therefore upsetting the manufacture, use and quality of the latter.

The applicants have surprisingly found that certain halogenated organic additives which have the reputation of slowing down or preventing the combustion of chemical polymers, such as polyesters, natural rubber, butadiene/styrene copolymers or ethylene/propylene copolymers have a catalytic action on the oxidation of bitumen. In particular, these additives notably accelerate the speed of the reaction, which shows itself in the practical sense in a considerable reduction of the residence time of the products in the oxidation reaction tower.

This reduction may amount to 35% of the residence time necessary for conversion under the same conditions of a feedstock, but in the absence of said halogenated additives.

The applicants have now developed a new process for the accelerated manufacture of petroleum bitumens possessing improved resistances to combustion and to flow and which are widely utilisable, particularly in the building industry, which comprises subjecting a heavy petroleum residue to a thermal treatment at elevated temperature in the presence of air or oxygen, known as "blowing" and in the presence of 0.1 to 10% wt by weight of the total mixture of a halogenated organic compound selected from the compounds obtained by the Diels and Alder condensation of a hexahalocyclopentadiene with a dienophilic compound.

The heavy petroleum residue used in the present invention may be at atmospheric distillation residue or vacuum distillation residue of crude oil or an asphalt coming from the deasphalting of the said residues by means of a light paraffinic solvent.

The properties of the heavy petroleum residue used according to the present invention may also be adjusted, for the purpose of the application envisaged, by the incorporation of a certain quantity of petroleum distillate either as it is or possibly modified by

physico-chemical treatments.

Thus a lighter petroleum cut may be incorporated in the abovementioned residues so as to obtain, by the blowing treatment to which the invention relates, bitumens which are capable of satisfying specifications connected with penetration and softening point (ring and ball method, NFT standard 66.008) imposed for particular applications.

Among these lighter petroleum cuts, known as "fluxes", suitable products are the heavy distillates coming from the vacuum distillation of crude oil and used as feedbacks for mineral lubricants, or the filtrate obtained in the operation of dewaxing at low temperature using an organic solvent (for example a ketone), or a raffinate obtained after removal, by a solvent (for example furfural, phenol etc.), of the aromatic hydrocarbons present in the phase known as "DAO" (de-asphalted oil), or more generally, any petroleum fraction obtained by any physical and/or chemical process, such as distillation, solvent extraction, dehydrocyclisation, isomerisation etc., capable of creating or increasing in the flux the necessary quantity of precursor of the cross-linked structure which is characteristic of the final bitumen, namely monocyclic or polycyclic napthenic or aromatic hydrocarbons.

The quantity of "flux" incorporated in the abovementioned residues may be between 5 and 80% by weight, according to the bitumen in question, and preferably between 25 and 70% by weight.

The halogenated organic compounds obtained by the Diels and Alder condensation of a hexaholocyclopentadiene with a dienophilic compound may be chlorendic acid or the analogous compound "Dechlorane 604". These are products marketed by the Belgian company HOOKER CHEMICAL S.A., resulting from the condensation by the Diels-Alder mechanism between hexachloropentadiene and maleic anhydride in the one case and hexahalocyclopentadiene and cyclooctatriene in the other. Chlorendic acid, whose chemical name is hexachloro-endo-methylene-tetrahydrophthalic acid, only contains chlorine as halogen, whereas Dechlorane 604 also contains some atoms of bromine.

The organic additive is preferably incorporated in the petroleum residue, prior to the blowing operation, in a quantity of between 0.25 and 3% by weight. This incorporation may be carried out by agitation by any known means, at an average temperature of 150 to 200°C.

In cases where it is intended also to incorporate a flux in the raw material, the incorporation of the organic additive is preferably carried out during the same operation.

The petroleum residue containing the organic additive and possibly the flux may be subjected to a known process of blowing at elevated temperature in the presence or air or oxygen, either continuously or discontinuously, at atmospheric pressure.

In a normal blowing operation, the raw material enters the blowing tower at the bottom and it is brought into contact at this level with the oxidising gas which provides both for the chemical conversion of the latter and also for the agitation of the mixture. At the end of the reaction, the bitumen obtained leaves the lower part of the tower at the side, Whilst the light products formed during the reaction are eliminated from the top of the tower.

A variant of the continuous process consists in incorporating the oxidising gas in the raw material, no longer inside the tower but in the feed pipe of the tower, by means of a mixer valve.

The operating conditions may be selected in such a way that the product of the treatment has a penetration of between 10 and 100 (NFT standard 66.004).

The average blowing temperature may be between 150 and 300°C, but preferably between 200 and 280°C.

The rate of flow of air, which depends not only on the temperature but also on the quality or grade or bitumen, may be between 50 and 10,000 m^3 per ton of charge, and preferably between 80 and 4,000 m^3 per ton of charge. For a reaction temperature of 150°C it is likely to be in the range from 200 to 10,000 m^3 per ton of charge and at 300°C it is likely to be in the range from 50 to 1,000 m^3 per ton of charge.

The products obtained according to the process of the present invention have an improved resistance to combustion, which may be assessed according to the adapted method used in the plastic materials industry for the determination of inflammability by measuring the oxygen limit index (AFNOR experimental standard NFT 51-071 of July 1973).

Instead of bars cut up into plates of plastic material, the applicants use test pieces of 125 mm in length and 13 mm in width cut out in a sheet of asbestos board 3 mm thick.

These test pieces are then dried in an oven at 150°C for 6 to 8 hours, placed in a desiccator until required and weighed just prior to the series of measurements.

The bitumen to be tested, placed in a tube of a height of 120 mm and a diameter of 45 mm is brought to the selected impregnation temperature by means of an oil bath and the samples are saturated with the bitumen over a minimum length of 70 mm.

The duration of impregnation is chosen according to the weight of the bitumen which it is desired to deposit on the sample: it may be determined by means of a few preliminary

impregnations.

The test pieces of asbestos board saturated with bitumen are withdrawn from the bath and placed to cool in a vertical position. The result is a slight flow of the bitumen, which leads to an excess of product at the bottom of the test piece. This is eliminated by means of a knife so as to adjust the quantity of bitumen to the desired weight.

When setting up the apparatus for measuring the oxygen limit index the base of the test pieces is placed between two metal plates of 40 mm in length and 20 mm in width to hold the test pieces. The useful length which can burn is therefore 85 mm.

The aim of this method of analysis is to find out the minimum content of oxygen in a mixture of oxygen and nitrogen which maintains combustion with a flame, in particular with a descending flammability of the candle type.

This content, expressed as a percentage, is called the oxygen limit (O.L.I.). The higher the OLI value of the bitumen, the better is its resistance to combustion.

The following Examples illustrate the invention.

Comparative Example:

A vacuum distillation residue of crude oil possessing the following properties:

- density at 25°C : 1.025
- kinematic viscosity at 100°C (cst) : 1370 (NFT standard 60-100)

was subjected to a continuous blowing operation in the presence of air under the following conditions:

- mean blowing temperature (°C) : 270
- rate of flow of air (m^3 per ton of charge) : 170

A product was obtained having the following properties:

- penetration (25°C/100 g/5s) : 30 mm /10
- softening point Ring and ball (°C) : 62

To this product was added 60 per cent by weight, reckoned on the total mixture, of a distillate flux oil obtained by the vacuum distillation of a crude petroleum and having the following properties:

- density at 15°C : 0.94
- kinematic viscosity at 100°C (cSt) : 14.5
- pour point (°C) : + 39 (NFT standard 60-105)

whilst agitating at about 160°C for 15 minutes.

This mixture constituted the petroleum feedstock which was then subjected to the process of blowing, operating under the following conditions:

- mean temperature : 260°C
- rate of flow of air : 560 m^3 per ton of charge
- duration of blowing : 4 hours 10 minutes.

The bitumen obtained in this case had the following properties:

- softening point (Ring and Ball) : 98°C
- penetration (25°C/100 g/5s) : 37
- flash point (°C) : 260°C
- ignition point (°C) : 290°C
- absolute viscosity at 180°C (cp) : 218
- absolute viscosity at 220°C (cp) : 32.1
- oxygen limit index (% by vol.of O_2) : 23

Example 1

Using the same vacuum distillation residue of crude oil as in the comparative example, a mixture was prepared in the same way containing, however, only 45 per cent by weight, reckoned on the total mixture, of chlorendic acid.

This petroleum raw material was then subjected to blowing under the following conditions:

- mean reaction temperature : 260°C
- rate of flow of air : 490 m^3 per ton of charge
- duration of blowing : 3 hours 30 minutes

The bitumen obtained was analysed. It had the following properties:

- softening point (Ring and ball) : 95°C
- penetration (25°C/100 g/5s) : 38
- flash point (°C) : 258 (NFT standard 60-118)
- ignition point (°C) : 292 (NFT standard 60-118)
- absolute viscosity at 180°C (cp) : 369
- absolute viscosity at 220°C (cp) : 57
- oxygen limit index (% by vol. of O_2) : 25

Example 2

The same raw materials were used as in Example 1, except for the halogenated organic additive, which in this case was Dechlorane 604 incorporated in the same quantity (0.5% per weight) in the mixture. The mixture was blown under the following conditions:

- mean temperature (°C) : 260°C
- rate of flow of air : 490 m^3 per ton of charge
- duration of blowing : 3 hours 15 minutes.

A bitumen was obtained having the following properties:

- softening point (Ring and ball) : 98°C
- penetration (25°C/100 g/5s) : 37
- flash point (°C) : 275°C
- ignition point (°C) : 301°C
- absolute viscosity at 180°C (cp) : 603
- absolute viscosity at 220°C (cp) : 79
- oxygen limit index (% by volume of O_2) : 25

From these examples it can clearly be seen that a small quantity of the chlorinated organic compound chosen, when added to the petroleum raw material makes it possible:

1) - to obtain a bitumen with given softening points and penetration under the most economical blowing conditions, particulary with a lower rate of flow of air,

2) - to obtain more rapidly a bitumen with given softening point and penetration,

3) - to raise the oxygen limit index of the bitumen obtained and in this way improve its resistance to combustion,

4) - to increase the absolute viscosity of such a bitumen,

5) - to reduce the quantity of flux incorporated in the raw material.

The halogenated organic additives also have a useful effect on the bitumen in that they give a very distinct increase in the duration of combustion, i.e. an effect of retarding combustion known as a "candle effect".

Furthermore, the above mentioned halogenated organic additives are totally miscible both in the petroleum raw materials described above and in the bitumens obtained by the blowing process and, contrary to the equivalent mineral additives used particularly to retard or prevent combustion of bitumens, the halogenated organic additives present in these same bitumens do not affect their quality, and in particular their ash content (NFT standard 60-111) or the level of solubility in certain solvents for particular application, but they increase still further the viscosity at high temperature, as can be seen from the Table below.

TABLE I

Bitumen 100/40	Viscosity in centipoises at 220°C
Known process	32
Blowing in the presence of 0.5% chlorendic acid	57
Blowing in the presence of 0.5% Dechlorane 604	79

In addition to their interesting physical properties, the bitumens obtained according to

the process of the present invention have a physico-chemical structure which is different from that of the bitumens prepared previously by the known processes.

One may in fact consider that the molecules of additive are more or less combined with the bitumen, which then contains halogenated molecules.

This explains the better behaviour to fire of the bitumens prepared in this way.

Furthermore, the distribution of chemical types in the bitumens obtained according to the process of the present invention is also different and is more favourable to a good behaviour from the point of view of sweating oil, as is clearly shown by the following Table.

TABLE II

Bitumen 100/40	Usual	Example 1	Example 2
Chemical Types: % wt.			
Asphaltenes	26.0	24.8	24.5
Saturates	22.0	21.2	20.5
Cyclo-aromatics	30.8	39.2	37.1
Resins	21.2	14.8	17.9
Ratio			
Asphaltenes + Saturates / Cyclic + Resins	0.92	0.85	0.82
Stain index (*) (ASTM method D 1328)	21	14	17

(*) This index is bound up with the stability of the colloidal structure of the bitumen and in particular with its staining or non-staining properties. The lower it is, the better the bitumen is.

WHAT WE CLAIM IS:-

1. A process for the accelerated manufacture of bitumens possessing an improved resistance to combustion, characterised in that it comprises subjecting a heavy petroleum residue to a thermal blowing treatment at elevated temperature in the presence of air or oxygen and from 0.1 to 10%, wt by weight of the total mixture of a halogenated organic compound selected from the compounds resulting from the Diels and Alder condensation of a hexahalocyclopentadiene and a dienophilic compound.

2. A process as claimed in claim 1, characterised in that the reaction is carried out at a temperature of 150 to 300°C, preferably between 200 and 280°C.

3. A process as claimed in claim 1 or 2 characterised in that the rate of flow of air is between 50 and 10,000 m^3 per ton of charge, preferably between 80 and 4,000 m^3 per ton of charge.

4. A process as claimed in any of claims 1 to 3, characterised in that the thermal blowing treatment is carried out in the presence of from 0.25 to 3 % wt of the halogenated organic compound.

5. A process as claimed in any of claims 1 to 4, characterised in that the heavy petroleum residue is selected from atmospheric distillation residues or vacuum distillation residues of crude oil, or asphalts obtained by de-asphaltisation by means of a light paraffinic solvent of the said residues.

6. A process as claimed in claim 5, characterised in that the properties of the heavy petroleum residue are modified by the incorporation of a lighter petroleum cut as a flux oil.

7. A process as claimed in claim 6, characterised in that the quantity of flux incorporated in the heavy petroleum residue is between 5 and 80 % wt, preferably between 25 and 70 % wt.

8. A process as claimed in claim 1 substantially as described in Examples 1 and 2.

9. Bitumen possessing improved resistance to combustion and to flow when prepared by a process as claimed in any of claims 1 to 8.

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Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1980.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY,from
which copies may be obtained.