Electrode Binder

The present invention relates to a process for preparing an electrode binder, and an electrode binder obtainable by said process.

Background of the Invention

Electrodes are used in smelting cells for the production of metals such as aluminium and steel, at present nearly all primary aluminium being produced by electrolysis of alumina (Al_2O_3) in electrolysis cells. In an electrolysis cell for aluminium production, aluminium is deposited in molten form onto a carbon cathode whilst simultaneously oxygen is released at, and eventually consumes, the cell's anode. The electrodes are prepared by mixing petroleum coke particles with a binder. Petroleum coke comprises nearly pure carbon and is formed during the refining of crude oil by high temperature carbonisation of heavy residues.

Two main categories of anode are employed in aluminium electrolysis cells, pre-baked anodes and so-called Soederberg anodes which are used in Soederberg cells. In Soederberg cells, a continuous mixture of petroleum coke and binder is fed into the cell, the anode being baked in situ by the heat generated in the cell. Pre-baked anodes are prepared by pressing a mixture of petroleum coke particles and binder into shape and then subjecting the anodes to baking or carbonisation in order to transform the binder into carbon.

The binder usually used in the production of such electrodes is coal-tar pitch. Coal-tar pitch is a

distillation product of coal tar, coal-tar being a product of the carbonisation of coal, and consists of hydrocarbon oils, and derivatives of phenols and bases such as pyridine and quinoline etc. Coal-tar pitch is used as a binder as its high carbon and aromatic content has meant that after carbonisation electrodes containing a coal-tar pitch binder contain few non-carbon impurities. This is important to the performance and life-time of the electrode as impurities (e.g. metals such as vanadium, nickel, etc.) in the electrode may similarly contaminate the product and increase the air- and carbon dioxide-reactivity of the electrode thus reducing its operational life-time. However, coal-tar contains an extremely high proportion of Polycyclic Aromatic Compounds (PAC), a typical coal-tar pitch having a PAC content of approximately 100,000 ppm. Some of these molecules are carcinogenic and for environmental and health and safety reasons it would be beneficial if there was an alternative material that could be used as an electrode binder in place of coal-tar pitch, but which has as low a PAC content as possible.

The need for a coal-tar pitch replacement has been increased by recent regulatory trends making it preferable that PAC levels in commercial materials be kept to a minimum. A large number of PAC molecules exist. In Europe certain substances (e.g. coal derived substances such as coal-tar pitch) are classified according to their content of specific PACs. One such PAC is benzo[a]pyrene, which is considered to be a useful marker of the overall PAC content of a substance. Accordingly, the classification of such products in

respect of carcinogenicity is generally based upon their benzo[a]pyrene content.

The use of heavy petroleum residues as electrode binders has been investigated. However, to date such binders have not been considered industry-acceptable replacements for coal-tar pitch as their performance with respect to coal-tar pitch in important parameters such as their carbon content and density, as well as the air-reactivity and carbon dioxide-reactivity of electrodes prepared from such binders has been unsatisfactory. Further, of the few reported means by which satisfactory electrode binders may be prepared, the petroleum feedstocks are highly aromatic, resulting in products having a PAC content which remains high and which is undesirable for environmental and health and safety reasons.

For example, EP-A 0378326 describes a binder pitch suitable for use in the preparation of graphite electrodes used in electric arc furnaces for the production of steel, by subjecting a petroleum aromatic mineral oil to hydrotreating; thermally cracking the hydrotreated aromatic mineral oil; subjecting residue from the thermal cracking to distillation and combining the topped residue with finely subdivided calcined premium coke particles having an average diameter between 1 and 40 μm. In this process, which relates specifically to the preparation of binder pitch for steel production, it is necessary to use a hydrotreated aromatic mineral oil feedstock i.e. a feedstock which has been pre-treated with hydrogen in the presence of a catalyst.

Canadian Patent publication 2009121 describes a process for the production of a high quality petroleum

tar pitch from an aromatic feedstock comprising the steps of, (a) providing a fresh aromatic feedstock; (b) pre-heating said feedstock in a furnace to a temperature of about between 380 to 480 °C; (c) feeding said heated feedstock to a reactor and treating said feedstock in said reactor under controlled conditions so as to promote condensation and polymerization reactions; (d) passing said treated feedstock to a fractionating tower wherein the feedstock is fractionated into (1) gases, (2) light distillates and (3) a bottom fraction stream; (e) dividing said bottom fraction stream into a recycle stream and a cracked fraction stream; and (f) feeding said cracked fraction stream to a reduced pressure distillation tower wherein said light cracked fraction is further fractionated into (1) light gas oil, (2) heavy gas oil and (3) a high quality petroleum tar pitch.

The feedstock of the process of CA 2009121 is a highly aromatic hydrocarbon stream having an aromatics content of 65-85% wt (page 4, lines 1-4 and page 6, line 21 to page 7, line 5). In the working example provided, the feedstock employed is a catalytic cracking decanted (clarified) oil having an aromatic content of 85 % wt. Further, in order to obtain a binder pitch having the correct properties, it is essential to recycle a part of the heavy cracked fraction using a recycle stream, it being stated that recycling is highly desirable in order to optimise the resulting pitch properties (page 10, lines 1 to 5). Therefore, from the teaching of CA 2009121 the person skilled in the art would be led to conclude that for an electrode binder to be prepared from a petroleum residue by thermal cracking of that residue, it is necessary to use a highly aromatic feedstock, even

requiring recycle of a part of the thermally cracked residue.

EP-A 1130077 describes a process for producing a so-called non-polluting petroleum pitch by subjecting a petroleum fraction or residue to heat treatment at a temperature between 350 and 470 °C, for a time of less than 120 minutes at a pressure of under 20 atmospheres. The feedstocks employed are a decanted oil obtained by catalytic cracking and a residue from the production of ethylene from naphtha. However, the pitches obtained still contain high quantities of polycyclic aromatic compounds, in particular benzo(a)pyrene, the levels of benzo (a)pyrene in the pitch typically being well above 1000 ppm.

It would be advantageous if there was a means by which an electrode binder having both industry-acceptable properties and a low PAC content could be prepared from a petroleum-based feedstock.

Summary of the Invention

It has now surprisingly been found possible to prepare from a petroleum residue an electrode binder which has properties approaching that of coal-tar pitch and a PAC content significantly lower than that of existing petroleum-based binders.

The present invention provides a process for preparing an electrode binder, which process comprises:-

(a) thermally cracking a non-hydrotreated thermal tar feedstock having an aromatic content of less than 65 % wt,

(b) separating the thermally cracked product of step (a) in a separator, into at least a top fraction and a bottom fraction, and

(c) subjecting the bottom fraction from step (b) to vacuum distillation, to yield as a vacuum distillation residue an electrode binder.

Detailed Description of the Invention

The present invention involves thermally cracking a non-hydrotreated thermal tar feedstock having an aromatic content of less than 65 % wt [step (a)]. Preferably, the aromatic content of the thermal tar feedstock is less than 60 % wt, more preferably less than 55 % wt, and most preferably less than 50 % wt, aromatic content being the total amount of mono to hexa$^+$ aromatic compounds as measured according to test method SMS 2783-95 (Research Disclosure 451104, November 2001, No. 451, pp 1918-1922). Preferably, the thermal tar feedstock has an aromatic content in the range of from 25 to 65 % wt, more preferably 30 to 60 % wt and most preferably 30 to 50 % wt.

Thermal tar is a residual product of thermal cracking of heavy hydrocarbon feeds; thermal cracking being a process wherein hydrocarbons are heated to high temperature (e.g. 400 to 550 °C) at which temperatures longer hydrocarbon molecules become unstable and break into smaller molecules. The major applications of thermal cracking of heavy hydrocarbon feeds in refineries are in visbreaking (i.e. viscosity reduction) and thermal gas oil production.

The thermal tar feedstock of the present invention is preferably obtained by thermal cracking of a heavy hydrocarbon feed at a temperature in the range of from 400 to 550 °C, more preferably 450 to 520 °C. The thermal tar feedstock is preferably obtained by thermal cracking of an atmospheric distillation residue of a

crude oil (long residue), a vacuum distillation residue (short residue) or a heavy or waxy distillate fraction.

It is particularly preferred that the thermal tar feedstock of the present invention is a residue from the thermal cracking of a heavy distillate feed, preferably a waxy distillate feed. Waxy distillates are distillate fractions having a boiling point range of from 220 °C to 650 °C. Waxy distillates may conveniently be obtained by vacuum distillation of a long residue, or from a thermal gas oil unit. Such thermal tar feedstocks are preferred as they contain fewer metal impurities than thermal tars obtained by cracking, for example, residual feeds.

Preferably, the thermal tar feedstock is a residue from a thermal gas oil unit. Most preferably the thermal tar feedstock of the present invention is obtained by thermally cracking a heavy, preferably a waxy, distillate feed in a thermal gas oil unit.

In a preferred embodiment of the present invention the thermal tar feedstock is obtained from a two-stage thermal gas oil unit in a process comprising:- i) thermal cracking of a residual feed, ii) separating the cracked feed into a gas fraction and a liquid fraction, iii) separating the gas fraction into at least a gas oil fraction and a waxy distillate fraction in a fractionator, iv) thermally cracking the waxy distillate fraction and v) separating the thermally cracked waxy distillate fraction to yield, as a residue, a thermal tar. The thermally cracked waxy distillate fraction may be conveniently separated in the fractionator of step iii).

In this preferred embodiment the residual feed is preferably thermally cracked at a temperature in the

range of from 400 to 500 °C, more preferably 430 to 480 °C: the residual feed preferably being a short residue. The residual feed may conveniently be cracked in a cracking furnace or in a soaker unit, wherein the feed is heated to the cracking temperature in a furnace and then subsequently transferred to a soaker (reaction chamber) where most of the cracking takes place. The cracked feed may be separated into at least a gas fraction and a liquid fraction by any convenient means, but the separation may very conveniently be performed in a cyclone. As will be understood by those skilled in the art, the temperature of the cracked residue entering the separation means is dependent upon the temperature used in the thermal cracking step, however, it will preferably be in the range of from 370 to 470 °C, more preferably 400 to 440 °C. The fractionator of step iii) of the preferred embodiment is preferably an atmospheric fractionator, and the waxy distillate fraction is preferably drawn from the fractionator at a temperature in the range of from 350 to 450 °C, more preferably of from 370 to 420 °C. The waxy distillate is preferably cracked at a higher temperature than the residual feed, preferably in the range of from 470 to 550 °C, more preferably 500 to 520 °C.

The thermal tar feedstock of the present invention is a non-hydrotreated feedstock. By non-hydrotreated it is meant that the feedstock has not been treated with hydrogen, as for example in a catalytic hydrotreater. Hydrotreating a feedstock lowers its carbon content and density. This is considered disadvantageous for the production of electrode binders as it is preferred that

electrode binders have a high carbon content, and thus a high density.

In step (a) of the present invention the thermal tar feedstock is subjected to thermal cracking. As will be understood by those skilled in the art, the cracking conditions used for step (a) may vary depending on the type of thermal tar feed, and the equipment used to perform the cracking. However, it is preferred that the thermal cracking is performed at a cracking temperature in the range of from 400 to 550 °C.

The thermal tar feedstock may conveniently be cracked in a cracking furnace. When a cracking furnace is employed the feedstock is preferably heated to a temperature in the range of from 400 to 550 °C, more preferably 450 to 500 °C. The residence time in the cracking furnace may vary depending on the feedstock and cracking temperature, however in refinery operations it may conveniently be in the range of from 1 to 10 minutes, preferably 1 to 5 minutes.

Preferably the thermal cracking of step (a) is conducted in a soaker unit. A soaker unit comprises a cracking furnace and soaker (reaction chamber). When cracked in a soaker unit the thermal tar is heated to the cracking temperature in the cracking furnace from where it is transferred to the soaker (reaction chamber) where most of the cracking takes place. When a soaker unit is employed the feedstock is preferably heated in the furnace to a temperature in the range of from 400 to 500 °C, more preferably 450 to 500 °C, and most preferably 475 to 500 °C and then transferred to the soaker reactor. The pressure in the soaker reactor is preferably controlled to be in the range of from 100 kPa to 1000

kPa, more preferably 150 to 500 kPa, and most preferably 200 to 300 kPa; and the residence time is preferably in the range of from 10 to 120 minutes, more preferably 15 to 60 minutes, and most preferably 20 to 40 minutes.

In the process of the present invention, thermal cracking in a soaker unit is particularly effective when the feedstock is a thermal tar from a thermal gas oil unit.

The thermally cracked product of step (a) is separated into at least a top fraction and a bottom fraction in a separator [step (b)].

The separator of the present invention may be any apparatus capable of separating the thermally cracked product into a top fraction and a bottom fraction i.e. a lighter fraction comprising lighter molecules (top fraction) and a residual fraction comprising heavy molecules (bottom fraction). Examples of apparatus that may be used as the separator include an atmospheric distillation unit and a cyclone. Regardless of the type of separator employed, the bottom fraction preferably comprises at least 80 % wt of components having an atmospheric boiling point of at least 300 °C. Separation step (b) is an important feature of the present invention as only by removing a proportion of lighter materials prior to vacuum distillation step (c) is it possible to prepare an electrode binder having industry-acceptable properties and a low PAC content.

Preferably, the separator of step (b) is a cyclone. When a cyclone is employed the thermally cracked product of step (a) is separated into a gas fraction (top fraction) and liquid fraction (bottom fraction). It is preferred to use a cyclone to separate the thermally

cracked product of step (a) as the high viscosity of this material (i.e. a thermally cracked thermal tar) is such that when introduced into distillation apparatus the thermally cracked product may block or even coke in the distillation apparatus.

As will be understood by those skilled in the art, the temperature of the cracked material entering the separator will be dependent upon the cracking conditions. However, when a cyclone is employed for separation step (b), the temperature of the thermally cracked product entering the cyclone is preferably in the range of from 350 to 450 °C, more preferably 380 to 430 °C; and the residence time in the cyclone will preferably be in the range of from 30 seconds to 20 minutes, more preferably 30 seconds to 8 minutes, even more preferably 1 to 6 minutes.

It is an advantageous feature of the present invention that it is not necessary to recycle any part of the bottom fraction of separation step (b) back through thermal cracking step (a). Accordingly, in a preferred process according to the present invention, no part of the bottom fraction of separation step (b) is recycled back through thermal cracking step (a).

The bottom fraction from the separator is subjected to vacuum distillation, the residue of said vacuum distillation being the electrode binder of the present invention [step (c)].

As will be understood by those skilled in the art, the conditions used for the vacuum distillation may vary depending upon the properties of the feed and the type and properties of the electrode binder to be produced, and a degree of experimentation may be required to

establish the optimum distillation conditions. However, the conditions of vacuum distillation are preferably such that they correspond to an atmospheric boiling point of from 450 to 550 °C, more preferably of from 480 to 520 °C, wherein conversion of atmospheric boiling point to sub atmospheric boiling point is made in accordance with the Maxwell-Bonell relationship as described in Ind. Eng. Chem., 49 (1957) pp 1187-1196).

In general, the vacuum distillation of the bottom fraction may conveniently be carried out at a pressure in the range of from 0.3 to 16 kPa, more preferably 1 to 10 kPa, even more preferably 1 to 8 kPa, and most preferably 3 to 7 kPa; and a distillation temperature preferably in the range of from 310 to 400 °C, more preferably 350 to 390 °C.

As is well known to those skilled in the art, it is preferred that the carbon content of an electrode binder be as high as practically possible. This is because in preparing the electrode the binder will be converted into carbon. Accordingly, the conditions employed in the thermal cracking, separation and vacuum distillation steps are preferably optimised such that the electrode binder has a Micro Carbon Residue Test (MCRT) value of at least 45 % wt; more preferably at least 50 % wt (as measured according to DIN EN ISO 10370).

The electrode binder of the present invention may comprise a vacuum distillation residue from a sole process stream according to the present invention or it may conveniently comprise a blend of two or more such vacuum distillation residues. Blends of two or more different vacuum distillation residues prepared according

to the present invention may be conveniently used to optimise the properties of the electrode binder.

It is an advantageous feature of the present invention that the electrode binders comprise only low levels of PAC molecules as compared to coal-tar pitch and the hereinbefore described petroleum-based binders. Preferably, an electrode binder according to the present invention has a benzo[a]pyrene content of less than 200 ppm, more preferably less than 100 ppm, and most preferably less than 50 ppm, as measured according to IP BN/93.

Preferably, the electrode binders have a PAC content of less than 2000 ppm, more preferably less than 1000 ppm, and most preferably less than 750 ppm, as measured according to IP BN/93 on the basis of the list of PAC molecules provided in respect of Examples 1-4.

It is a further preferred feature of the present invention that the electrode binders have a low sulphur content, the electrode binders preferably having a sulphur content of less than 2 % wt, more preferably less than 1 % wt, as measured according to ASTM 2622-94.

The present invention further provides for an electrode binder obtainable by the process of the present invention.

The present invention still further provides for an anode binder for use in aluminium production obtainable by the process of the present invention; and for the use of said anode binder in aluminium production.

The invention will be further understood from the following illustrative examples.

In the following Examples, unless otherwise stated, density values were measured at 25 °C by test method DIN

52004; Micro Carbon Residue Test (MCRT) values were measured by test method DIN EN ISO 10370; Sulphur content was measured by test method ASTM D 2622-94; Softening point was measured by test method DIN 52011; Viscosity values were measured at the specified temperature using a Dynamic Shear Rheometer.

Total aromatic content was determined according to Shell Method Series (SMS) 2783-95 (Research Disclosure 451104, November 2001, No. 451, pp 1918-1922) and is based on the total amount of mono to hexa$^+$ aromatic compounds present. SMS 2783-95 is a means of ultraviolet quantitative analysis based on ASTM E169-99. The ultraviolet spectrometer employed was a single beam instrument(Varian Cary 50), having a bandwith of 1.0 nm or less at 220 nm; a photometric repeatability of 0.5 % Transmission and a slit width of 2 nm. The spectrophotometer was fitted with a matched stoppered silica cell of certified pathlength. Absorbance maxima were measured at three wavelength positions: 190 to 205 nm (λ_1): 218 to 238 nm (λ_2): and 245 to 265 nm (λ_3): which positions correspond to the absorption bands of mono-, di-, and tri-aromatic compounds respectively. Wavelength positions were derived for higher aromatic compounds from the peak maxima for λ_3 as described in SMS 2783-95. Quantities of each aromatic type were calculated from the absorptivity of each absorbance maxima by correlating the data with those of a calibration sample of known concentration using the method described in SMS 2783-95, using calculation procedure number 1.

PAC content was determined according to IP BN/93, wherein test samples were sequentially filtered on silica

with toluene; filtered on silica with heptane; PAC species separated from aliphatics, naphthenics, mono- and diaromatic hydrocarbons by high performance liquid chromatography (HPLC); and finally identification and quantification of individual PAC species performed by GC-MS. In this analysis, 12Deutorated benzo[a]pyrene was employed as an internal standard. The PAC species measured in determining the PAC content were as follows:- fluoranthene; pyrene; benzo[a]fluorene; benzo[b+c]fluorene; benzo[b]naphto[2,1-d]thiophene; benzo[g,h,i]fluoranthene; benzo[a]anthracene; chrysene and triphenylene; 1+2+3+4+5+6 methylchrysene; benzo[b,j,k]fluoranthene; benzo[e]pyrene; benzo[a]pyrene; perylene; dibenz[a,j]anthracene; indeno[1,2,3-c,d]pyrene; dibenz[a,h+a,c]anthracene; benzo[b]chrysene; benzo[g,h,i]perylene; anthanthrene, and coronene.

Examples 1-4: Preparation of Electrode Binders

An electrode binder was prepared using a feedstock and process according to the invention (Example 1). In addition, comparative binders were prepared using alternative types of feedstock (Examples 2-4). The feedstocks employed in Examples 1-4 were:-

Example 1: (According to the Invention) Feedstock (A). A thermal tar from a two-stage thermal gas oil unit (aromatic content 49.5 % wt).

Example 2: (Comparative) Feedstock (B). Clarified oil; a highly aromatic oil (aromatic content 76.0 % wt) which is the residue from an atmospheric fractionator on a catalytic cracking unit.

Example 3; (Comparative) Feedstock (C). A short residue from a North Sea crude, which is the bottom product of a vacuum distillation unit (aromatic content 30.4% wt).

Example 4: (Comparative) Feedstock (D): An ethylene cracker residue (ECR), which is the residue from an atmospheric fractionator of an ethylene cracker unit (aromatic content 70.7% wt).

The properties of feedstocks A to D are shown in Table 1.

TABLE 1

Feedstock	Thermal Tar (A)	Clarified Oil (B)	Short Residue (C)	ECR (D)
Density (g/cm^3)	1.029	1.119	1.018	1.137
MCRT (% wt)	12.5	13.5	21.6	25.0
Sulphur (% wt)	0.72	2.50	2.20	0.23
Softening Point (°C)	Liquid	liquid	51.0	44.5
Viscosity 80 °C (mm^2/s)	248	56	32718	5191
PAC (ppm)	6800	20132	34	32472
Vanadium (ppm)	<5	3	95	<1
Nickel (ppm)	<5	3	25	<1
Total Aromatic (% wt)	49.5	76.0	30.4	70.7

Electrode binders were prepared from feedstocks A-D as follows.

Feedstock was passed through a filter manifold and stored in a heavy oil weight tank. From the weight tank, the feedstock was pumped to a cracking furnace. The cracking furnace comprised eight separate tube coils each immersed in a lead pot with each lead pot separately

heated by an electrical heater. The total volume of the coils was approximately 3000 cm^3. The residence time of the feedstock in the furnace was dependant upon the density of the feedstock and the feed rate, however a feed rate of 5Kg/h gave a residence time of approximately 40 minutes, and a feed rate of 2.5 Kg/h gave a residence time of approximately 80 minutes.

After passing through the cracking furnace the total thermally cracked product was fed into a flash column separator wherein overhead vapours, butane and lighter fractions were removed. The bottom fraction from the separator (fractionator bottoms) was then fed into a vacuum tower wherein it was further separated into two fractions by vacuum flash distillation, an over-head fraction and a residue fraction, which residue fraction was collected for use as an electrode binder.

The yields and properties of the electrode binders obtained are shown in Table 2, together with the conditions employed in the cracking furnace and vacuum flasher. For each Feedstock the conditions were optimised to obtain an electrode binder having a MCRT value of at least 45% wt. In Example 1 (Feedstock (A)), two runs were performed yielding two binders, (A1) and (A2). Similarly, in Example 2 (Feedstock (B)) two runs were performed yielding binders (B1) and (B2).

Table 2

	Example 1		Example 2 (comp.)		Example 3 (comp.)	Example 4 (comp.)
Feedstock	Thermal Tar (A)		Clarified Oil (B)		Short Residue (C)	ECR (D)
Binder Properties	A1	A2	B1	B2	C1	D1
PAC (ppm)	620	1390	2050	9748	5	20000
Benzo[a]pyrene (ppm)	51	120	200	590	1	1600
MCRT (% wt)	53.7	46.4	63.4	41.4	51.8	62.0
Density ($g/cm^{3)}$	1.150	1.142	1.203	1.222	1.094	1.213
Softening Point (°C)	133.0	110.0	159.0	97	138.5	>160
Viscosity 180 °C (mPas)	11818	1163	NT	118	23961	NT
Sulphur (%wt)	0.74	0.74	2.3	2.5	2.5	0.13
Vanadium (ppm)	<10	<10	<10	<10	245	<10
Nickel (ppm)	<10	14	26	24	81	14
Run						
Feed Rate (Kg/h)	2.5	2.5	2.5	2.5	5.0	2.5
Max Coil Temp (°C)	465	457	438	440	487	443
Vac. Tower Temp (°C)	363	362	347	349	373	347
Vac. Tower Pressure (kPa)	1.6	1.6	2.5	3.3	1.1	6.1
Binder Yield (%)	29	33	25	25	40	46

NT = Not Tested

WO 03/046111 PCT/EP02/13313

From Table 2 it can be seen that the electrode binders of Example 1, (A1) and (A2), prepared from a thermal tar feedstock, have a low sulphur content and low PAC / benzo[a]pyrene content. In this regard they compare favourably to the binders of Example 2, (B1) and (B2), prepared from a clarified oil feedstock, which have a high sulphur and PAC content, and to electrode binder (D1) prepared in Example 4 from an ethylene cracker residue feedstock which has an even higher PAC content. Whilst electrode binder (C1), prepared in Example 3 from a short residue feedstock had low PAC content, the density of the binder obtained was low.

Examples 5-9: Preparation and testing of laboratory electrodes

Test electrodes were prepared using the electrode binders of Examples 1-4.

In Example 5 (according to the invention) an electrode was prepared from a blend of binders (A1) and (A2). Similarly, in Example 6 a comparative electrode was prepared from a blend of binders (B1) and (B2). In Example 8, binder (D1) was blended with a small amount of over-head fraction (OH) obtained from the vacuum tower as the viscosity of D1 alone was too high to prepare a laboratory scale electrode. A further comparative electrode was prepared using a coal-tar pitch binder (Example 9). The composition and properties of the binders used to prepare the test electrodes are shown in Table 3.

Test electrodes were prepared as follows. Graded petroleum coke was preheated to a temperature of at least 110 °C greater than the softening point of the binder to be used. The petroleum coke was then placed in a similarly

preheated mixer and cold crushed binder blended into the preheated petroleum coke. Mixing was continued until a homogenous blend was obtained, after which the mixture was transferred to a preheated steel mould and the electrode shaped by means of a hydraulic press with an applied pressure of approximately 10 tonnes. The electrodes comprised 14 % wt binder, 19.7 % wt course petrol coke, 26.5 % wt medium petrol coke, 15.8 % wt fine petrol coke and 24 % wt dust petrol coke.

The electrodes were calcified by oven baking, applying a final temperature of 1190 °C, for 24 hours. During the baking process, the electrodes were protected against oxidation by a covering of petrol coke and by flushing the oven with nitrogen. The electrodes were then tested for air-reactivity, and carbon dioxide-reactivity according to the methods described in Fischer W.K. et al, Journal of Metals 39 (11), 43-45, 1987. Electrical resistance was tested according to test method DIN 51919. The results are shown in Table 3.

TABLE 3

	Example 5	Example 6 (comp.)	Example 7 (comp.)	Example 8 (comp.)	Example 9 (comp.)
Binder	A1 (85%wt) A2 (15%wt)	B1 (55%wt) B2 (45%wt)	C1 (100%wt)	D1 (87%wt) OH(13%wt)	Coal-Tar Pitch (100%)
PAC (ppm)	736	5514	5	20000	97800
Benzo[a]pyrene (ppm)	61	376	1	1600	10900
Viscosity 180 °C (mPas)	6.940	2.850	12.381	7.640	1.032
Softening Point °C	130.5	135.5	131	129	115.5
MCRT (% wt)	52.6	54.8	50.3	53.6	54.7
Electrode					
Air-Reactivity (% Residue) [a]	92.5	94.3	73.2	92.7	92.7
CO_2-Reactivity (% Residue) [b]	85.2	86.4	82.3	83.5	82.3
Electrical Resistance ($\mu\Omega m$)	70.4	69.0	80.9	79.5	78.5

a) Air Reactivity = 100 x (Mass before test/Mass after test)

b) CO_2 Reactivity = 100 x (Mass before test/Mass after test)

c) NT = Not tested.

WO 03/046111 PCT/EP02/13313

From Table 3 it can be seen that the electrode of Example 5, prepared according to the present invention, was prepared from a binder having a very low PAC/ benzo[a]pyrene content, and displayed a performance in terms of air-reactivity, carbon dioxide-reactivity and electrical resistance similar to that of a conventional electrode prepared from coal-tar pitch (Example 9).

The electrodes of Examples 6 and 8, were prepared from binders having a high PAC /benzo[a]pyrene content and their use would therefore be undesirable from an environmental and health and safety standpoint. Whilst the electrode of Example 7 was prepared from a binder with a low PAC content, it displayed very low air reactivity and thus the binder from which this electrode was prepared would not be considered acceptable as a replacement for coal-tar pitch by the aluminium and steel industry.

Example 10

An electrode binder was prepared from a thermal tar taken from the bottom of an atmospheric fractionator of a two-stage thermal gas oil unit (TGU). The electrode binder was prepared by thermally cracking the thermal tar through a cracking furnace (temperature 480 °C), passing the thermally cracked product through a soaker reactor (pressure 2.5 bar (250 kPa), residence time 25 to 35 minutes, temperature 450 °C), separating the thermally cracked product in a cyclone (inlet temperature 390 °C) into a top and bottom fraction, (residence time 4 to 6 minutes) and subjecting the bottom fraction to vacuum distillation in a vacuum flasher (temperature 370 °C, pressure 55 mbar (5.5 kPa). The properties of the thermal

tar feedstock and the electrode binder obtained are shown in Table 4.

An electrode was prepared from the electrode binder of Example 10 in the same manner as the electrodes of Examples 5-9 were prepared; and tested for air reactivity, carbon dioxide reactivity, and electrical resistance. The results are shown in Table 4.

From Table 4 it can be seen that the binder of Example 10 had a low PAC / benzo[a]pyrene content and the electrode prepared from the binder had air-reactivity, carbon dioxide-reactivity and electrical resistance similar to that of an electrode prepared from coal-tar pitch.

TABLE 4

Example 10	Thermal Tar Feedstock	Electrode Binder	Electrode
PAC (ppm)	1163	622	NT
Benzo[a]pyrene (ppm)	86	73	NT
Density (g/cm^3)	1.001	1.167	NT
MCRT (% wt)	11.5	51.6	NT
Sulphur (% wt)	1.11	1.2	NT
Softening Point (°C)	Liquid	127	NT
Total Aromatic (% w)	34	NT	NT
Viscosity 180 °C (mPas)	NT	4.468	NT
Air-Reactivity (% Residue)	NT	NT	91.8 (92.7)*
CO_2-Reactivity (% Residue)	NT	NT	84.1 (82.3)*
Electrical Resistance (μΩM)	NT	NT	79.8 (78.5)*

* Values shown in parenthesis are those of an electrode binder prepared from a coal-tar pitch binder (Example 9)

WO 03/046111 PCT/EP02/13313

Claims

1. A process for the preparation of an electrode binder, which process comprises:-

(a) thermally cracking a non-hydrotreated thermal tar feedstock having an aromatic content of less than 65 % wt,

(b) separating the thermally cracked product of step (a) in a separator, into at least a top fraction and a bottom fraction, and

(c) subjecting the bottom fraction from step (b) to vacuum distillation, to yield, as a vacuum distillation residue, an electrode binder.

2. A process as claimed in claim 1, wherein the thermal tar feedstock is a residue from a thermal gas oil unit.

3. A process as claimed in claim 1 or claim 2, wherein the thermal tar feedstock is a residue from the thermal cracking of a waxy distillate feed.

4. A process as claimed in any one of claims 1 to 3 wherein the separator of step (b) is a cyclone.

5. A process as claimed in any one of claims 1 to 4, wherein the thermal tar feedstock is thermally cracked in a soaker unit.

6. A process as claimed in any one of claims 1 to 5, wherein the electrode binder has a sulphur content of less than 2 % wt.

7. A process as claimed in any one of claims 1 to 6, wherein the electrode binder has a PAC content of less than 1000 ppm.

8. A process as claimed in any one of claims 1 to 7, wherein the electrode binder has a benzo[a]pyrene content of less than 200 ppm.

9. An electrode binder obtainable by a process as claimed in any one of claims 1 to 8.

10. An anode binder obtainable by a process as claimed in any one of claims 1 to 8 for use in aluminium production.