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(71) Applicant: **DOW BENELUX N.V.**
Aert van Nesstraat 45
NL-3012 CA Rotterdam(NL)

(72) Inventor: **Wiersma, Jacob Gerrit**
Wilhelminastraat 16
NL-4571 JM Axel(NL)

(54) Briquette binder.

(57) Binder suitable for producing briquettes or other shaped products, comprising a) an, optionally modified, polyaromatic component obtained as primary condensate in the steam cracking of light hydrocarbons, b) at least one component chosen from the group consisting of atmospheric and vacuum residues and distillates obtained in the refining and/or (hydro)cracking of petroleum or petroleum fractions. Use of the binder for producing briquettes, and briquettes comprising this binder and a bound substance.

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BRIQUETTE BINDER

The present invention relates to a binder which is suitable for the production of briquettes, to the use of this binder for the production of briquettes and to briquettes that are produced by using this binder.

Briquettes mainly consist of a solid substance, such as a combustible, like for example coal or cokes, or minerals such as iron oxide, magnesium carbonate and the like, and of a binder therefor. They are widely used for domestic heating and for the purpose of a more efficient utilization of industrial raw materials. These briquettes are manufactured by pressing a mixture of the solid substance and the binder into the proper form under appropriate temperature and pressure conditions. Usual binders include for example coal tar pitch and bitumen, optionally in combination with sulphite liquor.

A number of criteria should be borne in mind for the selection of a binder for coal briquettes, the latter in this connection meaning briquettes of solid fuels or combustibles such as coal, brown coal, cokes and the like.

An important aspect for the briquettes is their burning behaviour. This means, for instance, that a coal briquette, on the one hand, should be able to gently glow under conditions where relatively little combustibles and oxygen are present, whereas under other conditions the briquette should be able to burn with a clear flame and not fall apart unburned. This may be expressed as fuel efficiency in terms of the coal content of the ashes. Another aspect of the burning behaviour is that a good fuel efficiency is required. Of course, the former aspect of the burning behaviour can also be viewed as a mechanical requirement for the binder, i.e. the binder should be able to confer to the briquette during burning enough strength that it will not fall apart until used up for the greater part. Further, the (national) criteria regarding the the emission of environmentally objectionable substances should be met.

The binder should also provide the briquette with so much strength and elasticity that the latter will not break to pieces under the usual transport and storage conditions. On the one hand, this is a matter of dynamical strength, meaning that during manufacturing, transport and the like the briquette may not break to pieces or that the majority, i.e. at least 95% of the briquettes does not break. Furthermore, the briquette should have a static strength during the complete usage cycle, which means that the lowermost briquette may not collapse under the weight of the briquettes lying on top thereof, neither during stacking nor at high temperatures.

The selection of the binder is also determined by the sulfur content, the ash content and the emission of compounds during combustion or other processing.

Smell is a criterion which is more subjective than the above-mentioned criteria. It has been found, for example, that the acceptance of coal briquettes for domestic use largely depends on the extent to which the binder and the briquette give off an undesirable smell under storage or usage conditions. Strongly smelling briquettes generally are not accepted. This is, of course, related to the fact that the briquettes are often stored in storage spaces which often are badly ventilated, such as in basements, and in the proximity of food such as potatoes or other personal effects.

A conventional binder for coal briquettes is bitumen. Another type of coal briquette contains a special sulfite liquor (lignosulphonate) as binder, providing a so-called smokeless briquette. These types of briquettes have a similar, but relatively high sulfur content of about 4.5 to 6% by weight.

In some events it is still allowed to use coal tar as binder, but mostly a bituminous binder is used because of its lower benzo(alpha)pyrene content.

A summary of the known techniques and binders for the briquetting of coal is to be found in "Erdöl und Kohle-Erdgas-Petrochemie, vereinigt mit Brennstoff-Chemie" Band 40, No. 12, pages 521-526.

A totally different application for briquettes of solid substances is for the production of silicon. As described for example in British patents 2,150,128 and 2,088,840 silicon is produced from substantially pure silicon oxide, for example quartz sand, starting from briquettes containing on the one hand the silicon oxide and on the other hand a carbon source such as baking coal, cokes or bitumen. Such briquettes are then stacked in an electrical furnace and heated under pyrolysing conditions so that SiO_2 is reduced to SiO, SiC and Si. It will be evident, of course, that a binder for use in this type of briquettes should fulfil a number of requirements different than for binders for coal briquettes.

Binders for quartz briquettes should provide the briquette with a particularly good strength because often several tens of tons of briquettes are charged batchwise into a furnace. In addition, the binder should burn without producing a substantial amount of ashes, and more in particular, it should be free or virtually free of metals which may remain in the silicon and which are difficult or impossible to remove afterwards. In order to reduce emissions, binders having a low sulfur content are preferred, however, above all they should have good coke forming properties as is also the case for coal briquettes.

The above-mentioned briquette applications are the most important, but the briquette binders can also be used for briquettes of magnesium oxide or magnesium carbonate and briquettes of fly ash, generally metal-enriched dust. Finally, briquetting techniques are also used for the so-called partial briquetting, which means that low quality coals are briquetted with a relatively small proportion of binder, whereafter the briquettes are broken and subsequently mixed with quality coal or cokes for the production of metallurgic cokes grades.

It is the object of the present invention to provide a binder which may be used almost universally for the briquetting of various materials. The binder which is suitable for the production of briquettes or shaped forms, comprises

a) an, optionally modified, polyaromatic component obtained as primary condensate in the steam cracking of light hydrocarbons,

b) at least one component chosen from the group consisting of atmospheric and vacuum residues and distillates obtained in the refining and/or (hydro)cracking of petroleum or petroleum fractions.

Component a) of the binder according to the invention comprises a hydrocarbon mixture containing a relatively large proportion of polyaromatics having a structure which is comparable to the structure of asphaltenes or pseudo-asphaltenes. Component a) usually has a C/H atomic ratio of 0.9 to 2.0, an aromaticity of 2.5 to 10 and a ring and ball softening point of at least 100 °C. In this connection, aromaticity shall mean the ratio of the number of aromatic carbon atoms relative to the number of aliphatic carbon atoms. The aromaticity is preferably from 2.5 to 5.

Component a) is the by-product of the steam cracking of light hydrocarbons. Preferably, light petroleum fractions, such as LPG, gas oil or naphtha are cracked in a steam cracker, for example thermally or catalytically, preferably at a temperature of 700-2000 °C, whereby the polyaromatic fraction is obtained after removal of the components which are volatile at atmospheric pressure, as the primary condensate from the product stream. This polyaromatic fraction is particularly suitable as first component of the binder according to the invention. This component, also called pyrolysis oil can be used as such for component a) in the binder of the invention or be processed in different ways to produce a modified polyaromatic fraction. In this way binders may be produced with a wide range of functional properties for a great number of different briquette compositions (applications).

Component a) or the pyrolysis oil is preferably modified by subjecting it to one or more of the following treatments: extraction, distillation, flocculation/precipitation and oxidative treatment.

One preferred way to modify the polyaromatic pyrolysis oil, which preferably has an aromatic content of at least 60% (calculated as (aromatic-C/total-C) x 100%), is to substantially remove the low molecular fraction from the oil to obtain a pyrolysis oil fraction with a more narrow molecular weight distribution which improves the adhesive strenght and affinity with respect to the fines that are to be briquetted. Especially, this concerns reducing the fraction having a molecular weight (determined by GPC in THF) smaller than 1000, so that a product remains having a ring and ball softening point of at least 100 °C, preferably 110-170 °C. Preferably, the product has a molecular weight a distribution in which 95% by weight of the molecules have a molecular weight higher than 1000, and a weight averaged molecular weight of at least 1250, more preferably at least 2000. A binder based on a component a) modified this way is especially advantageous for producing magnesium carbonate or quartz briquettes.

The molecular weight distribution of the pyrolysis oil may be controlled by means of extraction with appropriate extraction agents, such as Freon 113, dichloro methane, hexane, cyclohexane, isopropyl chloride, tert.butyl chloride, dichloro ethane, dichloro propane and the like. By means of the following solvents and combinations thereof specific pyrolysis oil fractions can be separated, whereas the remaining material will be suitable for the binder preparation as mentioned above. In the following table the ratio "oil:solvent" indicates the weight ratio between the pyrolysis oil and the solvent used for separating or removing the desired fraction.

solvent	oil : solvent
n-hexane	1 : 6.5
cyclohexane	1 : 7.7
Freon-113	1 : 17
isopropyl chloride	1 : 18
tert.butyl chloride	1 : 2

The temperature in this preparation varies generally from room temperature to the respective boiling point.

In connection with the above-mentioned treatment, distillation, if required at decreased pressure, can be part of the process to remove the low molecular fraction until the desired composition of the remaining fraction is obtained. Appropriate conditions for this distillation include pressures of 5-50 mm Hg, at temperatures of 250-400 ° C, in order to remove 5-60% by weight of the starting pyrolysis oil material.

According to a different method one can use a flocculation/precipitation technique for a rough separation of the pyrolysis oil component a) of the binder, thereby obtaining a separation in two phases. Possible chemicals for achieving this purpose are for instance mixtures of dichloro methane and methanol.

By using such mixtures one can vary the average molecular weight of the insoluble fraction by varying the proportions of the chemicals with respect to each other and by varying the proportion of the chemicals with respect to the pyrolysis oil. The results of the examinations for the desired relative proportions are summarized in the following table. In this table the relative proportions in parts by weight are given for the pyrolysis oil (p.o.) and for the dichlore methane ($MeCl_2$) and methanol (MeOH). In the last column the average molecular weight is given for the pyrolysis oil fraction thus precipitated.

Table

test	p.o.	MeC12	MeOH	Av. Mw
1	5	45	50	2600
2	7	60	33	2000
3	10	70	20	1800
4	18	64	18	1300
5	28	60	12	650
6	42	50	8	400
7	50	45	5	175
8	98	1	1	150

If desired, the polyaromatic or pyrolysis oil component a) of the binder according to the invention, whether or not subjected to one or more of the treatments mentioned above, can be subjected to an oxidative treatment, preferably in the presence of for example 0.1-3% by weight of a crystalline or amorphous alumina-silicate catalyst, for example a FCC-catalyst. For this purpose preferably conditions are used known for the blowing of bitumen, for example at least 10 minutes, as required 150-500 minutes, at a temperature of at least 200 ° C, yet preferably not higher than 360 ° C.

The oxidative treatment has the advantage that one can remarkably increase the coke yield, particularly up to a value much higher than is usual for bitumen, while maintaining the desired strength of the briquette thus produced. By means of an oxidative treatment coke yields up to 80% may be achieved, whereas bitumen has a coke yield of at the most 30%. The oxidation should, however, not be carried on too long, as in that case a product will be obtained which is too brittle, which is undesired with respect to strength properties.

The second component b) of the binder according to the invention comprises at least one component chosen from the group consisting of atmospheric and vacuum residues and distillates obtained in the refining and/or (hydro)cracking of petroleum or petroleum fractions. This component b) which itself may be a mixture of two or more of the above-mentioned residues and distillates serves to improve the processibility of the binder, but also to affect the properties of the briquettes. Preferably, component b) of the binder comprises at least a vacuum residue of the refining and/or (hydro)cracking of petroleum cg. petroleum fractions. The advantage hereof is that a certain degree of plasticity is introduced, which enhances the dynamic strength properties of the binder. Preferably, at least 10% by weight of the vacuum residue is present, based on the binder. If, for example, a certain residue from this group is used for reasons of processibility then it may be necessary to use also a certain distillate from this group in order to improve the miscibility and compatibility of the several binder components a) and b). A useful composition for component b) of the binder contains 40-100% by weight of a vacuum residue of the petroleum refining and 60-0% by weight of a vacuum distillate of the petroleum refining.

The vacuum residue in component b) preferably contains a boiling hexane insolubles content of at least 20%. Preferably it also has a sulfur content not higher than 1.0% by weight, especially in the case when the binder is intended for use in coal briquettes. For the use for other briquettes the sulfur content is also of importance when during their use there can be some emission of objectionable substances in view of national regulations regarding environmental protection. Preferably, the vacuum residue in component b)

has a somewhat more paraffinic character than component a) of the binder according to the invention. This relatively higher paraffinic character is expressed in the C/H ratio in the vacuum residue, which is preferably between 0.7 and 1.0 (on atomic basis).

According to a preferred embodiment of the invention also an elasticity improving agent, such as atactic polypropylene or polyethylene wax, is added in an amount of 0.2 to 10% by weight, based on the binder. The advantage of this addition resides in the fact, that the elasticity of the binder is improved, which positively influences the dynamic strength of the briquettes manufactured therewith, so that breaking of briquettes under extreme conditions is avoided.

As indicated hereinbefore, component b) may also advantageously contain a further fraction serving to improve the miscibility and compatibility of the other components. For this purpose one can use a distillate, for example a vacuum distillate of the refining and/or hydrocracking of petroleum, cq. petroleum fractions. For the same purpose it is, however, also possible to add a mineral oil or a heavy gas oil, having an initial boiling point of preferably 260 °C or higher and more preferably between 365 and 500 °C at atmospheric pressure. It will be clear, that the necessity and the amounts for using each of these components or fractions depend on the nature and proportion of the respective components constituting the binder, as well as of the type of application. However, based on the above-described information a person skilled in the art can compose a binder suited for his purpose.

The relative proportion of the components is, as described, determined by the nature of the starting products and the specific application. Generally, the binder consists of 75-95 parts by weight of polyaromatic component a) and 5-25 parts by weight of component b) and optional other additives.

The binder is preferably substantially free of ashes, minerals, metals and in particular free of elements of the group IIIA and VA of the Periodic System of Elements, or compounds thereof. In this connection, with "substantially free" is meant that the content of the respective component is not higher than 0.05% by weight, based on the binder.

The binder according to the invention can be prepared in different ways, however, it should always be taken into account that the binder generally will have a softening point around 100 °C, more particularly between 80 and 150 °C. In practice, the binder should be prepared at a temperature which is clearly above its softening point in order to avoid problems regarding solidification or a too high viscosity. For example, the components can be supplied to a blender heated at 250 °C in which the components are mixed to obtain a homogeneous mass at this temperature. The binder thus obtained, to which optionally also an amount of lime is added, may be stored, transported and processed at this temperature.

The binder according to the invention has an excellent homogeneity and stability. More particularly, the binder fulfils the requirements of Dutch standard NEN 3965, which means, among other things, that no phase separation takes place during storage.

The invention further relates to the use of the binder as described above for the production of briquettes. This briquetting may be carried out in the usual way with the binder according to the invention and the solid substance to be bound. In this connection, it is referred to the methods which are usual in this area of technique, for example Perry (Chemical Engineers Handbook, 3rd Edition, page 1564).

Finally, the invention also relates to a briquette comprising a binder according to the invention and a bound component. This bound component may consist of a conventional solid combustible, such as coal or cokes, but also of a starting material for another reaction, such as magnesium oxide, magnesium carbonate or quartz sand. The substance to be bound may also consist of a product which should be brought into the form of a briquette, whether or not temporary, for storage. For this purpose one can think of fly ash or radioactive waste.

Depending on the application, the binder content in the briquette is chosen such that optimal results are achieved. These binder contents may vary between 1 and 15% by weight, based on the weight of the briquette. For the production of coal briquettes for combustion purposes this content will generally be about 8% by weight. When using the binder for quartz sand briquettes, as described in the two above-mentioned British patents, the binder content is also determined by the desired carbon/cokes-content of the briquette. It may be remarkably higher than the 15% by weight mentioned.

For partial briquetting, as described hereinbefore, the binder content may be less than 8% by weight, because for this application homogeneity is more emphasized than the briquette strength. Binder contents of 2-5% by weight are thereby possible.

The invention will be further explained by means of examples, without the scope of the invention being limited thereto.

Example 1

Starting from a pyrolysis oil obtained from the thermal steam cracking of naphtha after separation of the gaseous components, the main component of the binder was prepared by means of precipitation/flocculation.

One part by weight of pyrolysis oil was contacted with 1.5 parts by weight of a 1/1 mixture of methanol/dichloro methane. From this step 0.77 parts by weight of this mixture containing polyaromatic compounds were obtained as precipitate. After distillation of this mixture the component a) of the binder was obtained having a ring and ball softening point of 120 °C.

The aromaticity thereof was 3.6, whereas the C/H atomic ratio was 1.25.

This product was mixed at 175 °C with 15% by weight (based on the total binder) of a mixture (1/1) of vacuum residue and vacuum distillate.

The resulting binder was used in an amount of 6% by weight for the production of magnesium carbonate briquettes. The green briquettes were shown to have a satisfactory strength. The "heat" strength was satisfactory as well.

The static compression strength was at least 250 kg/cm^2, which is amply sufficient for magnesium carbonate briquettes.

Example 2

In a same manner analogous to the one described in Example 1 coal briquettes were produced from anthracite fines and 8%, based on the briquette weight, of a binder according to the invention. The binder contained 86% by weight of a pyrolysis oil fraction, 8% by weight of vacuum residue and 6% by weight of vacuum distillate and had a sulfur content of 0.33% by weight, an ashes content of 0.11% by weight, a softening point of 88 °C (ring and ball). The briquettes had a static strength of 133 kg, a dynamic strength of 91.3% and an emission of 265 ppm SO_2 in the flue gass.

Claims

1. Binder for use in the production of briquettes or shaped forms comprising

a) an, optionally modified, polyaromatic component obtained as primary condensate in the steam cracking of light hydrocarbons,

b) at least one component chosen from the group consisting of atmospheric and vacuum residues and distillates obtained in the refining and/or (hydro)cracking of petroleum or petroleum fractions.

2. Binder according to claim 1 comprising 75 to 95 parts by weight of component a) and 25 to 5 parts by weight of component b).

3. Binder according to claim 1 or 2 wherein component a) is obtained in the steam cracking of LPG, gas oil or naphtha.

4. Binder according to claims 1-3, wherein component a) is the product obtained by the catalytic or thermal steam cracking of light hydrocarbons at a temperature of 700-2000 °C, from which the components that are gaseous at atmospheric pressure are removed.

5. Binder according to claims 1-4, wherein component a) has been subjected to an extraction, distillation, flocculation/precipitation or oxidative treatment or combination of two or more of these.

6. Binder according to claims 1-5, wherein component b) contains 40-100% by weight of a vacuum residue of the petroleum refining and 60-0% by weight of a vacuum distillate of the petroleum refining.

7. Binder according to claims 1-6 further comprising up to 60% by weight, based on component b) of mineral oil or heavy gas oil.

8. Binder according to claims 1-7 further comprising 0.2-10% by weight of atactic polypropylene or polyethylene wax or a combination thereof, based on the weight of the binder.

9. Use of the binder according to claims 1-8 for the production of briquettes.

10. Briquette comprising a binder according to claims 1-8 and a bound substance.

11. Briquette according to claim 10, wherein the binder content lies between 1 and 20% by weight, based on the briquette.

12. Briquette according to claim 10 or 11, wherein the bound substance is selected from the group consisting of coal, magnesium oxide, magnesium carbonate, cokes, metal-enriched dust, quartz sand and mixtures of two or more of these products.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 20 0939

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.4)
X	GB-A- 960 912 (COMPAGNIE FRANCAISE DE RAFFINAGE) * Claims 1-7; page 3, lines 19-61 *	1-5,9-12	C 10 L 5/16
A	GB-A- 759 145 (GELSENKIRCHNER-BERGWERKS AG) * Claims 1-9; page 6, lines 95-109 *	1-12	
A	DE-C- 890 183 (GELSENKIRCHNER-BERGWERKS AG) * Claim 1 *	1,9-12	
A	FR-A-2 381 821 (RUTGERSWERKE) * Claims 1-10 *	1-4	
A	DE-A-1 645 735 (ESSO RESEARCH) * Claims 1,5-7,9; page 14, lines 11-17 *	1,5,9-12	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 10 L
C 22 B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	13-07-1989	MEERTENS J.

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
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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