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(54) **PETROLEUM COKING ADDITIVE**

(57) The problem addressed by the invention is that of improving the quality of coke by increasing the coking properties of a component of a coking feedstock (a coking additive), and by ensuring the stability of the coking properties of a component of a coking feedstock (a coking additive) when the coking additive constitutes up to 99% of the total volume of the coking feedstock. The technical result of the invention is an increase in the stability of a coking additive, and an increase in the coking properties of said coking additive. The claimed technical result is achieved in that in a petroleum coking additive consisting of a product of the delayed low temperature carbonization of heavy petroleum residues at temperatures of up to 500°C, said product being characterized by a 14 to 28% volatile substance content, the product of the delayed low temperature carbonization of heavy petroleum residues, obtained at a recycle ratio of from 1.05 to 1.2 in the coking chamber, is characterized by coking properties of not less than G on the Gray-King scale.

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Description

[0001] The invention relates to the by-product coke industry, specifically, to technologies of producing of furnace coke from feedstock which includes petrochemical products; the invention can be used in metallurgy, in particular, at by-product coke industry plants.

[0002] From RF Patent No. 2400518, a method of producing a coking feedstock by delayed carbonisation is known which includes feeding of a heated stock into a coking chamber, coking of the feedstock for 14-24 hours and the following discharging of the resultant coke as a coking additive, in realising whereof the feedstock is fed into the coking chamber with temperature 450-470°C, preferably with temperature 455-465°C, and with the recycle ratio not above 1.2. The problem addressed by the invention is that of improving the yield of the coking additive, that is, the coke with a high volatile substance content.

[0003] A method of producing coke is known from RF Patent No. 2174528, wherein coke is produced from a mixture of coals of various processing groups and by-product coke screenings. Into the coal feedstock, 6.1 - 15.0% of by-product coke screenings are added, with respective decrease of percentage of low-caking or non-caking coals. The disadvantage of this method is that the petroleum coke is used in the feedstock as a thinning additive, which deteriorates quality of the obtained coke and does not make it possible to add petroleum coke into the coal feedstock in large amounts.

[0004] An additive to coal feedstock is known, which are used for producing furnace coke according to RF Patent No. 2411283, the said additive being a product of product of the delayed low temperature carbonization of heavy petroleum residues at temperatures of up to 500°C, the said product being characterised by a 14 to 28% volatile substance content and a ductile temperature range not les than 120°C. This known additive to coal feedstock makes it possible to improve quality of the produced coke due to high caking properties per Roga index and due to a large ductile temperature range from 120 to 350°C.

[0005] The additive to coal feedstocks per RF Patent No. 2411283 has been selected as the most approximated analogue (prototype).

[0006] A disadvantage of the additive per RF Patent No. 2411283 is instability of its caking properties, insufficient coking properties of the additive and, consequently, instable quality of the obtained furnace coke, especially in the case of a high content of the additive in the coal feedstock (over 50%), and insufficient quality of the obtained coke conditioned by peculiarities of the additive coking properties.

[0007] The problem addressed by the invention is that of improving the quality of coke by increasing the coking properties of a component of a coking feedstock (a coking additive), and by ensuring the stability of the coking properties of a component of a coking feedstock (a coking additive) when the coking additive constitutes up to 99% of the total volume of the coking feedstock.

[0008] The technical result of the invention is an increase in the stability of a coking additive, and an increase in the coking properties of the said coking additive.

[0009] The claimed technical result is achieved in that in a petroleum coking additive consisting of a product of the delayed low temperature carbonisation of heavy petroleum residues at temperatures of up to 500°C, the said product being characterised by a 14 to 28% volatile substance content, according to the invention, the product of the delayed low temperature carbonisation of heavy petroleum residues obtained at a recycle ratio of from 1.05 to 1.2 in the coking chamber is characterised by coking properties of not less than G on the Gray-King scale.

[0010] Petroleum caking additives produced at various oil-processing plants differ considerably from each other, depending on the volatile substances yield. Table 1 shows parameters of caking of the additives achieved at various oil-processing plants, and indexes of quality of the coke produced from them.

[0011] Caking properties were determined by the method GOST R ISO 15585-2009 "Determining of caking index"; coking of the additives was performed in a Nikolayev furnace until the temperature in the middle of the charge was achieving 1000°C.

Table 1

No.	Manufacturer plant	Volatiles yield, %	Caking properties, G, units	CSR, %	CRI, %
1	Novoil	16.82		56.5	23.9
2	Novoil	15.42		66.2	26.0
3	Novoil	15.82		68.8	20.5
4	Ufaneftekhim	16.30		74.0	19.0
5	Ufaneftekhim	19.40		77.1	19.7
6	Ufaneftekhim	20.24		76.2	20.5

(continued)

No.	Manufacturer plant	Volatiles yield, %	Caking properties, G, units	CSR, %	CRI, %
7	Lukoil	15.72		74.1	23.0
8	Lukoil	18.71		76.1	20.8
9	Lukoil	19.41		77.0	20.0

[0012] Instability of caking additives quality, in the authors' view, is explained by the fact that they are manufactured on different equipment and at different technologies.

[0013] In process of work with coking additives produced according to the known technologies, it was found that they do not always possess good coking properties (as it is known, coking and caking properties differ from each other), which also does not make possible to produce a good furnace coke with the stable quality.

[0014] Thus, as it turned out, stability of properties of the coke produced with the content of the known coking additives will depend, to a large extent, not only upon the additive composition and the method of its producing but also upon the equipment and definite technologies which are used for producing the coking additives, upon the original (inherent) properties of the raw stock for producing the additive which are conditioned, among others, by the locality of the raw stock origin. In a word, the stability of the additive properties occurred to be to a large extent dependable on factors which seem to be second-rate, at first sight, and do not influence the additive properties in an obvious way.

[0015] According to the claimed method, a mixture of heavy oil residues is held for 14-24 hours at temperature 450-470°C, with the recycle ratio K_p = 1.05 - 1.2. The recycle ratio is a proportion of the newly-generated low-boiling coking products in relation to the total mass of the raw stock fed for coking which is returned back into the reactor. Involving of recycle fractions into the coking original stock wherefrom the coking additive is produced will contribute to improving of composition stability of the obtained product due to the fact that the recycle is a product of coking (more exactly, delayed carbonization, as it is realised at temperatures up to 500°C) which has already passed thermal conversions and, consequently, possesses improved thermal stability, and when it is recycled into the coking process it will be subject to the cracking (disintegration) reactions to a lesser extent. But increasing of the recycle ratio above 1.2 (i.e. when the coking process involves large amounts of thermally stable recycling fractions which have already passed thermolysis) results in receiving of a coking additive with a lesser percentage of volatiles. On the contrary, decreasing of the recycle ratio below 1.05 contributes to receiving of a coking additive with too large amount of volatiles. In the both cases, it will deteriorate coking properties of the additive.

[0016] The petroleum semi-coke produced at temperature 450-470°C with the recycle ratio K_p = 1.05 - 1.2 is characterised with high coking property values, which makes it possible to add in into a coal feedstock in any weight proportions - up to 99 wt %.

[0017] For conducting tests, samples of petroleum semi-coke were taken which were obtained at temperature 465°C with the recycle ratio K_p = 1.05 - 1.2, with different value of volatile substances yield (in %).

[0018] It is known that the index of coking property of hard coals is defined by Gray-King method (GOST 16126-91 (ISO 502-82)).

[0019] It is also known that the index of coking property defined by Gray-King method does not possess exact (direct or other) correlation with the volatiles percentage index or free swelling index. At various values of volatiles percentage the coking property index on the Gray-King scale can be identical, e.g. G.

[0020] In such a case, the authors of the invention believe that the index of coking property on the Gray-King scale characterises not only the additive coking property but also the qualitative composition of volatile substances. In particular, caking and coking properties of volatiles in the petroleum coking additive (PCA) will be defined by their aromaticity. The more aromatic volatile substances are the higher is extent of their caking and coking properties, even at their lesser percentage in PCA, and vice versa. In this connection, by increasing of the recycle ratio we will increase the extent of volatiles aromatising and thus improve caking and coking properties of the PCA itself. On the contrary, due to decreasing of the recycle ratio, substances remain in the coke which have not been completely subjected to cracking, consequently, the PCA will posses lesser caking and coking properties.

[0021] Samples of petroleum semi-coke obtained with various values of the recycle ratio and with various values of volatiles yield (within 11.2 - 28.5%) were taken for analysis. Identification of the type of petroleum semi-coke by Gray-King method was conducted in a tubular furnace per GOST 16126-91 (ISO 502-82). Results of the experiment are presented in Table 2.

Table 2

Sample No.	Volatiles yield, %	Recycle ratio	Coke type by Gray-King method
1	11.0	1.05	C
2	11.0	1.20	C
3	12.0	1.05	C
4	12.0	1.20	D
5	13.0	1.05	D
6	13.0	1.20	G
7	14.0	1.05	G
8	14.0	1.20	G
9	15.0	1.05	G1
10	15.0	1.20	G2
11	17.0	1.05	G3
12	17.0	1.20	G4
13	20.0	1.05	G5
14	20.0	1.20	G5
15	23.0	1.05	G3
16	23.0	1.20	G5
17	25.0	1.05	G3
18	25.0	1.20	G4
19	27.0	1.05	G1
20	27.0	1.20	G2
21	28.0	1.05	G
22	28.0	1.20	G

[0022] The following consistent pattern has been found during investigation: the semi-coke type per Grey-King scale improves as the value of volatiles yield increases and, tentatively, when the value of volatiles yield is equal to 14%, the coke residue of the petroleum coking additive will melt into strong or "normal" coke (of G type). It means that the coking additive with the volatiles yield over 14% can be added into coal feedstock without any quantitative limits.

[0023] When the volatiles value is equal to 28%, the coking property value per Grey-King becomes equal to G again (like at the volatiles percentage equal to 14%). As the volatiles percentage grow again, we observe decrease of the coking additive coking property below the "normal" G level.

[0024] As a result of conducted investigation related to identification of factors influencing stability of properties of the coke produced from such coking additive, it was found that of significance is not only the quantitative content of volatiles in the cocking additive but their qualitative composition as well which, in this case, is characterised by the coking property per Grey-King.

[0025] The quality of furnace coke produced from the mixture of industrial coal feedstock of Mechel PJSC with the offered petroleum coking additive is presented in Table 3. The coal feedstocks were coked in a Nikolayev furnace until the temperature in the middle of the charge was achieving 1000°C.

Table 3

No.	Feedstock composition	Coke type by Grey-King method from PCA	CRI, %	CSR, %	CBS, %
1	Coal feedstock - 100%	-	32.0	52.0	84.0
2	Feedstock 95% + PCA 5%	G4	31.2	54.6	84.2
3	Feedstock 85% + PCA 15%	G3	29.1	56.0	84.7

(continued)

No.	Feedstock composition	Coke type by Grey-King method from PCA	CRI, %	CSR, %	CBS, %
4	Feedstock 70% + PCA 30%	G3	27.5	58.9	85.2
5	Feedstock 50% + PCA 50%	G4	26.1	63.6	85.8
6	Feedstock 30% + PCA 70%	G3	23.6	66.7	86.0
7	Feedstock 5% + PCA 95%	G3	19.7	72.1	87.3

[0026] The obtained results show that use of the petroleum coking additive with the coking property value per Grey-King scale not lower than G will allow to produce furnace coke of high and stable quality at any weight proportion "coking additive - cola in feedstock".

[0027] Under stability we mean, first of all, mechanical strength of the coke: in all cases it is higher than that of the coke from a 100% coal feedstock. As for reacting power and hot strength, they both can be varied depending on certain needs of the coke consumers.

[0028] The price of a petroleum coking additive is lower than that of coking hard coals, so use of large amounts of the additive for producing of furnace coke (without deterioration of its quality) will make it possible to significantly improve economic efficiency indexes of by-product coke industry and metallurgical plants.

A product of the delayed coking of oil processing residues with the content of volatiles from 14 to 28% and the coke type not less than G on the Gray-King scale is applied as a petroleum coking additive (PCA) to coal feedstocks which are used for producing of furnace coke. The invention makes it possible to create an additive to coal feedstocks ensuring joint coking in coal feedstocks with adding in any weight proportions without the coke quality deterioration.

Claims

1. petroleum coking additive consisting of a product of the delayed low temperature carbonization of heavy petroleum residues at temperatures of up to 500°C, the said product being **characterised by** a 14 to 28% volatile substance content, and featured by the fact that the product of the delayed low temperature carbonization of heavy petroleum residues obtained at the recycle ratio in the coking chamber from 1.05 to 1.20 is **characterised by** coking properties of not less than G on the Gray-King scale.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/RU 2017/000020

A. CLASSIFICATION OF SUBJECT MATTER

C10B 55/00 (2006.01); C10B 57/04 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10B 55/00-55/10, 57/00-57/18, 47/00, 49/00, 51/00, 53/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatSearch (RUPTO internal), USPTO, PAJ, Esp@cenet, DWPI, EAPATIS, PATENTSCOPE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	RU 2411283 C1 (ZAKRYTOE AKTSIONERNOE OBSHCHESTVO "UPRAVLIAIUSHCHAIA KOMPANIIA "NKA-KHOLDING") 10.02.2011	1
A	RU 2563493 C1 (OBSHCHESTVO S OGRANICHENNOI OTVETSTVENNOSTIU "PROMYSHLENNYE INNOVATSIONNYE TEKHNOLOGII NATSIONALNOI KOKSOKHIMICHESKOI ASSOTSIATSII" (OOO "PROMINTEKH NKA")) 20.09.2015	1
A	RU 2469066 C1 (OBSHCHESTVO S OGRANICHENNOI OTVETSTVENNOSTIU "PROMINTEKH") 10.12.2012	1
A	US 4421604 A (RUHRKOHLE AKTIENGESELLSCHAFT) 20.12.1983	1

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
04 July 2017 (04.07.2017)	14 August 2017 (14.08.2017)
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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 2400518 A **[0002]**
- WO 2174528 A **[0003]**
- WO 2411283 A **[0004] [0005] [0006]**