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(54) PROCESS FOR THE IMPROVEMENT OF THE
COKING PROPERTIES OF COAL

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, 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 an improvement of the process to improve the coking properties of coal by the addition of a bituminous substance, namely mineral oil bitumen.

For the past several years and in an increasing measure, many coking plants depend on the supplementary use of coal having inadequate coking properties. The increasing shortage of good coking coals (fat coal and gas coal, according to their customary designation in the Ruhr region) means that the latter have to be extended with more highly carbonized types (steam coal and lean coal), which in themselves are less suitable or entirely unsuitable for coking. They have only a low caking and swelling capacity and yield a brittle coke having small lumps, which does not meet the requirements of the blast furnace and foundry.

A series of measures is known whereby it is nevertheless possible to produce a sufficiently tough blast furnace coke from coals having moderate coking properties. Employed individually or in combination, they enable the coking plants to use, for example, steam coal or coal mixtures containing a larger or smaller proportion of lean coal in addition to good coking coal. One of these measures which is frequently employed comprises the addition of bituminous substances to the coking coal before it is supplied to the coke oven. The most effective additives are coal tar pitch or mineral oil bitumen, but other and less expensive substances are also used, such as coal tar or low-temperature tar, heavy oil or long residue. The admixture is sometimes effected in solid, ground form, but it is better effected in molten form by spraying on to the stream of coal fines in a suitable conveying device. The

amount of additive depends on the requirements, but already for economic reasons alone it must be kept as low as possible; because of the relatively high price of what are precisely the most effective additives, it is necessary to make do with less than 10% by weight, and if possible with 5% by weight. A further reason for keeping the addition as low as possible is the relatively high sulphur content of many bituminous substances, which is of course undesirable in blast furnace coke.

It has now been found that the effect of such bituminous additives on the coking properties of coal can be improved considerably if the said additives are employed in the form of a special aqueous emulsion.

The invention therefore relates to a process for the improvement of the coking properties of coal by the addition of a bituminous substance, characterized in that the bituminous substance is added in the form of an aqueous emulsion of a mineral oil bitumen having a ring-and-ball softening point of at least 80°C.

Such emulsions are of the oil-in-water type and can be produced by means of a high-speed dispersing machine. The aqueous phase is suitably added to a minor amount of an emulsifier, such as the alkaline soap of a higher fatty acid. The finished emulsions preferably contain between 45 and 60% by weight, generally around 55% by weight of bitumen.

According to the invention the bitumen emulsion is admixed to the coal fines before being supplied to the coke oven. In the event of the coal fines being compacted by roller presses before being supplied, as is sometimes done for the further improvement of the coking properties, the emulsion should be added upstream of the presses. The emulsion is suitably sprayed on to the coal stream in a conveying device with mixing effect, such as an open screw conveyor. It is a distinct advantage of the process according to the invention that the coal need not be dried for this mixing operation. It has been found that the water introduced with the emulsion, for example 4—5% by weight of water at 10% by weight

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of emulsion added, has no adverse effect in the coke oven.

It is advantageous to use special emulsions which contain a bitumen, with a penetration value at 25° of preferably 5 or below. Especially advantageous is a special emulsion which does not contain the usual straight-run bitumen, but, for example, the residue from a thermal cracking treatment, brought to the said specification by high-vacuum distillation. Such cracking residues and related bitumens are characterized by a relatively high Conradson carbon residue value of 35 or above.

For emulsifiers there are a series of commercial products, some of which are used in acid medium, others in alkali medium and a few even in neutral medium. The selection depends on the operating conditions, consequently above all on whether the bitumen emulsion has to be stored before use or transported for lengthy distances. If the emulsion is produced on site and used immediately, i.e., if no storage stability is required the emulsifier can sometimes be omitted; even in that case, however, it is suitably used in order to facilitate the emulsifying operation. A particularly suitable emulsifier for the application according to the invention is an alkali naphthenate. The latter are the salts of the higher

molecular naphthenic acids, which approximately correspond in boiling range with the lubricating oil fractions. Normally these acids are neutralized in the column with a solution of caustic soda or caustic potash during the vacuum distillation of naphthenic mineral oils, and withdrawn as a side fraction. The crude product contains, for example, about 50% of unsaponifiable material, 25% of alkali naphthenates and 25% of water and excess alkali. It is suitably used in the crude state, by dispersing approximately 3% by weight, based on finished emulsion, in the water added.

For the following comparative experiments, the "determination of the coking degree of coal according to the dilatometer method" according to DIN 51 739 was used. A coal sample from the Saar region, with a coking degree of 2—3, i.e., a low to medium coking power (according to DIN 51 739) was mixed with a hard mineral oil bitumen, once in ground form and once in the form of an aqueous emulsion containing a proportion of approximately 55% by weight of bitumen. The bitumen was produced from a Middle East long residue by propane extraction and had a ring-and-ball softening point of 90°C and a penetration value at 25°C of 3.

TABLE I

Additive	% by wt.	Contraction	Dilation
—	—	22%	3%
Propane bitumen 90/3	2	24%	6%
" " "	4	24%	7%
" " "	6	24%	12%
Emulsion	4	25%	8%
"	8	26%	13%
"	12	24%	17%

It is clear that the dilation, i.e., the coking power, is increased more by a given quantity of bitumen in emulsified form than by dried, ground bitumen.

For a further comparative experiment a coal sample was used which exhibited only contraction in the dilatometer, i.e., coking degree 1—"very weakly coking" (according to DIN 51 739). By additives of the aforementioned type, its coking properties were nevertheless raised to coking degree 2—"weakly coking".

Further, a likewise hard, cracked bitumen was used, which had been produced from the residue of a thermal gas oil cracking treatment; ring-and-ball softening point 101°C, a penetration value at 25°C of 1—2, and a Conradson carbon residue value of 37. By these additives the dilation was substantially raised, when supplied in the emulsified form (55%w of bitumen) to coking degree 3—"moderately coking" according to DIN 51 739.

TABLE II

Additive	% by wt	Contraction	Dilation
—	—	27%	—27%
Propane bitumen 90/3	4	28%	—15%
" " "	6	26%	—12%
Emulsion hereof	8	30%	—18%
" " "	12	26%	—8%
Cracked bitumen 101/2	4	28%	—5%
" " "	6	27%	± 0%
Emulsion hereof	8	28%	+ 2%
" " "	12	26%	+ 9%

WHAT WE CLAIM IS:—

1. A process for the improvement of the coking properties of coal by the addition of a bituminous substance, characterized in that the bituminous substance is added in the form of an aqueous emulsion of a mineral oil bitumen having a ring-and-ball softening point of at least 80°C.

2. A process as claimed in claim 1, wherein the bitumen is a cracked bitumen having a Conradson carbon residue value of at least 35.

3. A process as claimed in claim 1 or 2, wherein the emulsion is produced with alkali naphthenate as emulsifier.

4. A process as claimed in any one of claims

1—3, wherein the emulsion contains 45—60%w of bituminous substance.

5. A process according to claim 1, substantially as hereinbefore described with special reference to the Examples.

6. Coal having improved coking properties whenever prepared according to the process of anyone of claims 1—5.

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