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(54) **COAL ANTI-OXIDATION AGENT AND COAL OXIDATION PREVENTION METHOD**

(57) Provided is an antioxidant capable of coating the surface layer of a coal deposit (coal pile) and further reducing the amount of oxygen permeation into the inside of the deposit. The present invention is an antioxidant for coal, containing an oil-in-water type resin emulsion having an average particle size of emulsion particles of 0.3 μm or more and 1.0 μm or less. The antioxidant prefer-

ably further contains a surfactant. The worker sprays the above antioxidant on the coal deposit. This forms a consolidated layer on the surface of the coal deposit that is highly effective in suppressing oxygen permeation. Therefore, the permeation of oxygen in the air atmosphere into the inside of the coal deposit is blocked, thus preventing the oxidation of the coal.

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Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to an antioxidant for coal and a method for preventing oxidation of coal. More specifically, the present invention relates to chemical agents and prevention methods that contribute to the prevention of heat generation, heat storage and spontaneous combustion associated with the oxidation of coal deposited in coal yards (yards, silos, etc.) of coal mines, steel mills, power plants, etc.

10 BACKGROUND ART

[0002] In steel mills and power plants, coal is left in piles in a coal yard. When left for a long period of time, carbon and sulfur contained in coal react with oxygen in the air, and spontaneous oxidation proceeds. Then, the reaction heat generated during this spontaneous oxidation accumulates inside the coal deposit as thermal energy, and the temperature
15 inside the coal deposit rises, leading to spontaneous combustion.

[0003] Conventionally, in order to prevent such spontaneous heat generation and spontaneous combustion, it has been proposed that when transferring and depositing coal, transferring and/or depositing are conducted while spraying SBR latex-containing liquid on the coal (see Patent Document 1). It has also been proposed to spray a resin solution containing white powder on the surface of a coal pile in the field to form a white coating film (see Patent Document 2).
20 It has also been proposed to spray an acrylic emulsion or a vinyl acetate emulsion on coal (see Patent Document 3).

Citation List

Patent Document

25

[0004]

Patent Document 1: Japanese Patent No. 3948447

Patent Document 2: Japanese Patent Publication No. 6-062974

30 Patent Document 3: Japanese Patent Publication No. 58-53037

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

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[0005] However, there is room for further improvement in suppressing oxygen permeability into the inside of coal deposits.

[0006] The present invention has been made in view of the above circumstances, and is intended to provide an antioxidant capable of coating the surface layer of coal deposits (coal piles) and further reducing the amount of oxygen
40 permeation into the inside of the deposits.

Means for Solving the Problems

[0007] The present inventors have found that the above problems can be solved by setting the average particle size of the resin emulsion sprayed on coal within a specific range, and have completed the present invention. Specifically,
45 the present invention provides:

(1) The present invention is an antioxidant for coal, containing an oil-in-water type resin emulsion having an average particle size of emulsion particles of 0.3 μm or more and 1.0 μm or less.

50 (2) The present invention is also the antioxidant for coal according to (1), further containing a surfactant.

(3) The present invention is also a method for preventing oxidation of coal, wherein an antioxidant for coal, containing an oil-in-water type resin emulsion having an average particle size of emulsion particles of 0.3 μm or more and 1.0 μm or less is sprayed on coal deposits.

55 (4) The present invention is also the method for preventing oxidation of coal according to (3), wherein the antioxidant for coal is prepared by mixing the oil-in-water type resin emulsion and a surfactant.

Effects of the Invention

[0008] According to the present invention, since the antioxidant for coal contains an oil-in-water type resin emulsion with a specific range of the average particle size of emulsion particles, when the antioxidant for coal is sprayed on the surface of the coal deposit, a consolidated layer having a high oxygen permeation suppressing effect is formed on the surface of the coal deposit. Therefore, the permeation of oxygen in the air atmosphere into the inside of the coal deposit is blocked, and the oxidation of coal can be prevented. Therefore, the spontaneous heat generation and spontaneous combustion due to oxidation reaction can be effectively prevented as compared with the conventional case. Therefore, it is possible to avoid accidents caused by spontaneous heat generation and spontaneous combustion of coal, and to reduce the burden of various maintenance work related to them.

[0009] In particular, the antioxidant for coal preferably further contains a surfactant. By adding a surfactant to the highly hydrophobic coal deposit, the permeability can be improved, allowing the chemical solution to spread and produce a uniform coal consolidated layer. As a result, the permeability of oxygen into the coal deposit is further reduced, and the antioxidant effect is further enhanced.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Figure 1 is a schematic diagram of the test apparatus used in the test using the antioxidant for coal of the present invention.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

[0011] Hereinafter, embodiments of the present invention will be described, but the present invention is not particularly limited thereto.

<Antioxidant for Coal>

[0012] The antioxidant for coal of the present invention contains an oil-in-water type resin emulsion having an average particle size of emulsion particles of 0.3 μm or more and 0.6 μm or less. The antioxidant for coal preferably further contains a surfactant.

[Oil-in-Water Type Resin Emulsion]

[0013] The type of resin in the resin emulsion is not particularly limited, but preferably includes one or more selected from acrylic acid-based, methacrylic acid-based, and vinyl acetate-based resins. In particular, it is more preferable to include one or more selected from a butyl acrylate copolymer and a vinyl acetate/acrylic acid copolymer. It is preferable to include one or more selected from butyl acrylate/methyl methacrylate copolymer, vinyl acetate/butyl acetate/2-ethylhexyl acrylate copolymer, butadiene/styrene/acrylic acid copolymer, vinyl acetate/butyl acetate/2-ethylhexyl acrylate copolymer and vinyl acetate/acrylic acid ester copolymer.

[0014] The lower limit of the average particle size of the emulsion particles in the resin emulsion is 0.3 μm or more. The lower limit of the average particle size is preferably 0.4 μm or more, and more preferably 0.5 μm or more. If the average particle size is too small, even if the antioxidant for coal is sprayed on the surface of the coal deposit, the expected antioxidant effect may not be obtained, which is not preferable.

[0015] The upper limit of the average particle size of the emulsion particles in the resin emulsion is 1.0 μm or less. The upper limit of the average particle size is preferably 0.9 μm or less, more preferably 0.8 μm or less, further preferably 0.7 μm or less, and particularly preferably 0.6 μm or less. If the average particle size is too large, even if the antioxidant for coal is sprayed on the surface of the coal deposit, the expected antioxidant effect may not be obtained, which is not preferable.

[0016] In the present invention, the average particle size of the emulsion particles in the resin emulsion means the average particle size measured using a laser analysis type particle size distribution measuring apparatus / Shimadzu SALD-7500 nano (manufactured by Shimadzu Corporation).

[0017] The production method of the resin emulsion is not particularly limited. For example, it can be easily prepared by emulsion polymerization of a monomer component. More specifically, it can be prepared by polymerizing the monomer component in micelles formed in water with an emulsifier with a polymerization initiator.

[Surfactant]

[0018] The antioxidant for coal preferably further contains a surfactant.

[0019] The type of the surfactant is not particularly limited, and may be any of an anionic, cationic, nonionic, and amphoteric surfactants. In particular, the surfactant is preferably a nonionic type or a cationic type, and particularly preferably a nonionic type. It is thought, because, due to the hydrophobic surface of the coal deposit, the use of nonionic or cationic surfactants further enhances the familiarity between the surface of the coal deposit and the resin emulsion, resulting in the formation of a denser consolidated layer.

[0020] Examples of the anionic surfactants include sulfonic acid-based surfactants, and more specifically, di-2-ethyl-hexyl sulfosuccinate sodium salt-based surfactants. Examples of the cationic surfactants include ammonium salt-based surfactants, and more specifically, trialkylbenzylammonium salt-based surfactants.

[0021] Examples of the nonionic surfactants include ether-based surfactants, and more specifically, polyoxyalkylene alkyl ether-based surfactants. Examples of the amphoteric surfactants include betaine-based surfactants, and more specifically fatty acid amide propyl betaine-based surfactants.

<Method for Preventing Oxidation of Coal>

[0022] In the method for preventing oxidation of coal according to the present embodiment, the above resin emulsion is sprayed on the coal deposit (coal pile). It is more preferable to spray a mixture of the above resin emulsion and the above surfactant onto the coal deposit (coal pile).

[0023] In the present embodiment, the "coal deposit" or "coal pile" includes all of the deposited coal and does not necessarily have to be a mountain-shaped deposit. In addition to coal deposits piled up in coal yard, all coal aggregates such as coal put into and deposited in a container are referred to as "coal deposit" or "coal pile".

[Preparation of Antioxidant for Coal]

[0024] In the present embodiment, the oil-in-water type resin emulsion may be used alone as an antioxidant for coal, or a mixture of the oil-in-water type resin emulsion and the surfactant may be used as an antioxidant for coal. When the oil-in-water type resin emulsion and the surfactant are mixed, a mixture in which the oil-in-water type resin emulsion and the surfactant are mixed in advance may be brought to the site, or the oil-in-water type resin emulsion and the surfactant may be brought individually to the site and the respective materials may be mixed at the site.

[0025] The concentrations of the resin emulsion and the surfactant are not particularly limited, but the lower limit of the solid content concentration of the resin emulsion as a concentration of the antioxidant for coal used when spraying on the coal deposit (coal pile) is preferably 0.005% by weight or more, more preferably 5% by weight or more, and further preferably 10% by weight or more with respect to the antioxidant for coal. The upper limit of the solid content concentration of the resin emulsion is preferably 50% by weight or less, more preferably 40% by weight or less, and further preferably 20% by weight or less with respect to the antioxidant for coal.

[0026] The lower limit of the solid content concentration of the surfactant is preferably 0.005% by weight or more, more preferably 0.01% by weight or more, and further preferably 0.1% by weight or more with respect to the antioxidant for coal. The upper limit of the solid content concentration of the surfactant is preferably 50% by weight or less, more preferably 10% by weight or less, and further preferably 1% by weight or less with respect to the antioxidant for coal.

[Spraying Antioxidant for Coal]

[0027] Subsequently, the antioxidant for coal is sprayed on the coal deposit (coal pile). As a means of spraying, a rain gun, a sprinkler truck, or a hose from a stacker or a reclaimer can be used.

[0028] The amount of the antioxidant for coal sprayed is not particularly limited, but in consideration of both the effect of preventing spontaneous heat generation and spontaneous combustion and the cost of chemical agents, as a guide, the amount of the active substance may be 0.5 to 2,000 g, preferably 10 to 1,500 g, and particularly preferably 100 to 1,000 g, per 1 m² of surface area of coal deposit (coal pile).

EXAMPLES

[0029] Hereinafter, the present invention is disclosed in more detail with reference to the Examples.

<Experimental Method>

[0030] After depositing coal with a particle size of 2.0 mm or less at a height of 5 cm, about 2 L of a 15% aqueous solution or an aqueous dispersion of each chemical agent (antioxidant for coal) shown in Table 1 was sprayed to the deposit, so as to have an active substance of 300 g/m² coal area, to make a test piece. The test piece was left at room temperature for one week.

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[0031] The test piece after being left for one week was housed in a device having the specifications shown in Figure 1 so that the test piece served as a boundary wall separating the two spaces. Then, as shown in Figure 1, of the two spaces having the test piece as the boundary wall therebetween, standard air was continuously sent to one space, and pure nitrogen was continuously sent to the other space. At this time, the flow rates of the standard air and the pure nitrogen were both 30 mL/min, and the temperatures of the standard air and the pure nitrogen were both room temperature. The oxygen concentration in the space on the nitrogen side was then measured after 4 hours of continuous feeding of the standard air and the pure nitrogen. An oxygen analyzer 3600sn (manufactured by Hach Company) was used to measure the oxygen concentration. The case where the oxygen concentration was 7.0% or less was designated as "○", and the case where the oxygen concentration exceeded 7.0% was designated as "x". The results are shown in Table 1.

[0032] Under the blank condition (Comparative Example 1), only water was sprayed on the coal.

[Table 1]

	resin emulsion		surfactant concentration		oxygen concentration (%)	oxygen reduction rate (%)	evaluation*
	average particle size (μm)	solid content concentration	type	dilution concentration	(after 4 hours)	(comparison with no chemical agent treatment)	
Example 1	0.3	15%	-	-	6.83	35.9	○
Example 2	0.3	15%	nonionic	0.2	5.39	49.4	○
Example 3	0.3	15%	cationic	0.2	5.76	45.9	○
Example 4	0.3	15%	anionic	0.2	6.08	42.9	○
Example 5	0.3	15%	amphoteric	0.2	5.52	48.2	○
Example 6	0.6	15%	-	-	6.21	41.7	○
Example 7	0.6	15%	nonionic	0.2	0.20	98.1	○
Example 8	0.6	15%	cationic	0.2	0.99	90.7	○
Example 9	0.6	15%	anionic	0.2	6.95	34.7	○
Example 10	0.6	15%	amphoteric	0.2	5.65	46.9	○
Comparative Example 1	-	-	-	-	10.65	-	×
Comparative Example 2	0.2	15%	-	-	7.34	31.1	×
Comparative Example 3	0.2	15%	nonionic	0.2	7.21	32.3	×
Comparative Example 4	1.4	15%	nonionic	0.2	8.91	16.3	×
Comparative Example 5	2.8	15%	nonionic	0.2	8.92	16.2	×
Comparative Example 6	-	-	nonionic	0.2	7.10	33.3	×

[0033] In Table 1, various materials are as follows. (A) Oil-in-Water Type Resin Emulsion

[0034] The oil-in-water type resin emulsion is an emulsion of an acrylic acid copolymer.

(B) Surfactant

[0035] The nonionic surfactant is a polyoxyalkylene alkyl ether-based surfactant.

[0036] The cationic surfactant is a trialkylbenzylammonium salt-based surfactant.

[0037] The anionic surfactant is a di-2-ethylhexyl sulfosuccinate sodium salt-based surfactant.

[0038] The amphoteric surfactant is a fatty acid amide propyl betaine-based surfactant.

<Discussion>

[0039] When the average particle size of the emulsion particles in the oil-in-water type resin emulsion contained in the antioxidant for coal is 0.3 μm or 0.6 μm , the amount of oxygen permeated through the coal deposit (coal pile) can be reduced by 35% or more (Examples 1 to 10) compared with the case in which the antioxidant for coal contains no resin emulsion (Comparative Example 1 in which the liquid after dispersion contains only water, or Comparative Example 6 in which the antioxidant for coal contains only water and a nonionic surfactant). From this result, it can be said that spraying the diluted solution of the resin emulsion on the surface of the coal being deposited can suppress the oxidation reaction of the coal, resulting in suppressing the spontaneous heat generation and prolonging the period of reaching the critical temperature for spontaneous combustion. This effect can be obtained as long as the antioxidant for coal contains a resin emulsion, even if it does not contain a surfactant (Examples 1 and 6).

[0040] When the antioxidant for coal contains a surfactant in addition to the resin emulsion, the antioxidant effect is further enhanced (Examples 2 to 5, 7 to 10). In particular, when the surfactant is nonionic or cationic, the antioxidant effect is further enhanced (Examples 2, 3, 7, 8). It is thought because, due to the hydrophobic surface of the coal deposits, the use of nonionic or cationic surfactants further enhances the familiarity between the surface of the coal deposits and the resin emulsion, resulting in the formation of a denser consolidated layer.

[0041] When the average particle size of the emulsion particles in the resin emulsion is 0.2 μm , even if the antioxidant for coal contains a nonionic surfactant, a sufficient antioxidant effect is not obtained (Comparative Examples 2 and 3). This is presumably because the average particle size of the emulsion particles was too small, thus a consolidated layer was formed only on the upper part of the coal layer, and a uniform consolidated layer could not be formed.

[0042] On the other hand, when the average particle size of the emulsion particles in the resin emulsion is 1.4 μm or 2.8 μm , even if the antioxidant for coal contains a nonionic surfactant, a sufficient antioxidant effect is not obtained (Comparative Examples 4 and 5). This is presumably because the average particle size of the emulsion particles was too large, thus the emulsion penetrated into the coal layer too much, and a dense consolidated layer could not be formed.

Claims

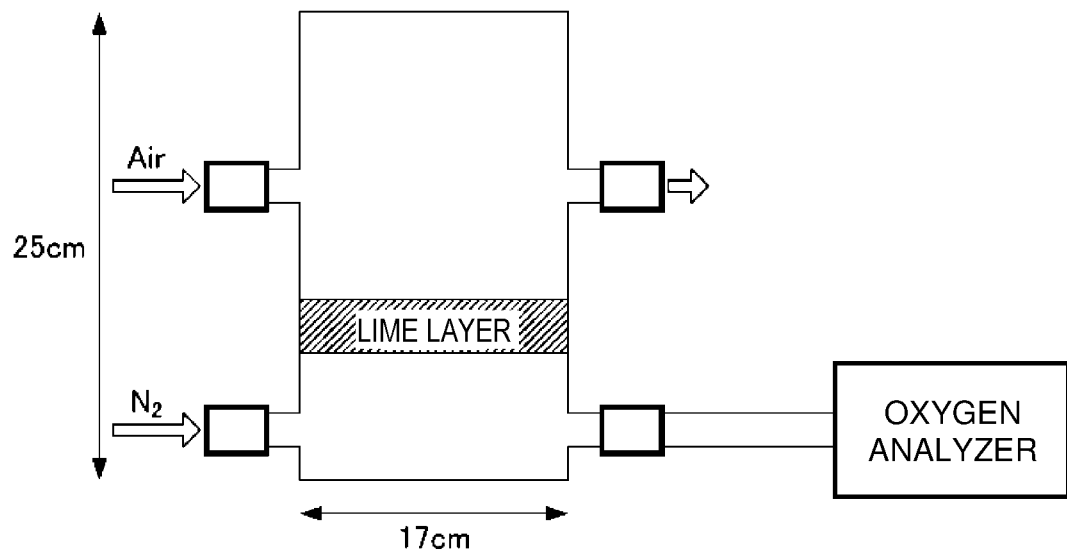
1. An antioxidant for coal, containing an oil-in-water type resin emulsion having an average particle size of emulsion particles of 0.3 μm or more and 1.0 μm or less.

2. The antioxidant for coal according to claim 1, further containing a surfactant.

3. A method for preventing oxidation of coal, wherein an antioxidant for coal, containing an oil-in-water type resin emulsion having an average particle size of emulsion particles of 0.3 μm or more and 1.0 μm or less is sprayed on coal deposits.

4. The method for preventing oxidation of coal according to claim 3, wherein the antioxidant for coal is prepared by mixing the oil-in-water type resin emulsion and a surfactant.

Fig. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2019/015786

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. C10L10/18 (2006.01) i

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)

Int. Cl. C10L10/18, C10L5/00, B65G3/02, C09K3/22

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

Published examined utility model applications of Japan 1922-1996

Published unexamined utility model applications of Japan 1971-2019

Registered utility model specifications of Japan 1996-2019

Published registered utility model applications of Japan 1994-2019

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2013-203525 A (KURITA WATER INDUSTRIES LTD.) 07 October 2013, claims 1-2, 4, paragraphs [0020], [0028], examples 1, 2 (Family: none)	1-4
Y	JP 2-88695 A (MITSUI CYANAMID KK) 28 March 1990, claims 1, 4-5, page 5, lower left column, lines 14-20 (Family: none)	1-4
Y	JP 2000-96040 A (LION CORP.) 04 April 2000, claim 1, paragraph [0017] (Family: none)	1-4
Y	JP 10-259390 A (NIPPON STEEL CORP.) 29 September 1998, claims, paragraphs [0002], [0005]-[0009] (Family: none)	1-4



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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"&" document member of the same patent family

Date of the actual completion of the international search
14.06.2019Date of mailing of the international search report
25.06.2019Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2019/015786

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 49-31589 A (KAO SOAP CO., LTD.) 22 March 1974, claims, page 1, lower right column, line 20 to page 2, upper left column, line 12, tables 1-3 (Family: none)	2, 4
A	JP 61-223084 A (CALGON CORPORATION) 03 October 1986, entire document & US 4650598 A, entire document & EP 195638 A2 & AU 5477486 A & CA 1274082 A & ZA 8601909 A	1-4
E, A	JP 6524480 B1 (TOYO INK SC HOLDINGS CO., LTD.) 05 June 2019, entire document (Family: none)	1-4

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 3948447 B [0004]
- JP 6062974 A [0004]
- JP 58053037 A [0004]