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FORM 1

APPLICATION ACCEPTED AND AMENDMENTS

SPRUSON & FERGUSON

ALLOWED 10.5.90

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

Henkel Kommanditgesellschaft auf Aktien, of Henkelstrasse 67, 4000 Dusseldorf, FEDERAL REPUBLIC OF GERMANY, hereby apply for the grant of a standard patent for an invention entitled:

Dispersants and Their Use in Aqueous Coal Suspensions  
which is described in the accompanying complete specification.

Details of basic application(s):-

<u>Basic Applic. No:</u>	<u>Country:</u>	<u>Application Date:</u>
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DATED this TENTH day of MARCH 1988

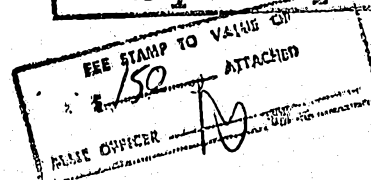
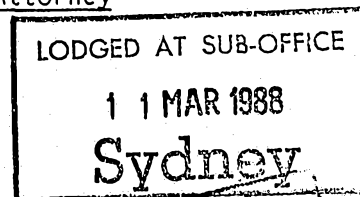
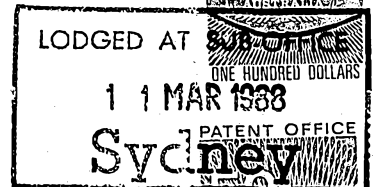
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**(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 599466**

(54) Title  
**DISPERSANTS AND THEIR USE IN AQUEOUS COAL SUSPENSIONS**

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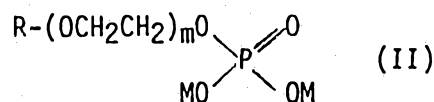
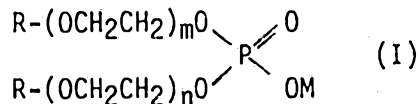
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(57) Claim

1. Dispersants containing lignin sulfonic acid and/or water-soluble salts thereof, characterized in that they comprise

(a) lignin sulfonic acid and/or alkali metal, alkaline-earth metal and/or ammonium salts thereof and

(b) one or more alkyl ether phosphates corresponding to general formulae (I) or (II) below



in which

R is a straight-chain or branched-chain C<sub>8</sub>-C<sub>22</sub> alkyl or alkenyl radical, M is hydrogen, an alkali metal, ammonium or an alkaline-earth metal and m and n are numbers from 1 to 15.

11. Dispersants as claimed in Claims 1 to 10, characterized in that they are present in aqueous coal suspensions in quantities of from 0.01 to 5 % by weight, based on the quantity of coal.

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FORM 10

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PATENTS ACT 1952

COMPLETE SPECIFICATION

This document contains the amendments made under Section 49 and is correct for printing.

(ORIGINAL)

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Complete Specification Lodged:  
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Related Art:

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Complete Specification for the invention entitled:

Dispersants and Their Use in Aqueous Coal Suspensions

The following statement is a full description of this invention, including the best method of performing it known to me/us

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Dispersants and their use in aqueous coal suspensions

This invention relates to dispersants containing lignin sulfonic acid and/or alkali metal or ammonium salts thereof and to their use in aqueous coal suspensions.

In view of the expected shortage of crude oil as a fuel on account of the decline in natural reserves worth producing on the one hand and the need to use them as a chemical raw material on the other hand, energy-recovery processes in which aqueous coal suspensions are subjected to high-temperature combustion have recently been gaining in importance. Aqueous coal suspensions offer the major advantage over coal in solid, albeit finely divided, form that they may be conveyed over relatively long distances at relatively low cost in transport systems known from the transport of crude oil, for example pipelines or overland pipelines. However, the disadvantage is that the dispersion medium, water, which is inert to combustion reduces the gross calorific value of aqueous coal suspensions. So far as the coal content of aqueous coal suspensions is concerned, an excessive coal content has to be avoided with transportability in mind whereas as high a coal content as possible is desired with the gross calorific value in mind.

It is known from the prior art that aqueous coal suspensions may be provided with additives which improve fluidity during transport in pipelines, but which on the



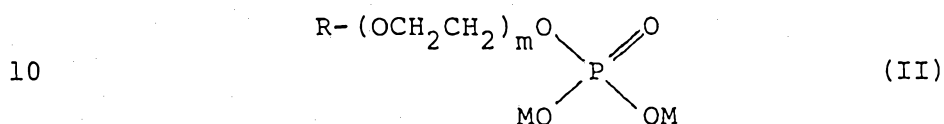
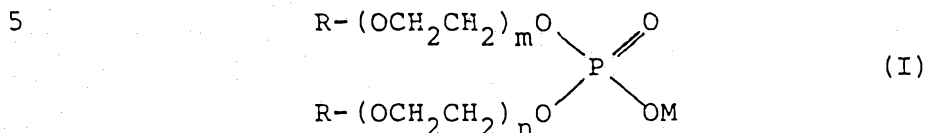
1 other hand allow an increase in the coal content of the  
aqueous coal suspensions and hence considerably increase the  
gross calorific value. Such additives also improve the  
combustion properties of the aqueous coal suspensions.  
5 For example, it is known from DE-C 27 27 943, from EP-B 0  
050 412, from EP-A 0 089 766 and from EP-A 0 092 353 that  
organic dispersants selected from the group comprising  
organic sulfonic acids and/or alkali metal, alkaline-earth  
metal or ammonium salts thereof, more especially lignin  
10 sulfonic acid and corresponding salts thereof, may be  
incorporated in aqueous coal suspensions to improve their  
fluidity and, at the same time, to increase their coal  
content. Providing the coal used to prepare the coal  
suspensions has a suitable sieve analysis, it is possible to  
15 produce readily pumpable suspensions having coal contents  
of from 10 to 50% by weight.

However, it is generally desired further to increase  
the coal content in order to increase the gross calorific  
value of aqueous coal suspensions, because aqueous coal  
20 suspensions can only be economically used for industrial  
combustion processes for energy recovery beyond a coal  
content of 65% by weight coal, based on the total weight of  
the suspension. In addition, it is desired further to  
reduce the viscosity of aqueous coal suspensions to provide  
25 for convenient transport, even through pipelines of compara-  
tively narrow cross-section.

It has now surprisingly been found that the viscosity of  
aqueous coal suspensions can be further reduced and their  
solids content further increased if, in addition to alkali  
30 metal and/or alkaline-earth metal lignin sulfonates as  
additives, alkyl ether phosphates are added as co-additives  
to aqueous coal suspensions.

The present invention relates to dispersants containing  
lignin sulfonic acid and/or water-soluble salts thereof  
35 which are characterized in that they contain lignin sulfonic

1 acid and/or alkali metal, alkaline-earth metal and/or ammonium salts thereof, one or more alkyl ether phosphates corresponding to general formulae (I) and/or (II) below:



in which

15 R is a straight-chain or branched C<sub>8</sub>-C<sub>22</sub> alkyl or alkenyl radical,  
M is hydrogen, an alkali metal, ammonium or alkaline earth metal and  
m and n are numbers of from 1 to 15,  
20 and optionally other auxiliaries of the type typically present in dispersants of the type in question.

The present invention also relates to the use of these dispersants in aqueous coal suspensions.

25 The dispersant according to the invention contains one or more compounds from the group comprising lignin sulfonic acid, alkali metal salts of lignin sulfonic acid, alkaline-earth metal salts of lignin sulfonic acid and ammonium salts of lignin sulfonic acid as anionic, surfactant-like component. These compounds may be present in the  
30 dispersants either individually or even in the form of mixtures of two or more of the compounds mentioned. In that case, the quantitative ratio between the individual compounds to one another is not critical. The primary object of these compounds is to reduce the interfacial  
35 tension between the coal particles and the aqueous phase



1 less wide chain-length range, the substituents R in general  
formulae (I) and (II) are normally mixtures of alkyl and  
alkenyl radicals of different structure and chain length.  
In this connection, it is possible to use compounds which,  
5 depending on their origin, contain from certain native fats  
and oils alkyl radicals R which correspond to the entire  
spectrum of fatty alkyl radicals of such fats and  
oils. However, it is also possible to select suitable  
fractions within a limited chain-length range. Compounds  
10 corresponding to general formulae (I) and (II) also include  
individual, synthetically obtained and hence pure compounds  
(I) and/or (II). For example, it is possible to use alkyl  
ether phosphates (I) and/or (II) of which the alkyl radical  
R emanates from fatty alcohols or fatty alcohol mixtures of  
15 the type formed in the known Ziegler and oxo reactions.

In preferred embodiments, the dispersants according to  
the invention contain one or more alkyl ether phosphates  
corresponding to general formulae (I) and/or (II) above,  
in which R is a straight-chain alkyl or alkenyl radical.  
20 This is particularly the case when the fatty alcohols (ROH)  
on which the synthesis of the compounds corresponding to  
general formulae (I) and (II) is based are of the type  
obtained from native fats and oils, for example via the  
transesterification of the triglycerides with methanol,  
25 followed by catalytic hydrogenation of the fatty acid methyl  
ester. In the natural mixtures, the straight-chain radicals  
R predominate.

In another embodiment, alkyl ether phosphates in which  
R is a straight-chain  $C_{12}$ - $C_{18}$  alkyl or alkenyl radical are  
30 preferably used in the dispersants according to the invention.  
Apart from their convenient availability, the  $C_{12}$ - $C_{18}$  alkyl  
or alkenyl radicals occurring particularly frequently in the  
natural chain length spectrum have the further major  
advantage that they may be components in dispersants which  
35 are particularly effective in reducing the viscosity of

1 aqueous coal suspensions.

The alkyl ether phosphates corresponding to general formulae (I) and (II) present in the dispersants according to the invention may be used either as free acids of the  
5 monoesters (II) or diesters (I), in which case M in the general formulae is hydrogen. However, the corresponding water-soluble alkali metal, alkaline-earth metal and/or ammonium salts of the particular free acids may also be used. In this case, M in the above general formulae is an  
10 alkali metal, an alkaline-earth metal or ammonium. Preferred alkali metals are lithium, sodium and potassium; preferred alkaline-earth metals are magnesium, calcium and strontium. Of the meanings mentioned for M in the general formulae, the alkali metals, particularly sodium, are preferred.

15 In general formulae (I) and (II), the indices m and n are numbers of from 1 to 15. The number of ethoxy groups corresponding to the indices results from reactions of the fatty alcohols with ethylene oxide, m and n indicating the ratio of ethylene oxide to alcohol on which the reaction is  
20 based. It is known that not only pure substances, but also mixtures of substances differing from one another in the number of ethoxy groups added are formed in the course of such reactions. Accordingly, m and n represent only average values and, in practice, may be whole or broken numbers  
25 within the range mentioned. In particularly preferred embodiments, the dispersants according to the invention contain one or more compounds corresponding to general formulae (I) and (II), in which m and n are numbers in the range from 2 to 12 and, more preferably, in the range from  
30 8 to 10.

In other particularly preferred embodiments, the dispersants according to the invention contain one or more alkyl ether phosphates corresponding to general formulae (I) and/or (II), in which  
35 R represents straight-chain  $C_{12}$ - $C_{18}$  alkyl or alkenyl radicals,

1 M is sodium and  
m and n are numbers of from 8 to 10.

5 Phosphoric acid mono- or diester salts such as these,  
together with the lignin sulfonic acid and/or water-soluble  
salts thereof, provide for a particularly distinct reduction  
in the viscosity of aqueous coal suspensions, despite a  
high coal content. In addition, aqueous suspensions such  
as these have the high gross calorific value required.

10 In preferred embodiments of the invention, the aqueous  
dispersants contain lignin sulfonic acid and/or salts thereof  
and one or more alkyl ether phosphates corresponding to  
general formulae (I) and (II) in a ratio by weight in the  
range from 4 : 1 to 20 : 1. By virtue of the particularly  
good results they provide in reducing the viscosity of aqueous  
15 coal suspensions, it is of advantage to use dispersants in  
which lignin sulfonic acid and/or salts thereof and one or  
more alkyl ether phosphates are present in a ratio by weight  
of from 4 : 1 to 10 : 1.

20 In addition to the components mentioned above, the  
dispersants according to the invention may also contain other  
components which are not absolutely essential to the disper-  
sing effect of the dispersants. Such components may be,  
for example, stabilizers, foam inhibitors, biocides and/or  
corrosion inhibitors which are known as such for this purpose  
25 and which are also used in dispersants known from the prior  
art. For example, guar or guar derivatives, cellulose or  
cellulose derivatives, xanthan or the like are added as  
stabilizers. The foam inhibitors emanate from the group  
comprising adducts of propylene oxide and/or ethylene oxide  
30 with fatty alcohols and/or long-chain fatty acids, for example  
with behenic acid. Biocides or corrosion inhibitors which  
may be used with advantage are also known from the prior  
art.

35 The dispersants according to the invention are prepared  
by methods known per se from the prior art, for example in

1 ball mills or conventional stirring vessels. Pastes or highly viscous liquids are normally formed, being formulated either as such or in admixture with water, preferably in a ratio by weight of 1 : 1.

5 To prepare aqueous coal suspensions, the dispersants formulated in paste or highly viscous liquid form are stirred into the aqueous phase in which they are then normally present in quantities of from 0.01 to 5% by weight, based on the quantity of coal.

10 Over the entire concentration range indicated, they provide for a distinct reduction in the viscosity of aqueous coal suspensions compared with suspensions of the type in which - as known from the prior art - sodium lignin sulfonate is used on its own as additive, i.e. without any other  
15 additives. Suspensions such as these have viscosity values which enable them to be pumped without difficulty through pipes and pipelines and delivered to the combustion furnaces. By virtue of their high coal content of 65% and higher, they have a very high gross calorific value, making aqueous  
20 coal suspensions of the type in question inexpensive and economical to use in power stations.

The invention is illustrated by the following Examples.

EXAMPLES 1 to 3

25 A German coal sample was ground to an average particle size of  $100\% < 200 \mu\text{m}$  and separated from coarser coal particles by means of a sieve. Aqueous coal suspensions containing 65% coal were prepared using sodium lignin sulfonate (source: Lignin-Chemie, Waldhof-Holmen) and a  
30 mixture of alkyl ether phosphates (mixture of the sodium salts of phosphoric acid mono- and diesters containing from 8 to 18 carbon atoms in the alkyl radical and on average 9.5 ethoxy groups (source: Forlanit<sup>(R)</sup> P, Henkel KGaA). The concentration of dispersant according to the invention was  
35 1% by weight, based on the quantity of coal.

1           The apparent viscosity of the suspensions was measured  
as a function of the shear rate using a rotational viscosi-  
meter (Contraves Rheomat 30) in the shear rate range from  
0 s<sup>-1</sup> to 200 s<sup>-1</sup>.

5           The results are shown in the following Table.

Table

10           Viscosities of aqueous coal suspensions at different shear  
rates and for different ratios of lignin sulfonate to alkyl  
ether phosphate

Example	Ratio of lignin sulfonate to alkyl ether phosphate	Viscosity (mPa.s)		
		at 50 s <sup>-1</sup>	at 100 s <sup>-1</sup>	at 200 s <sup>-1</sup>
1	19 : 1	492	456	422
2	9 : 1	485	447	413
3	4 : 1	446	410	382
Comp.	1 : 1	500	456	477

Result:

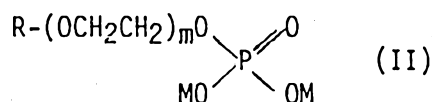
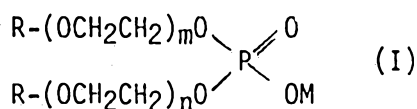
25           Over the entire shear rate range, the apparent viscosity  
of aqueous coal suspensions is distinctly lower than where  
pure lignin sulfonate is used (cf. following Comparison  
Example).

COMPARISON EXAMPLE

30           The procedure was the same as in Examples 1 to 3 using  
a dispersant containing only sodium lignin sulfonate as  
additive. The result is shown in the preceding Table  
(under "Comp.").

The claims defining the invention are as follows:

1. Dispersants containing lignin sulfonic acid and/or water-soluble salts thereof, characterized in that they comprise
  - (a) lignin sulfonic acid and/or alkali metal, alkaline-earth metal and/or ammonium salts thereof and
  - (b) one or more alkyl ether phosphates corresponding to general formulae (I) or (II) below



in which

R is a straight-chain or branched-chain C<sub>8</sub>-C<sub>22</sub> alkyl or alkenyl radical, M is hydrogen, an alkali metal, ammonium or an alkaline-earth metal and m and n are numbers from 1 to 15.

2. Dispersants as claimed in Claim 1, characterized in that they comprise one or more compounds (I) or (II), in which R is a straight-chain C<sub>12</sub>-C<sub>18</sub> alkyl or alkenyl radical.
3. Dispersants as claimed in Claims 1 and 2, characterized in that they comprise one or more compounds (I) or (II), in which M is an alkali metal.
4. Dispersants as claimed in Claim 3, characterized in that they comprise one or more compounds (I) or (II), in which M is sodium.
5. Dispersants as claimed in Claims 1 to 4, characterized in that they comprise one or more compounds (I) or (II), in which m and n are numbers in the range from 2 to 12.
6. Dispersants as claimed in Claim 5, characterized in that they comprise one or more compounds (I) or (II), in which m and n are numbers in the range from 8 to 10.
7. Dispersants as claimed in Claims 1 to 6, characterized in that they comprise one or more compounds (I) or (II), in which R is a straight-chain C<sub>12</sub>-C<sub>18</sub> alkyl or alkenyl radical, M is sodium and m and n are numbers from 8 to 10.
8. Dispersants as claimed in Claims 1 to 7, characterized in that they are comprising lignin sulfonic acids and/or salts thereof and one or more alkyl ether phosphates in a ratio by weight of from 4 : 1 to 20 : 1.



9. Dispersants as claimed in Claim 8, characterized in that they are comprising lignin sulfonic acids and/or salts thereof and one or more alkyl ether phosphates in a ratio of from 4 : 1 to 10 : 1.
10. Dispersants as claimed in Claims 1 to 9, characterized in that they additionally contain one or more compounds from the group comprising stabilisers, foam inhibitors, biocides and corrosion inhibitors.
11. Dispersants as claimed in Claims 1 to 10, characterized in that they are present in aqueous coal suspensions in quantities of from 0.01 to 5 % by weight, based on the quantity of coal.
12. The use of dispersants claimed in Claims 1 to 11 in aqueous coal suspensions.
13. The use of dispersants claimed in Claims 1 to 11 for reducing the viscosity of aqueous coal suspensions.
14. Dispersants substantially as hereinbefore described with reference to any one of Examples 1 to 3.

DATED this TWENTY-SIXTH day of MARCH 1990  
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Patent Attorneys for the Applicant  
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