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(54) Aqueous suspensions of slightly soluble particulate materials.

(57) There is disclosed an aqueous suspension comprising at least 40% by weight of a slightly water-soluble particulate inorganic material, at least 0.5% by weight of a hydrophilic polymeric material, at least 0.1% by weight of a natural or synthetic zeolite and at least 0.1% by weight of a dispersing agent, the percentages by weight of the hydrophilic polymer, zeolite and dispersing agent being based on the weight of the dry slightly soluble particulate material. Also disclosed is a process for preparing the aqueous suspension and the use of the aqueous suspension in a paper coating composition.

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AQUEOUS SUSPENSIONS OF SLIGHTLY SOLUBLE PARTICULATE MATERIALS

This invention relates to stable aqueous suspensions of slightly water-soluble particulate inorganic materials such as calcium sulphate or gypsum, to a process for preparing such suspensions and to the use of such compositions in paper coating compositions.

By slightly water soluble, there is meant herein a solubility in the range of from 0.1 to 10 grams per litre at 20°C.

In order to prepare a stable suspension of a particulate material, i.e. a suspension which remains fluid, does not form a gel and from which the particles, especially the coarsest particles present, do not sediment appreciably with time, it is generally necessary to incorporate in the suspension a dispersing agent for the particulate material. The dispersing agent generally functions by applying a similar electric charge to substantially the whole of the surface of each particle of material so that the particles repel each other. Commonly used dispersing agents include alkali metal or ammonium salts of polyphosphoric or polysilicic acids or polyelectrolytes such as alkali metal or ammonium salts of poly(acrylic acid) or derivative thereof.

Where the particulate material is slightly soluble in water such that divalent or multivalent cations pass into solution, it has been found difficult to prepare, using conventional dispersing agents, a stable suspension which has a sufficiently low viscosity for a given solids content. One such example of a slightly soluble material which is present in a large number of industrial processes is calcium sulphate or gypsum. Calcium sulphate dihydrate has a solubility of 2 grams per litre at 20°C. To form an aqueous suspension containing a high percentage by weight of calcium sulphate and having acceptable rheological properties, it is necessary to use a very large quantity of the dispersing agent. As dispersing agents are generally expensive, this process is commercially unattractive. If the dispersing agent is of the polyelectrolyte type, it has also been found that suspensions containing a high percentage by weight of calcium sulphate tend to form a gel on prolonged storage.

According to a first aspect of the present invention, there is provided a stable aqueous suspension comprising a slightly water-soluble particulate inorganic material and a dispersing agent, characterised in that the slightly soluble particulate inorganic material is present in an amount of at least 40% by weight and the dispersing agent is present in an amount of at least 0.1% by weight, and in that the suspension further comprises at least 0.5% by weight of a hydrophilic polymer and at least 0.1% by weight of a natural or synthetic zeolite, the percentages by weight of the dispersing agent, hydrophilic polymer and zeolite being based on the weight of the dry slightly soluble particulate inorganic material.

The present invention is particularly suitable for a mineral such as natural calcium sulphate or for synthetic calcium sulphate.

When the water-soluble particulate material is calcium sulphate, it is believed that the hydrophilic polymer forms what amounts to a sealing film over the surface of the particles of calcium sulphate thus greatly reducing the passage of calcium ions into the aqueous medium. The zeolite then scavenges the calcium ions which are already present in the aqueous medium and thus protects the dispersing agent from the formation of calcium complexes.

The hydrophilic polymeric material is preferably used in an amount no greater than 5.0% by weight, based on the weight of the dry slightly soluble particulate material and is preferably a carbohydrate polymer such as starch, a starch derivative or a cellulose derivative. Especially preferred are sodium carboxymethyl cellulose and starch phosphates.

The zeolite is preferably used in an amount no greater than 1.0% by weight, based on the weight of dry slightly soluble particulate material, and preferably has a cation exchange capacity of at least 200 milliequivalents per 100g, more preferably at least 500 milliequivalents per 100g. The exchangeable cations of the zeolite should desirably be alkali metal or ammonium ions. Examples of suitable zeolites are the synthetic faujasites (zeolites X and Y) and the natural zeolites clinoptilolite, phillipsite and mordenite. The natural zeolite chabazite is also suitable if it is in the alkali metal or ammonium ion exchanged form. Especially preferred is zeolite 4A which generally has a cation exchange capacity in the region of about 500 to 550 meq/100g.

The dispersing agent is preferably used in an amount no greater than 1.0% by weight, based on the weight of dry slightly soluble particulate material. Examples of especially suitable dispersing agents are tetrasodium pyrophosphate (TSPP) and sodium or ammonium salts of poly(acrylic acid) or poly(methacrylic acid) having a number average molecular weight in the range from 500 to 10,000. Of the two preferred types of dispersing agent the polyphosphate type, e.g. TSPP, is less sensitive to the presence of calcium ions in solution but very sensitive to high temperatures and shearing forces. It is therefore unsuitable if the suspension is to be used as a wet grinding feed. The sodium polyacrylate dispersing agents are much

more resistant to heat and shear and therefore ideal for wet grinding, but are extremely sensitive to calcium ions with which they form complexes with consequent loss of their dispersing ability. The present invention makes it possible to use sodium polyacrylate dispersing agents in the wet grinding of calcium sulphate of high solids concentrations.

The stable aqueous suspensions of the first aspect of the present invention may be used as a component of a paper coating composition, as a feed suspension for a wet grinding process to increase the fineness of the particulate material or as an article of commerce which is a concentrated aqueous suspension of the particulate material which can be pumped, stored or transported in containers without appreciable increase in viscosity with time or sedimentation of solids.

As mentioned, the aqueous suspension of the first aspect of this invention may be used as a component of a paper coating composition. Of the many varieties of coated papers produced today, the majority are principally coated with a composition, sometimes known as the coating colour, which essentially comprises an adhesive, also known as a binder, and a pigment. A discussion of the constituents of paper coating compositions and of the methods of applying such compositions to paper is given in Chapter XIX, Volume III, of the 2nd Edition of the book by James P. Casey entitled "Pulp and Paper: Chemistry and Technology". The adhesive used can be, for example, starch, casein or a synthetic resin latex; the particular adhesive used will depend, for example, on the printing process to be used, e.g. offset lithography requires the adhesive to be water-insoluble.

According to a second aspect of the present invention there is provided a paper coating composition which comprises a stable suspension of a slightly water-soluble particulate inorganic material in an aqueous medium containing an adhesive, wherein the particulate material constitutes at least 45% by weight of the composition, and wherein the composition additionally comprises at least 0.5% by weight of a hydrophilic polymer, at least 0.1% by weight of a natural or synthetic zeolite and at least 0.1% by weight of a dispersing agent, the percentages by weight of the hydrophilic polymer, zeolite and dispersing agent being based on the weight of the dry slightly soluble particulate material. The slightly water-soluble particulate material may be used in the paper coating composition in combination with other conventional paper coating pigments, for example clay. Preferably, the particulate material should constiute at least 50% by weight of the composition.

According to a third aspect of the present invention there is provided a process for preparing a stable aqueous suspension of a slightly water-soluble particulate inorganic material, which process comprises mixing with the slightly water-soluble material at least 0.5% by weight of a hydrophilic polymeric material, at least 0.1% by weight of a natural or synthetic zeolite and at least 0.1% by weight of a dispersing agent, the percentages by weight of the hydrophilic polymer, zeolite and dispersing agent being based on the weight of the dry slightly soluble particulate material, and the particulate material being used in an amount such as to provide at least 40% by weight of the aqueous suspension.

It has been found that most advantageous results are obtained if the slightly soluble particulate material is mixed first with the hydrophilic polymeric material and then with the zeolite. However the dispersing agent may be added either simultaneously with, or subsequently to, the zeolite.

In preferred embodiments of the third aspect of this invention, the hydrophilic polymeric material, zeolite and dispersing agents are added to an aqueous suspension of the particulate material.

It is believed that slightly soluble particulate materials when mixed with water release into solution multivalent cations which form complexes with the dispersing agent which is used, thus reducing the effectiveness of the dispersing agent in becoming attached to the surface of the particulate material thereby ensuring that substantially the whole of the surface carries the same electric charge. The addition of a zeolite is believed to effect the exchange of the multivalent cations released into solution for the exchangeable cations, for example alkali metal or ammonium ions, in the zeolite which do not have a deleterious effect on the dispersing agent.

The invention is illustrated by the following Examples.

EXAMPLE 1

A sample of dry calcium sulphate dihydrate was mixed with sufficient water to form a suspension containing 59% by weight of the dry material and with 2.5% by weight, based on the weight of the dry material, of sodium carboxymethyl cellulose. The viscosity of the resultant mixture was then measure by means of a Brookfield Viscometer at a spindle speed of 100 rpm. The mixture was then divided into two portions and, to one portion, there was added 1% by weight, based on the weight of dry calcium sulphate dihydrate, of sodium zeolite 4A having a cation exchange capacity in the region of about 550 meq/100g.

The viscosity of the suspension was then measured again. Small additions of tetrasodium pyrophosphate (TSPP) dispersing agent were then made sequentially to each portion of the suspension and the viscosity of the suspension was measured after each addition.

The results obtained are set forth in Table I

TABLE I

% by weight of TSPP	Viscosity at 100 rpm (Pa.S)	
	With zeolite	Without zeolite
0	3.7	7.4
0.1	1.4	2.15
0.2	1.35	1.5
0.3	1.3	1.3
0.4	1.35	1.3
0.5	1.35	1.3

These results show that the addition of 1% by weight, based on the weight of dry calcium sulphate dihydrate, of zeolite to the suspension of calcium sulphate and sodium carboxymethyl cellulose caused the viscosity to drop to about half its value in the absence of the zeolite. Furthermore a smaller addition of TSPP was required to achieve a minimum viscosity when the zeolite was present in the suspension.

EXAMPLE 2

The experiment described in Example 1 was repeated except that the TSPP dispersing agent was replaced by a sodium polyacrylate dispersing agent of number average molecular weight of 1680.

The results obtained are set forth in Table II below:-

TABLE II

% by weight sodium polyacrylate	Viscosity at 100 rpm (Pa.S)	
	With zeolite	Without zeolite
0	3.9	7.6
0.1	3.65	8.4
0.2	2.95	7.65
0.3	2.9	6.7
0.4	2.1	5.95
0.5	1.55	4.6
0.6	1.65	3.1
0.7	1.35	2.8
0.8	1.05	2.1
0.9	1.0	1.75
1.0	0.95	-

It can be seen from these results that the addition of a small quantity of sodium polyacrylate to a suspension of calcium sulphate and sodium carboxymethyl cellulose in the absence of zeolite actually causes an increase in viscosity. In the presence of zeolite not only is the viscosity substantially reduced even before any sodium polyacrylate is added but the thickening effect of a small addition of sodium polyacrylate is not observed. Also, in the presence of zeolite, a smaller addition of sodium polyacrylate is required to reduce the viscosity to the minimum value which was obtained using TSPP than would be required in the absence of zeolite.

The effect of omitting the hydrophilic polymer from the aqueous suspension of the present invention

would be that a very much larger proportion of zeolite would be required to achieve an acceptable viscosity. In fact the amount of zeolite required would be so large that it would affect the packing of the slightly soluble material and thus have a harmful effect on the viscosity of the suspension.

Claims

1. A stable aqueous suspension comprising a slightly water-soluble particulate inorganic material and a dispersing agent, characterised in that the slightly soluble particulate inorganic material is present in an amount of at least 40% by weight and the dispersing agent is present in an amount of at least 0.1% by weight, and in that the suspension further comprises at least 0.5% by weight of a hydrophilic polymer and at least 0.1% by weight of a natural or synthetic zeolite, the percentages by weight of the dispersing agent, hydrophilic polymer and zeolite being based on the weight of the dry slightly soluble particulate inorganic material.

2. An aqueous suspension according to Claim 1, comprising no more than 5.0% by weight, based on the weight of the dry slightly soluble particulate material, of the hydrophilic polymeric material.

3. An aqueous suspension according to Claim 1 or 2, wherein the hydrophilic polymer material is a carbohydrate polymer.

4. An aqueous suspension according to any preceding claim, wherein the zeolite is present in an amount no greater than 2.0% by weight, based on the weight of the dry slightly soluble particulate material.

5. An aqueous suspension according to any preceding claim, wherein the zeolite has a cation exchange capacity of at least 200 milliequivalents per 100g, preferably at least 500 milliequivalents per 100g.

6. An aqueous suspension according to any preceding claim, wherein the dispersing agent is present in an amount no greater than 1.0% by weight, based on the weight of dry slightly soluble particulate material.

7. An aqueous suspension according to any preceding claim, wherein the dispersing agent is an alkali metal or ammonium salt of a polyphosphoric acid or of poly(acrylic acid), a derivative thereof or a mixture of such salts.

8. An aqueous suspension according to any preceding claim, wherein the slightly water-soluble particulate material is calcium sulphate.

9. A process for preparing a stable aqueous suspension of a slightly soluble particulate inorganic material, which process comprises mixing with the slightly soluble material at least 0.5% by weight of a hydrophilic polymeric material, at least 0.1% by weight of a natural or synthetic zeolite and at least 0.1% by weight of a dispersing agent, the percentages by weight of the hydrophilic polymer, zeolite and dispersing agent being based on the weight of the dry slightly soluble particulate material, and the particulate material being used in an amount such as to provide at least 40% by weight of the aqueous suspension.

10. A process according to Claim 9, in which the slightly soluble material is first mixed with the hydrophilic polymer and, subsequently, with the zeolite.

11. A process according to Claim 9 or 10, wherein the dispersing agent is added simultaneously with, or subsequently to, the zeolite.

12. A process according to any one of Claims 9 to 11, in which the slightly soluble particulate material is in the form of an aqueous suspension into which is mixed the hydrophilic polymeric material, zeolite and the dispersing agent.

13. A paper coating composition which comprises a stable suspension of a slightly water-soluble particulate inorganic material in an aqueous medium containing an adhesive, wherein the particulate material constitutes at least 45% by weight of the composition, and wherein the composition additionally comprises at least 0.5% by weight of a hydrophilic polymer, at least 0.1% by weight of a natural or synthetic zeolite and at least 0.1% by weight of a dispersing agent, the percentages by weight of the hydrophilic polymer, zeolite and dispersing agent being based on the weight of the dry slightly soluble particulate material.

Claims for the following Contracting State : ES

1. A process for preparing a stable aqueous suspension of a slightly soluble particulate inorganic material, which process comprises mixing with the slightly soluble material at least 0.5% by weight of a hydrophilic polymeric material, at least 0.1% by weight of a natural or synthetic zeolite and at least 0.1% by weight of a dispersing agent, the percentages by weight of the hydrophilic polymer, zeolite and dispersing agent being based on the weight of the dry slightly soluble particulate material, and the particulate material being used in an amount such as to provide at least 40% by weight of the aqueous suspension.

2. A process according to Claim 1, in which the slightly soluble material is first mixed with the hydrophilic polymer and, subsequently, with the zeolite.

3. A process according to Claim 1 or 2, wherein the dispersing agent is added simultaneously with, or subsequently to, the zeolite.

4. A process according to any one of Claims 1 to 3, in which the slightly soluble particulate material is in the form of an aqueous suspension into which is mixed the hydrophilic polymeric material, zeolite and the dispersing agent.

5. A process according to any one of Claims 1 to 4, wherein no more than 5.0% by weight, based on the weight of the dry slightly soluble particulate material, of the hydrophilic polymeric material is employed.

6. A process according to any preceding claim, wherein the hydrophilic polymer material is a carbohydrate polymer.

7. A process according to any preceding claim, wherein the zeolite is employed in an amount no greater than 2.0% by weight, based on the weight of the dry slightly soluble particulate material.

8. A process according to any preceding claim, wherein the zeolite has a cation exchange capacity of at least 200 milliequivalents per 100g, preferably at least 500 milliequivalents per 100g.

9. A process according to any preceding claim, wherein the dispersing agent is employed in an amount no greater than 1.0% by weight, based on the weight of dry slightly soluble particulate material.

10. A process according to any preceding claim, wherein the dispersing agent is an alkali metal or ammonium salt of a polyphosphoric acid or of poly(acrylic acid), a derivative thereof or a mixture of such salts.

11. A process according to any preceding claim, wherein the slightly water-soluble particulate material is calcium sulphate.

12. A process for making a paper coating composition which comprises the step of combining a stable suspension of a slightly water-soluble particulate inorganic material in an aqueous medium prepared by a process as claimed in any one of Claims 1 to 11 with an adhesive, wherein the stable suspension employed contains sufficient of the particulate inorganic material to provide at least 45% by weight of the particulate inorganic material in the final paper coating composition.

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EUROPEAN SEARCH REPORT

Application Number

EP 88 30 0520

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)
Y	US-A-4 606 503 (J.A. BLEECK) * Whole document *	1,4,6,7,9,11-13	C 09 C 1/02 D 21 H 1/22
Y	GB-A-2 034 729 (SUPRA) * Pages 1-4 *	1-3,6,8,9,13	
Y	DE-A-3 203 067 (KEMIRA) * Claims 1,10-12; page 4; examples 1-10 *	1-3,6-9,12,13	
P,Y	EP-A-0 216 516 (ECC INTERNATIONAL) * Pages 3-14 *	1-3,6-9,12,13	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 09 C
D 21 H

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	24-05-1988	NESTBY K.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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