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(54) **Aluminosilicate slurries.**

(57) Stable, pumpable aqueous slurries of water-insoluble sodium aluminosilicate, containing 10% to 60% solids, are prepared by incorporating effective amounts of a water-soluble non-ionic polymer and a water-soluble anionic surfactant which adsorbs onto the polymer. Polyethylene oxide of high molecular weight and sodium dodecyl sulphate (SDS) are suitable as polymer and surfactant. The stabilised suspensions may be used for preparing particulate detergent compositions.

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FIELD OF THE INVENTION

This invention relates to the production of slurries or suspensions of water-insoluble sodium aluminosilicates which are pumpable and stable, that is, redispersible after standing.

BACKGROUND OF THE INVENTION

Such aluminosilicates are commonly manufactured and supplied for use in slurry form. For example, cation exchange aluminosilicate suspensions containing from 10% to 60%, typically 40% to 50%, aluminosilicate are made in bulk for use as detergency builders. These suspensions, being slurries of fine particles, are not always stable with the passage of time, e.g. during storage or transport. The tendency of the particles to settle, together with the lubricating effect of the repulsion caused by their negative surface charges, gives rise to a sediment which may be difficult to redisperse. Indeed, caked sediments of aluminosilicate formed in this way may be impossible to treat in such a way as to recover the original suspension. This is a serious disadvantage because the suspensions frequently need to remain pumpable.

This problem is known, and various additives to suspensions have been proposed which to varying degrees lessen the tendency to form hard-caked sediment. Certain of the existing proposals involve addition of polymers. GB 2 053 880 (Montedison SpA) describes addition of anionic ethyl acrylate/methacrylic acid copolymers to stabilise zeolite slurries. GB 2 048 841 describes use of high molecular weight polyacrylamides in the same way. JP-B-86 021168 (Nippon Kagako Kogyo) describes use of a nonionic polymer, polyethylene oxide, for stabilisation of a zeolite slurry.

GENERAL DESCRIPTION OF THE INVENTION

The present invention seeks to provide a new stabilisation system using a polymeric component.

According to the invention, an aqueous slurry or suspension of water insoluble aluminosilicate is stabilised by the presence in effective amounts of a water-soluble nonionic polymer in combination with a water-soluble anionic surfactant.

In particular there is provided a pumpable stable aqueous suspension of water-insoluble sodium aluminosilicate having a cation exchange capacity of at least 150mg/g as calcium oxide, containing from about 10% to about 60% by weight of the aluminosilicate and a stabilising effective amount of a synergistic combination of a water-soluble nonionic polymer of average molecular weight between 10^4 and 10^7 , and a water-soluble anionic surfactant containing at least one long chain (C10 to C18) hydrocarbon group which is capable of interacting with the nonionic polymer.

The surprising and useful discovery has been made that, although anionic surfactants on their own are not generally effective in stabilising suspensions, when they are added to suitable nonionic polymers in the aqueous phase there is a synergistic effect whereby the effectiveness of the nonionic polymer in stabilising a suspension is increased. It is believed that the surfactant adsorbs onto the polymer and these together form a "pseudo-polyelectrolyte" which is more effective than nonionic polymer in aggregating suspended particles. The mechanism of aggregation is understood to be depletion flocculation as described for simple polymers in "polymeric stabilisation of Colloidal Dispersions" by Donald H. Napper (Academic Press 1983). The process of flocculation inhibits hard sediment formation.

The nonionic polymer used should preferably therefore be a water-soluble polymer or copolymer capable of adsorbing an anionic surfactant. Suitable polymers include e.g. polyethylene oxide (PEO), derivatised celluloses such as hydroxyethylcellulose (which may be hydrophobically modified), polyvinylpyrrolidone and polyvinylalcohol.

The polymer molecular weight is preferably in the range from 10^4 to 10^7 , more preferably 10^5 to 10^7 , and it may be used in an amount of from 0.01% to 10%, more preferably from 0.1% to 1%, by weight of the aqueous phase. For a given polymer an upper practical limit may be imposed by the increasing viscosity of the polymer solution which clearly should not be too high. Generally, the higher the polymer molecular weight the less the amount of polymer required. Preferably the polymer should be non-adsorbing with respect to the dispersed particles.

The anionic surfactant should be water-soluble, and capable of producing a synergistic stability-increasing effect with the polymer. In accordance with the mechanism proposed above, it should be capable of being adsorbed by the selected nonionic polymer. Commonly this can be demonstrated by increase in polymer solution viscosity on addition of surfactant, which provides a simple test for identifying polymer/surfactant combinations which may be effective in the invention. Examples of suitable surfactants are linear alkyl or alkyl aryl sulphates, sulphonates and carboxylates containing at least one long (C10 to

C18) hydrocarbon chain. Sodium dodecyl sulphate works well. Such surfactant/polymer combinations are described by I. D. Robb in E. H. Lucassen-Reynders "Anionic Surfactants, Physical Chemistry of Surfactant Action", Chapter 3 pp109-127, Marcel Dekker 1981.

It has been found that with some surfactant/polymer combinations the synergistic effect is a temporary one; after a period of time the sediment forms substantially as it would with polymer alone. However since the period of time may be several days or more, the effect is still a useful one in practice.

The preferred amount of surfactant is from 0.001% to 10%, more preferably from 0.01% to 6%, by weight of the aqueous phase. The amount of surfactant is preferred to be between about 0.1 and about 3 times the amount of nonionic polymer.

In one aspect the invention provides a suspension consisting of the aluminosilicate plus the polymer and surfactant in the aqueous phase. Generally in this aspect the suspension will be free of other major constituents such as e.g. large quantities of surfactant for spray-drying to form detergent compositions. So, aluminosilicate will be essentially the only solid component.

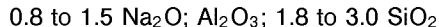
In another aspect, the invention provides a transport or storage container containing an aqueous aluminosilicate suspension incorporating nonionic polymer and anionic surfactant as stabiliser.

In further aspects, the invention provides methods for making stabilised suspensions. In one version the polymer and surfactant may be included in water used for slurring; alternatively they may be added to a pre-existing slurry or filter cake of solid e.g. wet freshly-made zeolite.

The aqueous aluminosilicate suspension may be used in a process for preparing a particulate detergent composition, in which one or more further detergent ingredients are added to the suspension which is then dried, preferably by spray-drying.

The aluminosilicate may be of the zeolite type, e.g. prepared as described in US 2 882 243 (Union Carbide) or the amorphous type e.g. prepared as described in EP 97512 (Unilever), or mixtures of these types.

There seems to be no criticality in the type of aluminosilicate or method of preparation in the application of the present invention. Preferably the anhydrous form of the aluminosilicate has the general formula:



and may be either crystalline or amorphous or a mixture thereof.

The aluminosilicate suspension will usually have a pH in the range from about 10 to about 12 to ensure that the optimum cation exchange capacity required to provide detergency building properties is obtained. The average particle size is preferably in the range from 0.1 μm to 10 μm , more preferably 0.5 μm to 6 μm , as measured by a Micromeritics Sedigraph No. 5000D.

Unless the context requires otherwise, references herein to a suspension as being stabilised include a situation in which an aggregated sediment has formed but is nevertheless readily dispersible to re-form a pumpable suspension.

Embodiments of the invention are now described by way of example, with comparative tests to show the effects obtained. Proportions are by weight unless stated otherwise.

A. ZEOLITE WITH POLYETHYLENE OXIDE

(1) 25g of a 48% w/w slurry of zeolite (Degussa Wessalith-P) i.e. 40% anhydrous sodium aluminosilicate, was allowed to settle under gravity in a 25ml measuring cylinder. After four days the sediment occupied 73% of the total volume and remained at that level thereafter. It could not be probed with a glass rod or redispersed by end-over-end rotation.

(2) An identical slurry was made up containing 0.2% polyethyleneoxide (PEO, 4×10^6 molecular weight). After five days the sediment occupied 84% of the total volume and remained at this level thereafter. The sediment could be probed, and redispersed by end-over-end rotation.

(3) Example A(2) was repeated using only 0.1% PEO, and 0.5% sodium dodecylsulphate. The sediment occupied 83% of the total volume after five days and 79% of the total volume after 26 days. The sediment could be probed easily, and redispersed by end-over-end rotation.

(4) Example A(1) was repeated with the addition of 0.5% w/w sodium dodecylsulphate (but no polymer). After four days the sediment occupied 74% of the total volume and remained at this level thereafter. The sediment could not be probed, nor redispersed by end-over-end rotation.

It should be noted from A(4) that SDS on its own showed no significant stabilising effect, but it substantially improves the stabilising effect of PEO so that in A(3) only half the PEO used in A(2) produced

comparable results.

Another interesting feature is that the improvement over PEO alone provided by addition of SDS is not a permanent one, although it lasts long enough to be very useful. Example A(3) shows that after 26 days the sediment height was similar to that which would be obtained with 0.1% PEO alone. The table shows this effect over a range of SDS concentrations. The experiments were performed as in Example A(3), but using 0.15% PEO.

TABLE

40% zeolite slurry with 0.15% PEO.

SDS (% w/w v.water)	<u>Sediment vol. (%)</u>	
	After 5 days	After 26 days
0.0	81	81
0.25	81	81
0.5	84	81.5
0.75	84	82

B. ZEOLITE WITH POLYVINYLPYRROLIDONE

(1) 12.5g of zeolite 4A powder were slurried in 12.5g of pH 11 water. 23.5g of this slurry were transferred to a 25ml stoppered measuring cylinder which was left to stand in a temperature-controlled cabinet at 35 °C. After standing for one day the sediment occupied 70% of the total slurry volume and remained at this level thereafter. The sediment could be neither probed with a glass rod nor redispersed by end-over-end rotation of the measuring cylinder.

(2) 6.25g of a 3.3% w/w PVP solution (made up at pH 11, molecular weight 360,000), were diluted with 6.25g of pH 11 water and mixed thoroughly. 12.5g of zeolite powder were mixed with this solution, and 23.5g of the slurry were transferred into a 25ml measuring cylinder and left to stand at 35 °C. After five days the sediment occupied 74.2% of the total slurry volume, and remained unchanged for a further five days. The slurry did not flow very easily on inverting the measuring cylinder, and did not redisperse upon end-over-end rotation of the measuring cylinder.

(3) 6.25g of the same 3.3% PVP solution were mixed with 6.25g of a 10% SDS solution (pH 11) and the procedure described in B(2) was repeated with this solution. After five days, the sediment volume occupied 83.5% of the total slurry volume, and remained at this level for a further five days. After this time the slurry flowed readily and redispersed as the measuring cylinder was inverted.

The addition of SDS rendered the previously rather ineffective PVP effective in maintaining a readily dispersible slurry. With this polymer there did not seem to be the same tendency to revert to polymer-only degree of stabilisation as with PEO.

C. ZEOLITE WITH HYDROPHOBICALLY-MODIFIED HYDROXYETHYLCELLULOSE

(1) 12.5g of zeolite 4A powder were slurried in 12.5g of pH 11 water. 23.5g of this slurry were transferred to a 25ml stoppered measuring cylinder which was left to stand in a temperature-controlled cabinet at 35 °C. After standing for one day the sediment occupied 69.8% of the total slurry volume and remained at this level thereafter. The sediment could not be redispersed by 50 end-over-end rotations of the measuring cylinder.

(2) Example C(1) was repeated using 12.5 ml of a 0.2% w/w HMHEC solution. After five days the slurry sediment volume occupied 70.3% of the total volume and remained at this level thereafter. The sediment

could not be redispersed by 50 end-over-end rotations of the measuring cylinder.

(3) Example C(1) was repeated using 12.5 ml of a 0.2% w/w HMHEC solution which contained in addition 0.028% w/w SDS. After five days the sediment occupied 80.0% of the total slurry volume and remained at this level for a further five days. The sediment could be redispersed almost completely by end-over-end rotation. After 50 rotations of the measuring cylinder, the sediment occupied 7% of the undisturbed ten-day sediment volume.

(4) Example C(3) was repeated with a 0.2% HMHEC solution which contained 0.056% w/w SDS. After five days the sediment occupied 81.1% of the total slurry volume, which value decreased to 80.0% after 10 days. The sediment was completely redispersed after 40 end-over-end rotations of the measuring cylinder.

(5) Example C(3) was repeated with a 0.2% HMHEC solution which contained 0.4% w/w SDS. After five days the sediment occupied 78.2% of the total slurry volume, which value decreased to 76.6% after 10 days. After 50 end-over-end rotations the residual sediment occupied 36% of the undisturbed ten-day sediment volume.

In the absence of surfactant, we found that a concentration of HMHEC between 0.2 and 0.5% was needed to affect the sediment volume of the slurry. Although concentrations of HMHEC below 0.2% w/w had no effect on sediment volume, addition of SDS to slurries containing between 0.1% and 0.2% w/w HMHEC did cause an increase in sediment volume. The effect of SDS with HMHEC is not a simple one, and some simple tests may be needed to determine the optimum relative and absolute proportions of the stabiliser components to suit the context.

Sediment volume with SDS/HMHEC seems not to decrease significantly between five and ten days' standing.

D. AMORPHOUS ALUMINOSILICATE WITH PEO

(1) 9.8g of AAS powder were mixed with 20.6g of distilled water whose pH had been adjusted to pH 11.3 through addition of NaOH solution. 27.7g of this slurry were transferred into a 25ml stoppered measuring cylinder, placed inside a temperature-controlled cabinet at 31 °C, and the sediment volume was monitored over a period of time. After five days, the sediment occupied 70.6% of the total slurry volume.

(2) 12.0g of AAS powder were mixed with 23.2g of a 0.1% 4×10^6 molecular weight polyethyleneoxide solution whose pH was 11.3. 27.1g of this slurry were decanted into a 25ml stoppered measuring cylinder and left to stand as above. After five days the sediment occupied 72.6% of the total slurry volume.

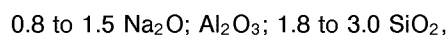
(3) 12.0g of AAS powder were slurried with 23.0g of a 0.1% 4×10^6 molecular weight PEO solution which also contained 0.3% w/w of sodium dodecylsulphate. 24.8g of this slurry were transferred to a 25ml stoppered measuring cylinder and allowed to sediment under the same conditions. After five days the sediment occupied 74.4% of the total slurry volume.

So, with amorphous aluminosilicate a synergistic effect is obtained similar to that with zeolite.

Claims

1. A pumpable stable aqueous suspension of water-insoluble sodium aluminosilicate having a cation exchange capacity of at least 150mg/g as calcium oxide, containing from about 10% to about 60% by weight of the aluminosilicate and a stabilising effective amount of a synergistic combination of a water-soluble nonionic polymer of average molecular weight between 10^4 and 10^7 , and a water-soluble anionic surfactant containing at least one long chain (C10 to C18) hydrocarbon group which is capable of interacting with the nonionic polymer.

2. An aqueous suspension according to Claim 1 in which the aluminosilicate is crystalline zeolite, amorphous aluminosilicate, or a mixture thereof, with the general formula:



for the anhydrous material.

3. An aqueous suspension according to any preceding claim wherein the pH of the suspension is in the range from about 10 to about 12.

4. An aqueous suspension according to any preceding claim containing aluminosilicate in the range from about 30% to about 50%.
- 5 5. A suspension according to any one of the preceding claims in which the aluminosilicate has average particle size of 0.1μ to 10μ , preferably 0.5μ to 6μ .
6. A suspension according to any one of the preceding claims in which the amount of nonionic polymer present is from 0.01% to 10% by weight, preferably from 0.1% to 1% by weight, of the aqueous phase.
- 10 7. A suspension according to any one of the preceding claims, in which the anionic surfactant is adsorbed onto the nonionic polymer.
8. A suspension according to any one of the preceding claims, in which the polymer has an average molecular weight in the range of 10^5 to 10^7 .
- 15 9. A suspension according to any one of the preceding claims, in which the polymer is a polymer or copolymer of polyalkylene oxide, polyvinylalcohol, derivatised cellulose, or polyvinylpyrrolidone.
- 20 10. A suspension according to any one of the preceding claims, in which the amount of anionic surfactant is from 0.001% to 10% by weight, preferably 0.01% to 6%, of the aqueous phase.
11. A suspension according to any one of the preceding claims in which the anionic surfactant is a linear alkyl or alkyl aryl sulphate, sulphonate or carboxylate.
- 25 12. A suspension according to any one of the preceding claims, in which the aluminosilicate is essentially the only solid.
13. Use, as a storage and/or transport stabilising system for an aqueous suspension of sodium aluminosilicate, of effective amounts of a nonionic polymer and an anionic surfactant combined.
- 30 14. A method of forming a stabilised aqueous suspension of sodium aluminosilicate for storage and/or transport, comprising forming the slurry to contain amounts of a nonionic polymer and an anionic surfactant effective for stabilisation.
- 35 15. A method according to claim 14 comprising slurring the aluminosilicate in water containing the nonionic polymer and anionic surfactant.
16. A method according to claim 14 comprising dispersing the nonionic polymer and anionic surfactant in a pre-existing slurry of the aluminosilicate.
- 40 17. Use or a method according to any one of claims 13 to 16, wherein the suspension is in accordance with any one of claims 1 to 12
- 45 18. A process for the preparation of a particulate detergent wherein a suspension according to any one of claims 1 to 12 is mixed with other detergent components and water is removed from the mixture, preferably by spray-drying.

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