(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
20 December 2001 (20.12.2001)

PCT

(10) International Publication Number
WO 01/96239 A1

(51) International Patent Classification⁷: C01F 5/14, C08K 3/22, C02F 1/00, 1/52, B01D 53/50, C02F 1/66, G05D 21/02

(21) International Application Number: PCT/EP01/06353

(22) International Filing Date: 5 June 2001 (05.06.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0014519.3 15 June 2000 (15.06.2000) GB

(71) **Applicant** *(for all designated States except US)*: **CIBA SPECIALTY CHEMICALS WATER TREATMENTS LIMITED** [GB/GB]; Cleckheaton Road, Low Moor, Bradford, West Yorkshire BD12 0JZ (GB).

(72) **Inventor; and**
(75) **Inventor/Applicant** *(for US only)*: **BUTTERS, Martin** [GB/GB]; 21 Leys Close, Thackley, Bradford, West Yorkshire BD10 8NJ (GB).

(74) **Common Representative: CIBA SPECIALTY CHEMICALS WATER TREATMENTS LIMITED**; Patents Department, Cleckheaton Road, Low Moor, Bradford, West Yorkshire BD12 0JZ (GB).

(81) **Designated States** *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) **Designated States** *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

**Published:**
- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

WO 01/96239 A1

# (54) Title: STABILISED MAGNESIUM HYDROXIDE SLURRIES

(57) **Abstract:** Compositions comprising an aqueous magnesium hydroxide slurry with solids loading of 25-75 wt%, an acidic polymer or water-soluble salt thereof and a co-additive (preferably boric acid or water soluble salts thereof) are prepared. Also claimed are methods for the preparation thereof. The polydispersity and molecular weight of the polymer are well-defined. The composition has a low viscosity and remains flowable after several days.

# Stabilised Magnesium Hydroxide Slurries

This invention relates to magnesium hydroxide slurries, and a method of preparing magnesium hydroxide slurries which are low in viscosity and which remain flowable after several days.

Magnesium hydroxide is used in large quantities in various industrial and agricultural applications such as acid effluent neutraliser, crop supplement and as a pigment in the paper industry. It is desirable to be able to ship and store magnesium hydroxide as a high solids aqueous slurry of low viscosity. However, such slurries are fairly unstable and form either gels or hard-pack sediment upon standing, thereby rendering the slurries difficult to off-load at the point of use after transportation.

Magnesium hydroxide and magnesium oxide slurry stability has been the subject of extensive research and has been a long standing problem for the magnesium hydroxide industry. The art has addressed the problem by focusing on methods of reducing the viscosity of high solids magnesium hydroxide slurries. US 4,230,610 teaches a method of reducing the viscosity of magnesium oxide slurries by using 0.1 to 5.0 percent by weight of poly(acrylic acid) neutralised to a pH of from about 8.0 to about 12.0. US 4,375,526 teaches a method of reducing the viscosity and enhancing the stability of magnesium hydroxide slurries by using anionic polymers and copolymers. US 4,430,248 teaches a method of reducing the viscosity of magnesium hydroxide slurries by using cationic polymers and copolymers.

Those approaches are somewhat effective in reducing the viscosity of magnesium oxide and magnesium hydroxide slurries but are not generally satisfactory for maintaining the stability of the slurries over an extended period of time. It is an object of this invention to provide aqueous slurries of magnesium hydroxide having an improvement over prior art in that they are more stable and lower in viscosity at a given solids content at optimum additive dosages.

Accordingly in one aspect the present invention provides an aqueous slurry comprising from 25 to 75 percent by weight magnesium hydroxide; from 0.05 to 5 percent by weight, based on the weight of magnesium hydroxide, of at least one acidic polymer or salt thereof, hereafter described as an anionic polymer; and from 0.05 to 5 percent by weight, based on the weight of magnesium hydroxide, of at least one or more co-additives selected from boric acid and water soluble salts of boric acid.

The one or more anionic polymers which are suitable for the present invention are anionic polymers which are effective at dispersing aqueous slurries of magnesium hydroxide.

Anionic dispersants based on the following product types may be used for preparing the magnesium hydroxide slurry:

a) homopolymers and copolymers prepared from addition polymerisation
b) anionic condensation polymers
c) polymers derived from natural sources e.g. anionic polysaccharides from starches etc.

Useful group a) polymers prepared by addition polymerisation could be defined as polymers prepared using at least one ethylenically unsaturated monomer containing at least one acidic or acidic functional group. Homopolymers would, of course, be prepared from just one monomer containing an acidic or anionic functional group. Copolymers would be prepared from two or more monomer types, at least one of which contains an acidic or anionic functional group.

Homopolymers may be prepared using one acidic monomer such as acrylic acid, methacrylic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, itaconic anhydride, aconitic acid, crotonic acid, isocrotonic acid, mesaconic acid, vinyl acetic acid, hydroxyacrylic acid, undecylenic acid, allyl sulphonic acid, vinyl sulphonic acid, allyl phosphonic acid, vinyl phosphonic acid, 2-acrylamido-2-methyl propanesulphonic acid or 2-acrylamidoglycolic acid

Copolymers are prepared using at least one monomer from the above group and optionally one or more non-acidic monomers such as acrylamide, acrylic acid esters, acrolein, methacrylic acid esters, maleic acid esters, itaconic acid esters, fumaric acid esters, vinyl acetate, acrylonitrile, styrene, alpha-methyl styrene, N-vinyl pyrrolidone, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, dimethyl acrylamide, N-(hydroxymethyl)acrylamide or vinyl formamide.

Polymers useful in this invention will be in the form of the water-soluble free acid partial or full alkali metal or ammonium salt or mixed salt. Preferred anionic polymers are made from acrylic acid with one other monomer selected from acrylamide, dimethylacrylamide, methacrylic acid, maleic acid or AMPS (sodium salts) in a preferred composition of 100:0 to 50:50 (on a weight basis) and fully neutralised as the sodium salt. More preferred anionic polymers include polyacrylic acid fully neutralised as the sodium salt.

Selected monomers are polymerised in a suitable solvent The solvent may typically comprise:

i) water or
ii) organic solvent (eg. propan-2-ol) or
iii) organic solvent + water

A preferred solvent system is water or organic solvent and water, more preferred is propan-2-ol and water or just water.

A solvent containing an alcohol with an alpha-hydrogen (such as propan-2-ol) will function as a chain-transfer reagent in addition to the role as a solvent (see below).

The polymerisation uses a suitable initiator, which include materials that when subjected to heat or chemical inducement, break-down to provide a source of free-radicals. Generally suitable initiators are:.

i) Persulphates e.g. ammonium persulphate
ii) Peroxides e.g. hydrogen peroxide and organic peroxides
iii) Azo compounds e.g. 4,4-azobis(4-cyanavaleric acid)

Such oxidising initiators may be used in combination with a reducing agent (known as a "redox" process) to speed-up the formation of free-radicals. The initiators must be soluble in the reaction solvent.

Preferred initiators are persulfates, a more preferred initiator is ammonium persulfate.

The polymerisation may also incorporate a chain-transfer reagent to help control the molecular weight. Typical chain-transfer reagents are materials with so-called "labile hydrogen". These compounds are typically:

i) alcohols with an alpha-hydrogen (eg. propan-2-ol)
ii) compounds containing -SH group(s) i.e. mercaptans such as thioglycollic acid and 2-mercaptoethanol.
iii) hypophosphorous acid and alkali metal salts, e.g. sodium hypophosphite.

Monomers for polymerisation may be in the form of the free-acid or partial or full alkali metal or ammonium salt or mixtures of different salts.

Polymerisation reactions will normally be conducted at elevated temperature. Where an organic solvent is used, this may be removed after polymerisation by a distillation process. The resultant solution may then be fully neutralised to the full or partial alkali metal or ammonium salt, or mixed salt, with one or more suitable base(s) if necessary.

Fully neutralised polymers are preferred. A preferred base is an alkali metal hydroxide, sodium hydroxide being more preferred.

Group b) Anionic condensation polymers derived from the polymerisation of e.g. amino acids in the form of the free acid, full or partial alkali metal or ammonium salt or mixed salt, may be used. Such products include polyaspartic acid and salts.

Group c) polymers derived from natural products include polycarboxylic acids derived from polysaccharides from plant sources or produced by micro-organisms. As with other types of polyelectrolyte, the polysaccharide may be used in the form of the free acid, full or partial alkali metal or ammonium salt or mixed salt. An oxidation step is usually required as part of the process to produce acidic/anionic polysaccharides. Examples include Inulin derivatives, such as Dicarboxyinulin, and Alginic acid.

Useful polymers for the present invention generally have a weight average molecular weight (Mw) of from about 1,000 to about 500,000 as measured by aqueous gel permeation chromatography (gpc). Where "Mw" appears, it refers to the Mw as measured by aqueous gpc. Preferred dispersants have a weight average molecular weight of from 1,500 to 250,000, more preferred are dispersants having a weight average molecular weight of from 2,000 to 100,000.

The method of preparing anionic polymers is well known to those skilled in the art. The anionic addition polymers can be prepared by organic solvent, aqueous, or organic solvent/aqueous processes. The art of preparing anionic polymers has also employed various methods of controlling the molecular weight of polymers to produce polymers having Mw below about 50,000. These methods include the use of chain transfer agents, metal activators such as $Fe^{2+}$ in redox initiator systems, control of reaction time and monomer concentration, increased levels of initiators etc.

The co-additive may be selected from boric acid, having the formula $B(OH)_3$, and water soluble salts of boric acid. Preferred co-additives include alkali metal salts of boric acid. A co-additive which is more preferred is sodium tetraborate, otherwise known as Borax.

The slurries of this invention contain from 25 to 75 percent, preferably from 30 to 70 percent by weight of magnesium hydroxide and more preferably from 35 to 65 percent by weight of magnesium hydroxide.

The one or more anionic polymers are added to the magnesium hydroxide slurry to a level of from 0.05 to 5 percent by weight, and preferably from 0.10 to 4.0 percent by weight based on the weight of magnesium hydroxide, and more preferably from 0.2 to 3.0 percent by weight based on the weight of magnesium hydroxide.

The boric acid and/or water soluble salts of boric acid are added to the magnesium hydroxide slurry to a level of from 0.05 to 5.0 percent by weight, based on the weight of magnesium hydroxide, preferably from 0.10 to 4.0 percent by weight based on the weight of magnesium hydroxide and more preferably from 0.2 to 3.0 percent by weight based on the weight of magnesium hydroxide.

The addition of anionic polymer and boric acid and/or water soluble salts of boric acid to the magnesium hydroxide slurry may affect the viscosity of the slurry. It is desirable to add the boric acid and/or water soluble salts of boric acid to provide an initial slurry viscosity of between 50 and 2,500, preferably between 100 and 1,500, and more preferably between 150 and 1,000.

In another aspect the invention provides a method of preparing a stabilised aqueous slurry comprising from 25 to 75 percent by weight magnesium hydroxide; from 0.05 to 5 percent by weight, based on the weight of magnesium hydroxide, of at least one polymeric anionic dispersant or salt thereof; and from 0.05 to 5 percent by weight, based on the weight of magnesium hydroxide, of at least one or more co-additives selected from boric acid and water soluble salts of boric acid.

The method of preparing a stabilised aqueous slurry may comprise of adding the $Mg(OH)_2$ to an aqueous solution of anionic polymer and co-additive, and applying agitation during, after or both during and after the addition to form a homogenous slurry. Agitation is preferably applied during and after the addition.

The method of preparing a stabilised aqueous slurry may comprise of adding anionic polymer and co-additive directly to a $Mg(OH)_2$ slurry and applying agitation during, after or both during and after the addition to form a homogenous slurry. Agitation is preferably applied during and after the addition.

The method of preparing a stabilised aqueous slurry may comprise any method above whereby the anionic polymer and co-additive are added individually or together as a combined solution or mixture.

The method of preparing a stabilised aqueous slurry may comprise any method above whereby the anionic polymer and co-additive are added individually or combined, in two or more stages at any point during the preparation of the slurry.

The method of preparing a stabilised aqueous slurry may comprise adding a portion of the total amount of the magnesium hydroxide to a portion of the solution of anionic polymer and co-additive then adding the second portion of the solution of anionic polymer and co-additive followed by the remaining portion of the magnesium hydroxide.

A preferred method comprises adding the Magnesium Hydroxide to a solution of anionic polymer and co-additive, applying agitation both during and after the addition of Magnesium Hydroxide.

A further aspect of the invention is a composition comprising an aqueous slurry comprising from 25 to 75 percent by weight magnesium hydroxide; from 0.05 to 5 percent by weight, based on the weight of magnesium hydroxide, of at least one polymeric anionic dispersant or salt thereof having a relatively low polydispersity.

Low polydispersity anionic polymers according to the invention may have a molecular weight of from 2000 to 3999, and a polydispersity of less than or equal to 2.2, preferably a polydispersity of less than or equal to 2.0, more preferably a polydispersity of less than or equal to 1.9.

Other low polydispersity anionic polymers according to the invention may have a molecular weight of from 4000 to 5999, and a polydispersity of less than or equal to 2.3, preferably a polydispersity of less than or equal to 2.1, more preferably a polydispersity of less than or equal to 2.0.

Other low polydispersity anionic polymers according to the invention may have a molecular weight of from 6000 to 7999, and a polydispersity of less than or equal to 2.4, preferably a polydispersity of less than or equal to 2.2, more preferably a polydispersity of less than or equal to 2.1.

Other low polydispersity anionic polymers according to the invention may have a molecular weight of from 8000 to 10000, and a polydispersity of less than or equal to 2.5, preferably a polydispersity of less than or equal to 2.3, more preferably a polydispersity of less than or equal to 2.2.

The polydispersity factor is the weight average molecular weight of the polymer divided by the number average molecular weight of said polymer, and indicates the spread of molecular weights of polymeric molecules in the samples.

The one or more anionic polymers which are suitable for the present invention are anionic polymers which are effective at dispersing aqueous slurries of magnesium hydroxide.

Low polydispersity anionic polymers based on homopolymers and copolymers prepared from addition polymerisation may be used for preparing the magnesium hydroxide slurry:

Useful polymers prepared by addition polymerisation could be defined as polymers prepared using at least one ethylenically unsaturated monomer containing at least one acidic or anionic functional group. Homopolymers would, of course, be prepared from just one monomer containing an acidic or anionic functional group. Copolymers would be prepared from two or more monomer types, at least one of which contains an acidic or anionic functional group.

Homopolymers may be prepared using one acidic monomer such as acrylic acid, methacrylic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, itaconic anhydride, aconitic acid, crotonic acid, isocrotonic acid, mesaconic acid, vinyl acetic acid, hydroxyacrylic acid, undecylenic acid, allyl sulphonic acid, vinyl sulphonic acid, allyl phosphonic acid, vinyl phosphonic acid, 2-acrylamido-2-methyl propanesulphonic acid or 2-acrylamidoglycolic acid

Copolymers are prepared using at least one monomer from the above group and optionally one or more non-acidic monomers such as acrylamide, acrylic acid esters, acrolein, methacrylic acid esters, maleic acid esters, itaconic acid esters, fumaric acid esters, vinyl acetate, acrylonitrile, styrene, alpha-methyl styrene, N-vinyl pyrrolidone, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, dimethyl acrylamide, N-(hydroxymethyl)acrylamide or vinyl formamide.

Polymers useful in this invention will be in the form of the water-soluble free acid partial or full alkali metal or ammonium salt or mixed salt. Preferred anionic polymers are made from acrylic acid with one other monomer selected from acrylamide, dimethylacrylamide, methacrylic acid, maleic acid or AMPS (sodium salts) in a preferred composition of 100:0 to 50:50 (on a weight basis) and fully neutralised as the sodium salt. More preferred anionic polymers include polyacrylic acid fully neutralised as the sodium salt.

Selected monomers are polymerised in a suitable solvent The solvent may typically comprise:

i) water or
ii) organic solvent (eg. propan-2-ol) or
iii) organic solvent + water

A preferred solvent system is water or organic solvent and water, more preferred is propan-2-ol and water, or just water.

A solvent containing an alcohol with an alpha-hydrogen (such as propan-2-ol) will function as a chain-transfer reagent in addition to the role as a solvent (see below).

The polymerisation uses a suitable initiator, which include materials that when subjected to heat or chemical inducement, break-down to provide a source of free-radicals. Generally suitable initiators are:.

i) Persulphates e.g. ammonium persulphate
ii) Peroxides e.g. hydrogen peroxide and organic peroxides
iii) Azo compounds e.g. 4,4-azobis(4-cyanavaleric acid)

Such oxidising initiators may be used in combination with a reducing agent (known as a “redox” process) to speed-up the formation of free-radicals. The initiators must be soluble in the reaction solvent.

Preferred initiators are persulfates, a more preferred initiator is ammonium persulfate.

The polymerisation may also incorporate a chain-transfer reagent to help control the molecular weight. Typical chain-transfer reagents are materials with so-called "labile hydrogen". These compounds are typically:

i) alcohols with an alpha-hydrogen (eg. propan-2-ol)
ii) compounds containing -SH group(s) i.e. mercaptans such as thioglycollic acid and 2-mercaptoethanol.
iii) hypophosphorous acid and alkali metal salts, e.g. sodium hypophosphite.

Monomers for polymerisation may be in the form of the free-acid or partial or full alkali metal or ammonium salt or mixtures of different salts.

Polymerisation reactions will normally be conducted at elevated temperature. Where an organic solvent is used, this may be removed after polymerisation by a distillation process. The resultant solution may then be fully neutralised to the full or partial alkali metal or ammonium salt, or mixed salt, with one or more suitable base(s) if necessary.

Fully neutralised polymers are preferred. A preferred base is an alkali metal hydroxide, sodium hydroxide being more preferred.

These types of anionic polymers generally have a weight average molecular weight (Mw) of from about 2,000 to about 10,000 as measured by aqueous gel permeation chromatography (gpc).

Preferred anionic polymers have a weight average molecular weight (Mw) of from about 3,000 to about 9,000 as measured by aqueous gel permeation chromatography (gpc).

More preferred anionic polymers have a weight average molecular weight (Mw) of from about 4,000 to about 8,000 as measured by aqueous gel permeation chromatography (gpc).

These types of anionic polymers generally have a polydispersity of from 0.01 to 3.0, particularly from 1.5 to 3.0.

Preferred anionic polymers have a polydispersity from 1.7 to 2.6, more preferred dispersants have a polydispersity from 1.9 to 2.5.

The method of preparing anionic polymers is well known to those skilled in the art. The anionic polymers can be prepared by organic solvent, aqueous, or organic solvent/aqueous processes.

A process is known by which a water soluble acidic polymer can be fractionated into higher and lower molecular weight fractions and in which the molecular weight in each fraction can be freely selected simply by appropriate selection of the fractionation conditions. This process is therefore useful for preparing polymers of low polydispersity suitable for use in the preparation of Magnesium Hydroxide slurries according to one aspect of the invention.

In this process a solution is formed in a blend of water and a polar solvent of a water soluble polymer containing neutralised acid groups and the solution is separated into an aqueous phase containing a higher molecular weight fraction of the polymer and an organic phase containing a lower molecular weight fraction of the polymer, and in this process the polar solvent is a $C_1$ to $C_5$ alcohol, the acid groups are neutralised with cations selected from sodium, potassium, lithium and ammonium and the molar proportion of neutralised acid groups is 10 to 55% when the cation is selected from sodium and potassium, 10 to 70% when the cation is ammonium and 30 to 90% when the cation is lithium.

The precise split between the lower and higher molecular weight fractions can be selected by altering the process conditions and in particular the degree of neutralisation, and so a simple process exists by which an acidic, water soluble, polymer can be fractionated into preselected molecular weight fractions. Both fractions of polymer are commercially useful and so are recovered and used, the fraction in the organic phase being useful where lower molecular weights are desired and the fraction in the aqueous phase being useful where higher molecular weights are desired.

The polymer in each fraction will have lower polydispersity than the starting polymer. Each of the polymer solutions can be used in the form in which it is obtained by phase separation, for instance simply by mixing the solution into the water or other liquor to be treated, or the polymer can be recovered from the solution by evaporation, precipitation or other conventional recovery techniques. The polymer in each of the separated solutions is generally in a partially neutralised state and can be acidified or fully neutralised in conventional manner if desired.

The degree of neutralisation of the acid groups controls the fractionation. The results obtained in any particular process will depend upon, inter alia, the concentrations, the polymer type and the solvent, but there is a minimum degree of neutralisation below which substantially no fractionation occurs and the system may instead remain as a homogenous solution. When the cation is sodium, potassium or lithium the degree of neutralisation will normally be at least 10%, often at least 15% and preferably at least 25% whilst if the cation is lithium the degree of neutralisation will normally have to be at least about 30%, preferably at least 40% and generally at least 50%. If the degree of neutralisation is too high the size of the lower molecular weight fraction is unacceptably low. When the cation is sodium or potassium the degree of neutralisation will normally be below 55%, preferably below 50% and most preferably below 40%. When the cation is ammonium the degree of neutralisation will normally be below 70%, preferably below 60% and most preferably below 50%. When the cation is lithium the degree of neutralisation will normally be below 90%, and preferably below 70%.

In any particular process the size of, for instance, the higher molecular weight fraction can be increased (with consequential reduction in its average molecular weight and consequential reduction in the size and the average molecular weight of the lower molecular weight fraction) by increasing the amount of alkali and conversely the size of the low molecular weight fraction can be increased by reducing the amount of alkali.

The process conditions are preferably selected such that each fraction contains from 20 to 80%, and most preferably 30 to 70%, by weight of the starting polymer.

The partial neutralisation of the acidic polymer is normally achieved by adding a compound that will provide the chosen cation, the compound usually being a hydroxide, in the selected amount to the dissolved polymer. Mixtures of two or more of the four cations may be utilised, in which event the proportions will be selected such that they have the same effect as the amounts specified for the individual cations.

For any particular polymer, the degree of fractionation is dependent not only on the degree of neutralisation and the type of cation but also upon the concentration of the polymer and the choice and amount of the alcohol. The alcohol is preferably isopropanol but propanol and other alcohols, especially $C_2$ to $C_5$ alcohols, may be used. The proportion water:alcohol by weight is preferably from 1:0.2 to 1:5, most preferably 1:0.5 to 1:2 with best results generally being achieved, especially when the alcohol is isopropanol and the cation is sodium, when the proportion is about 1:1. The proportions should be selected such that, having regard to the degree and nature of neutralisation, each of the phases will have a polymer concentration of at least 15% by weight of the phase.

The amount of the polymer (measured as the acid polymer) is normally at least 5% by weight based on the weight of polymer, alcohol, and water (including water introduced with the alkali) and preferably is at least 10%. The concentration must not be so high that the system is so viscous that mixing and phase separation is significantly impeded and so is generally below 30%. Preferably the concentration is 15 to 25% by weight.

The phase separation may also be affected by the temperature at which the process is conducted. This may be between 15°C and 80°C, but preferably is between 30°C and 70°C.

The process may be conducted by combining the essential components of the solution in any convenient manner, for instance by adding aqueous alkali to the aqueous organic reaction product obtained by polymerisation of the monomer or monomers in aqueous organic solution. The process may be conducted continuously or batchwise. Depending upon the degree of neutralisation and type and strength of base, the concentration of the polymer, the amount of solvent and the temperature the phase separation may occur rapidly or slowly. For instance it may occur substantially instantaneously or it may be necessary to leave the system to stand for periods of, for instance, 5 minutes to 2 hours, typically 30 minutes to 1 hour. The separation may be conducted batchwise or continuously, with the mix being fed through a conventional separation column or separation reactor.

The two phases are kept separate, may be fully neutralised with the same or different alkali and organic solvent may be stripped from the organic phase by distillation.

The slurries of this invention contain from 25 to 75 percent, preferably from 30 to 70 percent by weight of magnesium hydroxide, and more preferably from 35 to 65 percent by weight of magnesium hydroxide.

The one or more anionic polymers are added to the magnesium hydroxide slurry to a level of from 0.05 to 5 percent by weight, and preferably from 0.1 to 4.0 percent by weight based on the weight of magnesium hydroxide, and more preferably from 0.2 to 3.0 percent by weight based on the weight of magnesium hydroxide.

The low polydispersity polymer composition may additionally comprise from 0.01 to 5 percent by weight, based on the weight of magnesium hydroxide, of one or more co-additives selected from boric acid and water soluble salts of boric acid, such as alkali metal borates, $C_2$ to $C_{10}$ carboxylic acids containing 2 or more acid groups including salts thereof, alkali metal hydroxides, alkali metal halides, alkali metal carbonates, alkali metal sulfates, alkali metal nitrates, alkali metal phosphates or alkali metal silicates.

Suitable $C_2$ to $C_{10}$ carboxylic acid salts include alkali metal oxalates, alkali metal malonates, alkali metal succinates, alkali metal glutarates, alkali metal adipates, alkali metal fumarates, alkali metal maleates, alkali metal phthalates.

Preferred co-additives are one or more selected from alkali metal carbonates, boric acid or borates, more preferred are sodium carbonate, sodium tetraborate or boric acid.

The one or more co-additives are added to the magnesium hydroxide slurry to a level of from 0.01 to 5.0 percent by weight, based on the weight of magnesium hydroxide, more preferably 0.01 to 4.0 percent by weight, based on the weight of magnesium hydroxide, most preferably 0.01 to 3.0 percent by weight, based on the weight of magnesium hydroxide.

The addition of low polydispersity anionic polymer and optionally one or more co-additives to the magnesium hydroxide slurry may affect the viscosity of the slurry. It is desirable to add the co-additives to provide an initial slurry viscosity of between 50 and 2,500, preferably between 100 and 1,500, and more preferably between 150 and 1,000.

In another aspect the invention provides a method of preparing an aqueous slurry comprising from 25 to 80 percent by weight magnesium hydroxide; from 0.05 to 5 percent by weight, based on the weight of magnesium hydroxide, of at least one polymeric anionic dispersant or salt thereof having a low polydispersity, and optionally 0.01 to 5.0 percent by weight, based on the weight of magnesium hydroxide, of one or more co-additives selected from boric acid and water soluble salts of boric acid, such as alkali metal borates, $C_2$ to $C_{10}$ carboxylic acids containing 2 or more acid groups including salts thereof, alkali metal hydroxides, alkali metal halides, alkali metal carbonates, alkali metal sulfates, alkali metal nitrates, alkali metal phosphates or alkali metal silicates.

The method of preparing a stabilised aqueous slurry may comprise of adding the $Mg(OH)_2$ to an aqueous solution of anionic polymer and/or co-additive, and applying agitation during, after or both during and after the addition to form a homogenous slurry. Agitation is preferably applied during and after the addition.

The method of preparing a stabilised aqueous slurry may comprise of adding anionic polymer and/or co-additive directly to a $Mg(OH)_2$ slurry followed and applying agitation during, after or both during and after the addition to form a homogenous slurry. Agitation is preferably applied during and after the addition.

The method of preparing a stabilised aqueous slurry may comprise any method above whereby the anionic polymer and co-additive (where required) are added together as a combined solution or mixture.

The method of preparing a stabilised aqueous slurry may comprise any method above whereby the anionic polymer and co-additive (where required) are added individually or combined, in two or more stages at any point during the preparation of the slurry.

All the aqueous slurries of the present invention have a relatively low viscosity and a relatively improved stability over an extended period of time.

The slurries may be utilised in various applications including:

(a) use in relation to treatment of industrial effluent or waste water;
(b) use as a commercial alkali for pH control;
(c) flue gas desulphurisation;
(d) use of adsorptive properties of magnesium hydroxide to remove inorganic or organic contaminants; and
(e) treatment of boiler and cooling water to reduce levels of impurities

The following examples further illustrate the present invention:

## Example 1

Preparation of "Polymer A"

Acrylic acid monomer was converted to polyacrylic acid in a polymerisation reaction in a water/propan-2-ol solvent mixture using ammonium persulphate as thermal initiator. After polymerisation the propan-2-ol was removed by passing the solution through a distillation column. The resulting aqueous polyacrylic acid solution was then fully neutralised with NaOH and the polymer concentration adjusted to approximately 40% to give the final product.

## Example 2

Preparation of "Polymer B"

Acrylic acid monomer was converted to polyacrylic acid in a polymerisation reaction in a water/propan-2-ol solvent mixture using ammonium persulphate as thermal initiator. After polymerisation the polymer solution was partially neutralised with sodium hydroxide and the solution allowed to separate into two layers, a propan-2-ol rich upper layer and a water rich lower layer. The upper layer contained polymer comprising mainly lower molecular weight material from the original polymer and the lower layer contained polymer comprising mainly higher molecular weight material from the original polymer. The layers were separated and the lower layer passed through a distillation column to remove propan-2-ol. The resulting aqueous polyacrylic acid solution was then fully neutralised with NaOH and the polymer concentration adjusted to approximately 40% to give the final product.

## Example 3

The molecular weight characteristics of the Polymers A and B were determined by Gel Permeation Chromatography (GPC). Data obtained from GPC techniques are not absolute but dependent on the "system" used i.e. the particular type of equipment, the operating conditions and in particular the standards used to calibrate the GPC system. Data obtained from different systems are not necessarily comparable. The molecular weight data in this example were obtained as follows. The GPC system used included a set of GPC columns comprising of a TSK PWXL guard column, a G4000 and G3000 column from Toso Haas Corporation, a differential refractive index detector, pump and column oven. The system included a computer with software for data collection, construction of calibration curves and determination of molecular weight data. The operating conditions used for calibration and sample analysis involved the use of a mobile phase of 0.2M sodium chloride buffered with 0.005M dipotassium hydrogen phosphate (prepared in purified water), a flow-rate of 0.5 ml/min and column temperature of 40°C. The system was calibrated with a range of at least 6 polyacrylic acid (sodium salt) standards of molecular weight within the range 1,000 to 800,000. From the analysis of standards, the computer software constructed a calibration curve of retention time versus the logarithm of molecular weight (third order polynomial fit). Samples to be analysed were diluted in mobile phase solution to an approximate concentration of 0.15% w/v. This solution was filtered through a 0.45 micron filter and then injected into the system for analysis. Data collection and determination of molecular weight data in the form of weight and number averages and polydispersity were handled by the computer software. Ethylene glycol was added to each sample to monitor and correct for minor changes in flow rate.

Molecular weight data obtained is shown in Table 1:

Table 1

| **Polymer** | **A** | **B** |
|---|---|---|
| weight average molecular weight (Mw) | 4960 | 5570 |
| number average molecular weight (Mn) | 2030 | 2850 |
| Polydispersity (Mw/Mn) | 2.44 | 1.95 |

Polydispersity indicates the spread of molecular weights of polymeric molecules in the samples. The samples differ in polydispersity due to differences in the methods of preparation.

## Example 4

A sample of Mg(OH)2 in the form of a paste was obtained. Samples of paste were taken for the subsequent preparation of suspensions (described below). The Mg(OH)2 content of each paste sample was determined using a dry weight test (drying 1 gram of slurry at 110°C for 1 hour) and were generally in the range 50 - 55% w/w. Using the paste samples aqueous suspensions at 45% w/w Mg(OH)2 content were prepared. An aqueous phase was prepared containing water and additives comprising anionic polymer (AP) and, where required, an inorganic co-additive eg. sodium tetraborate. The liquid was stirred to dissolve the additives followed by the addition of Mg(OH)2 paste with agitation applied to produce a homogenous suspension. Agitation was applied during addition of Magnesium Hydroxide and after addition to a total mixing time of 30 minutes. The solids content of the suspension was then determined using a dry weight technique (drying 1 gram of suspension at 110°C for 1 hour).

The suspension was adjusted to a temperature of 25°C followed by the measurement of viscosity using a Brookfield RVT viscometer (spindle 3 at 50rpm).

The stability of the suspension was determined using the following technique. Glass bottles of approximately 250ml capacity with straight sides to just over 200ml were used for conducting stability tests on the Mg(OH)2 suspensions. Into a glass bottle was added approximately 200 ml of suspension of known solids content (Starting Solids). The weight of suspension added was recorded (Starting Weight). The bottle was capped and left undisturbed at room temperature for 7 days. When the storage time had elapsed the cap was removed from the bottle and the bottle inverted 180 ° directly over a pre-weighed beaker and the contents of the bottle allowed to drain for 2 minutes. During this draining period,.the bottle was moved gently in an arc without sudden jerks. The weight of fluid collected (Recovered Weight) was determined and the suspension was then homogenised by stirring with a spatula. The solids content was then determined (Recovered Solids) and a % Recovery calculated as follows:

% Recovery = (RW x RS)/(SW x SS) x 100.

RW = Recovered Weight SW = Starting Weight
RS = Recovered Solids SS = Starting Solids

The % recovery is a measure of stability, i.e. the higher the % recovery, the more stable the slurry.

The results are shown in table 2 below:

Table 2

**Results For Comparisons**

| Polymer | Polymer Dose | Co-Additive | Co-additive Dose (%) | Solids (%) | Viscosity (cP) | Recovery (%) |
|---|---|---|---|---|---|---|
| A | 0.5 | None | 0.0 | 45.5 | 1280 | 72.4 |
| A | 0.5 | $Na_2CO_3$ | 0.5 | 44.9 | 750 | 88.0 |
| A | 0.5 | $Na_2CO_3$ | 1.0 | 44.8 | 668 | 83.6 |
| A | 0.5 | $Na_2CO_3$ | 2.0 | 45.4 | 622 | 82.2 |

**Polymer and Sodium Tetraborate**

| Polymer | Polymer Dose | Co-Additive | Co-additive Dose (%) | Solids (%) | Viscosity (cP) | Recovery (%) |
|---|---|---|---|---|---|---|
| A | 0.5 | $Na_2B_4O_7$ | 0.5 | 45.1 | 712 | 85.1 |
| A | 0.5 | $Na_2B_4O_7$ | 1.0 | 45.1 | 588 | 89.8 |
| A | 0.5 | $Na_2B_4O_7$ | 2.0 | 45.2 | 468 | 92.5 |

**Low Polydispersity Polymer**

| Polymer | Polymer Dose | Co-Additive | Co-additive Dose (%) | Solids (%) | Viscosity (cP) | Recovery (%) |
|---|---|---|---|---|---|---|
| B | 0.5 | None | 0.0 | 45.0 | 792 | 89.5 |
| B | 0.5 | $Na_2B_4O_7$ | 0.5 | 45.0 | 556 | 90.2 |

Polymer and co-additive dosages are based on dry/anhydrous additive on Mg(OH)2 solids.

The % recovery values and viscosity measurements in table 2 demonstrate the improved properties of the present magnesium hydroxide slurries.

## Claims

1. Composition comprising an aqueous slurry comprising from 25 to 75 percent by weight magnesium hydroxide; from 0.05 to 5 percent by weight, based on the weight of magnesium hydroxide, of at least one acidic polymer or salt thereof; and from 0.05 to 5 percent by weight, based on the weight of magnesium hydroxide, of at least one co-additive selected from boric acid and water soluble salts of boric acid.

2. Composition according to claim 1, wherein the acidic polymer or salt thereof is a homopolymer or copolymer of one or more of Acrylic acid, Methacrylic acid, Maleic acid, Maleic anhydride, Fumaric acid, Itaconic acid, Itaconic anhydride, Aconitic acid, Crotonic acid, Isocrotonic acid, Mesaconic acid, Vinyl acetic acid, Hydroxyacrylic acid, Undecylenic acid, Allyl sulphonic acid, Vinyl sulphonic acid, Allyl phosphonic acid, Vinyl phosphonic acid, 2-acrylamido-2-methyl propanesulphonic acid, 2-acrylamidoglycolic acid, Acrylamide, Acrylic acid esters, Acrolein, Methacrylic acid esters, Maleic acid esters, Itaconic acid esters, Fumaric acid esters, Vinyl acetate, Acrylonitrile, Styrene, $\alpha$ Methyl styrene, N-Vinyl pyrrolidone, 2-Hydroxyethyl acrylate, 2-Hydroxyethyl methacrylate, Dimethyl acrylamide, N-(hydroxymethyl)acrylamide or Vinyl formamide.

3. Composition according to claim 1, wherein the acidic polymer or salt thereof is a condensation polymer derived from the polymerisation of amino acids in the form of the free acid, full or partial alkali metal or ammonium salt or mixed salt.

4. Composition according to claim 1, wherein the acidic polymer or salt thereof is a polycarboxylic acid derived from a polysaccharide.

5. Composition according to any of claims 1 to 4, wherein the acidic polymer or salt thereof has a weight average molecular weight of 1,000 to 500,000.

6. Composition according to any of claims 1 to 5, wherein the co-additive is an alkali metal salt of boric acid.

7. Method of preparing an aqueous slurry comprising from 25 to 75 percent by weight magnesium hydroxide; from 0.05 to 5 percent by weight, based on the weight of magnesium hydroxide, of at least one acidic polymer or salt thereof; and from 0.05 to 5 percent by weight, based on the weight of magnesium hydroxide, of at least one or more co-additives selected from boric acid and water soluble salts of boric acid.

8. Composition comprising an aqueous slurry comprising from 25 to 75 percent by weight magnesium hydroxide; from 0.05 to 5 percent by weight, based on the weight of magnesium hydroxide, of at least one acidic polymer or salt thereof selected from:

(a) an acidic polymer or salt thereof having a molecular weight of from 2000 to 3999 and a polydispersity of less than or equal to 2.0

(b) an acidic polymer or salt thereof having a molecular weight of from 4000 to 5999 and a polydispersity of less than or equal to 2.3

(c) an acidic polymer or salt thereof having a molecular weight of from 6000 to 7999 and a polydispersity of less than or equal to 2.4

(d) an acidic polymer or salt thereof having a molecular weight of from 8000 to 10000 and a polydispersity of less than or equal to 2.5.

9. Composition according to claim 8, wherein the acidic polymer or salt thereof is a homopolymer or copolymer of one or more of Acrylic acid, Methacrylic acid, Maleic acid, Maleic anhydride, Fumaric acid, Itaconic acid, Itaconic anhydride, Aconitic acid, Crotonic acid, Isocrotonic acid, Mesaconic acid, Vinyl acetic acid, Hydroxyacrylic acid, Undecylenic acid, Allyl sulphonic acid, Vinyl sulphonic acid, Allyl phosphonic acid, Vinyl phosphonic acid, 2-acrylamido-2-methyl propanesulphonic acid, 2-acrylamidoglycolic acid, Acrylamide, Acrylic acid esters, Acrolein, Methacrylic acid esters, Maleic acid esters, Itaconic acid esters, Fumaric acid esters, Vinyl acetate, Acrylonitrile, Styrene, $\alpha$ Methyl styrene, N-Vinyl pyrrolidone, 2-Hydroxyethyl acrylate, 2-Hydroxyethyl methacrylate, Dimethyl acrylamide, N-(hydroxymethyl)acrylamide or Vinyl formamide.

10. Composition according to any of claims 8 to 9, wherein the acidic polymer or salt thereof has a weight average molecular weight of 2,000 to 500,000.

11. Composition according to any of claims 8 to 10, which additionally comprises from 0.01 to 5 percent by weight, based on the weight of magnesium hydroxide, of at least one co-additive selected from the group consisting of boric acid and water soluble salts of boric acid, such as alkali metal borates, $C_2$ to $C_{10}$ carboxylic acids containing 2 or more acid groups including salts thereof, alkali metal hydroxides, alkali metal halides, alkali metal carbonates, alkali metal sulfates, alkali metal nitrates and alkali metal phosphates.

12. Method of preparing an aqueous slurry comprising from 25 to 75 percent by weight magnesium hydroxide; from 0.05 to 5 percent by weight, based on the weight of magnesium hydroxide, of at least one acidic polymer or salt thereof having a low polydispersity, and optionally one or more co-additives selected from the group consisting of boric acid and water soluble salts of boric acid, such as alkali metal borates, $C_2$ to $C_{10}$ carboxylic acids containing 2 or more acid groups including salts thereof, alkali metal hydroxides, alkali metal halides, alkali metal carbonates, alkali metal sulfates, alkali metal nitrates, alkali metal phosphates and alkali metal silicates.

# INTERNATIONAL SEARCH REPORT

Inte l Application No
PCT/EP 01/06353

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C01F5/14 C08K3/22 C02F1/00 C02F1/52 B01D53/50
C02F1/66 G05D21/02

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)
IPC 7 C01F C08K C02F B01D G05D

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

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

EPO-Internal, WPI Data, PAJ, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | EP 0 592 169 A (ROHM & HAAS)<br>13 April 1994 (1994-04-13)<br>page 1, line 22 -page 2, line 21 | 13 |
| A | page 2, line 44 -page 3, line 40<br>--- | 1-12 |
| X | US 4 375 526 A (ZUPANOVICH JOHN D ET AL)<br>1 March 1983 (1983-03-01)<br>cited in the application<br>the whole document<br>--- | 13 |
| X | DATABASE WPI<br>Section Ch, Week 198132<br>Derwent Publications Ltd., London, GB;<br>Class A97, AN 1981-57549D<br>XP002179544<br>& JP 56 073623 A (NIPPON SHOKUBAI KAGAKU KOGYO CO LTD), 18 June 1981 (1981-06-18)<br>abstract<br>---<br>-/-- | 13 |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

| | |
|---|---|
| Date of the actual completion of the international search<br>9 October 2001 | Date of mailing of the international search report<br>19/10/2001 |
| Name and mailing address of the ISA<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL – 2280 HV Rijswijk<br>Tel. (+31–70) 340–2040, Tx. 31 651 epo nl,<br>Fax: (+31–70) 340–3016 | Authorized officer<br>Raming, T |

# INTERNATIONAL SEARCH REPORT

Int  l Application No
PCT/EP 01/06353

**C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category ° | Citation of document, with indication,where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | US 5 281 270 A (TOTTEN PATTY L ET AL)<br>25 January 1994 (1994-01-25)<br>example 1<br>----- | 1-7 |

# INTERNATIONAL SEARCH REPORT

rmation on patent family members

Inte nal Application No
PCT/EP 01/06353

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| EP 0592169 A | 13-04-1994 | US 5877247 A | 02-03-1999 |
| | | AT 193696 T | 15-06-2000 |
| | | AU 672625 B2 | 10-10-1996 |
| | | AU 4878593 A | 21-04-1994 |
| | | CA 2107410 A1 | 06-04-1994 |
| | | CN 1086233 A ,B | 04-05-1994 |
| | | DE 69328810 D1 | 13-07-2000 |
| | | DE 69328810 T2 | 16-11-2000 |
| | | EP 0592169 A1 | 13-04-1994 |
| | | JP 6115930 A | 26-04-1994 |
| | | NZ 248855 A | 26-05-1995 |
| US 4375526 A | 01-03-1983 | NONE | |
| JP 56073623 A | 18-06-1981 | JP 1388871 C | 14-07-1987 |
| | | JP 61056168 B | 01-12-1986 |
| US 5281270 A | 25-01-1994 | US 5213161 A | 25-05-1993 |
| | | US 5220960 A | 22-06-1993 |
| | | CA 2089854 A1 | 20-08-1993 |
| | | EP 0558232 A1 | 01-09-1993 |
| | | NO 930509 A | 20-08-1993 |
| | | US 5298069 A | 29-03-1994 |
| | | CA 2094897 A1 | 01-02-1994 |
| | | EP 0582367 A1 | 09-02-1994 |
| | | NO 931443 A | 01-02-1994 |