⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 253 676**
A2

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: **87306355.6**

㉒ Date of filing: **17.07.87**

(51) Int. Cl.^{4}: **C 11 D 1/75**
C 11 D 1/40, C 11 D 1/58,
C 11 D 17/00, C 11 D 7/08

㉚ Priority: **17.07.86 AU 6989/86**

㊸ Date of publication of application:
20.01.88 Bulletin 88/03

㉞ Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

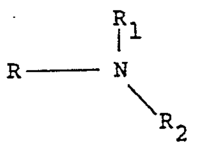
㉑ Applicant: **R & C PRODUCTS PTY. LIMITED**
845 Pacific Highway
Chatswood New South Wales (AU)

㉒ Inventor: **Silvester, Raymond Neville**
8 Millar Crescent
Dural New South Wales (AU)

㉔ Representative: **Allard, Susan Joyce et al**
BOULT, WADE & TENNANT 27 Furnival Street
London EC4A 1PQ (GB)

(54) Amine-acid thickening compositions.

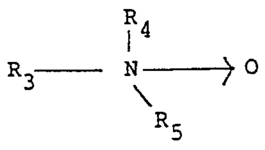
(57) A thickened aqueous composition comprising at least one compound acid or acidic salt, a thickening agent which is at least one of the compounds selected from the group consisting of compounds of the formula:



$$R-\overset{\displaystyle R_1}{\overset{|}{N}}\diagdown R_2$$

(I)

or



$$R_3-\overset{\displaystyle R_4}{\overset{|}{N}}\rightarrow O \quad \diagdown R_5$$

(II)

wherein R, R_1 R_2, R_3, R_4 and R_5 are specified substituent groups, and optionally a strong ionic salt, the thickening agent and the acid or acidic salt being together substantially water soluble, and wherein
the thickened aqueous composition has a viscosity of not less than 30 centipoise at 25°C when measured with a Brookfield RVT viscometer at 50 rpm using a No. 1 spindle.

EP 0 253 676 A2

Bundesdruckerei Berlin

Description

AMINE-ACID THICKENING COMPOSITIONS

The present invention relates to aqueous compositions of acids or acidic salts and more particularly to novel compositions of these acids or acidic salts which include a thickening agent.

As used in the specification acidic salts refer to those compounds which in an aqueous solution liberate protons.

Aqueous solutions of acids and acidic salts have long been used in compositions for cleaning. Such compositions include toilet bowl cleaners, metal cleaners and brighteners, rust stain removers, denture cleansers, metal descalers, general hard surface cleaners and disinfectants.

It has been found that a desirable property of many of the aforementioned compositions is that they have sufficient viscosity so as to allow the composition to be effectively applied to surfaces, for example, by brushing, or to allow the composition to remain in contact with the surface for a sufficient time to act. The latter function has particular relevance to the cleaning of angular surfaces such as those found in toilet bowls where prolonged contact between the composition and the bowl is required for effective cleaning.

There are many such compositions known in the art that have the requisite viscosity characteristics. Most of such compositions achieve their viscosity through the use of one or more of the following thickening agents:-

(a) cellulose derivatives exemplified by sodium carboxymethyl cellulose, hydroxyethyl cellulose, methyl hydroxyethyl cellulose, methyl cellulose, hydroxypropylmethyl cellulose, hydroxybutylmethyl cellulose;
(b) gums such as xanthan gum,
(c) acrylic acid polymers such as Carbopol (Registered Trade Mark of B.F. Goodrich)
(d) nonionic surfactants such as nonyl phenol ethoxylates;
(e) poly(ethylene oxide) resins such as Polyox (Registered Trade Mark of Union Carbide);
(f) anionic surfactants such as alkylbenzene sulfonates and alkyl ether sulfates; and
(g) sodium silicates such as sodium metasilicate.

Most of these thickeners whilst able to effectively increase the viscosity of aqueous acid or acidic salt compositions do have some disadvantages in use.

The cellulose derivatives and gums tend to hydrolyse on storage which results in a reduction in viscosity of the composition. They are also generally difficult to dissolve, in some cases intensive mixing being required in order to bring them into solution.

Acrylic acid polymers are generally only useful in solutions which have a pH near neutral and above. They also tend to hydrolyse on storage and to achieve viscosity, need to be neutralized with a fairly strong alkali.

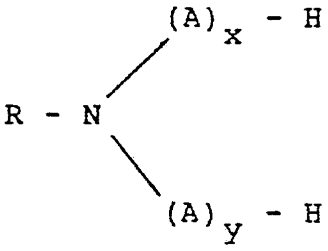
Nonionic surfactants have the disadvantage that usually high levels of about 5-10% are required to achieve satisfactory viscosity, thus making them expensive to use.

The poly(ethyleneoxide) water soluble resins also require generally high levels to achieve desirable composition viscosity and additionally, in some acid solutions show significant instability.

Sodium silicates are able to produce aqueous acid or acidic salt gel compositions. However, in developing viscosity in a composition, it has been noted that the viscosity generally develops over a long period of time, for example, as much as twelve hours. In commercial manufacturing processes, this is often inconvenient. It is also to be noted that on storage, such gels tend to break down into small pieces which in many instances is undesirable.

Other thickening agents and compositions disclosed in the art which relate to an aqueous acid and/or acidic salt compositions include:-

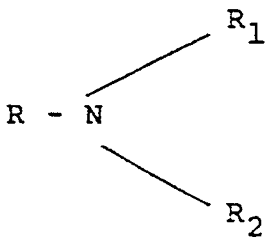
GB1,443,244 (Reckitt & Colman Products Limited) which discloses a thickening agent of the formula:



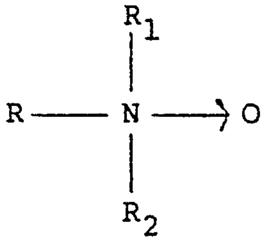
for thickening aqueous compositions of mineral acids and acid salts of strong inorganic acids.

GB2,071,688 (Jeyes Limited) which discloses as a thickening agent a mixture of: (a) a substantially acid insoluble compound of the formula (I) or (II); and

(b) a substantially acid soluble cationic or nonionic surfactant, for thickening aqueous compositions of inorganic acids or acid salts of strong inorganic acids.



(I)



$$R-\overset{R_1}{\underset{R_2}{N}}\rightarrow O$$

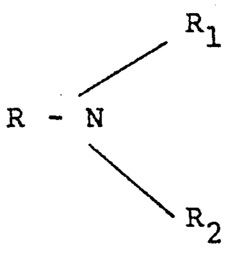
(II)

US 3,786,091 (Bolsing) which discloses a phosphoric acid containing base paste, produced by preparing a finely divided aqueous dispersion of a long chain amine, preheating this dispersion, introducing preheated phosphoric acid thereinto with vigorous agitation, at elevated temperature until neutral and then stirring the resulting mixture until cold.

US 4,021,377 (Borchert et al) which discloses a citric acid-amine reaction product obtained by mixing citric acid and water soluble or water dispersible amine in water until all the citric acid is dissolved. Generally the reaction is accompanied by a rise in temperature to about 40° C over an hour. The resultant solution containing amine salts of citric acid and citric acid amides is viscous. It is to be noted that the concentrations of citric acid and the amines exemplified are particularly high, the amines exemplified being in the range 12-45% W/W and the citric acid, 19.2% W/W. Further, only the amines monoethanolamine, diethanolamine and triethanolamine are exemplified.

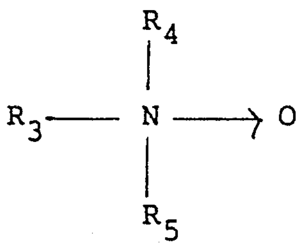
The present inventor has recognized the difficulties of the prior art thickening agents for such aqueous acid or acidic salt compositions. Accordingly, the present invention seeks to provide alternative compositions to those of the prior art.

The present invention consists in a thickened aqueous composition comprising at least one compound selected from the group consisting of acids and acidic salts, a thickening agent which is at least one of the compounds selected from the group consisting of compounds of the formula:



(I)

or



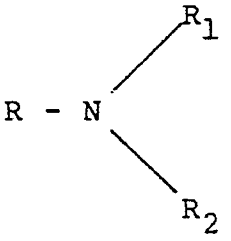
$$R_3-\overset{R_4}{\underset{R_5}{N}}\rightarrow O$$

(II)

in which R, R_3 is a substituted or unsubstituted alkyl, aryl, alkaryl, aralkyl or alkenyl group, R_1 is hydrogen, a substituted or unsubstituted alkyl, aryl, alkaryl, aralkyl or alkenyl group, R_2 is hydrogen, a substituted or unsubstituted alkyl, aryl, alkaryl, aralkyl or alkenyl group, R_4 is a substituted or unsubstituted alkyl, aryl, alkaryl, aralkyl or alkenyl group, R_5 is a substituted or unsubstituted alkyl, aryl, alkaryl, aralkyl or alkenyl group, or R_1 and R_2 or R_4 and R_5 when taken together comprise a substituted or unsubstituted heterocyclic ring, provided that if either R, R_1 or R_2 is an alkyl or alkenyl group derived from a fatty acid obtained from a natural oil or fat or an equivalent synthetic fatty acid, or is an alkaryl group containing from 8 to 12 carbon atoms in the alkyl moiety, then the other substituents are not respectively of the formulae: $[A]_x - H$ and $[A]_y - H$ where A is either ethoxy or propoxy and x, y are independently 1, 2 or 3, and optionally a strong ionic salt, said thickening agent and the at least one compound selected from the group consisting of acids and acidic salts being together substantially water soluble, and wherein

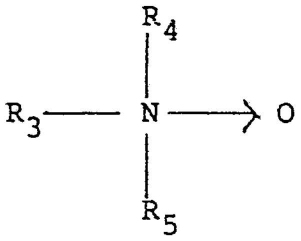
said thickened aqueous composition has a viscosity of not less than 30 centipoise at 25°C when measured with a Brookfield RVT viscometer at 50 rpm using a No. 1 spindle.

In a second aspect, the present invention consists in a method of forming a thickened aqueous solution, comprising dissolving in water (a) at least one compound selected from the group consisting of acids and acidic salts (b) a thickening agent which is at least one of the compounds selected from the group consisting of compounds of the formula:



(I)

or



(II)

in which R, R_3 is a substituted or an unsubstituted alkyl, aryl, alkaryl, aralkyl or alkenyl group, R_1 is hydrogen, a substituted or unsubstituted alkyl, aryl, alkaryl, aralkyl or alkenyl group, R_2 is hydrogen, a substituted or unsubstituted alkyl, aryl, alkaryl, aralkyl or alkenyl group, R_4 is a substituted or unsubstituted alkyl, aryl, alkaryl, aralkyl or alkenyl group, R_5 is a substituted or unsubstituted alkyl, aryl, alkaryl, aralkyl or alkenyl group, or R_1 and R_2, or R_4 and R_5 when taken together comprise a substituted or unsubstituted heterocyclic ring, provided that if either R, R_1 or R_2 is an alkyl or alkenyl group derived from a fatty acid obtained from a natural oil or fat or an equivalent synthetic fatty acid, or is an alkaryl group containing from 8 to 12 carbon atoms in the alkyl moiety, then the other substituted are not respectively of the formulae:

$[A]_X$-H and $[A]_Y$-H

where A is either ethoxy or propoxy and X, Y are independently 1, 2 or 3, and optionally (c) a strong ionic salt, said thickening agent and the at least one compound selected from the group consisting of acids and acidic salts being together substantially water soluble, in amounts sufficient to produce a viscosity of not less than 30 centipoise at 25°C when measured with a Brookfield RVT viscometer at 50 rpm using a No. 1 spindle.

In the context of this specification, substantially water soluble means that a thickening agent and an acid or acidic salt selected in accordance with the invention, will together either be soluble in water at 25°C or at most will form a hazy soluble that does not separate into two phases during normal storage.

It will be appreciated that the compositions of the present invention may be readily distinguished over those disclosed in the aforementioned patent application GB2071688 (Jeyes Limited) in that the compositions claimed therein are directed towards substantially acid insoluble amines or amine oxides, which require a substantially acid soluble cationic or nonionic surfactant to achieve thickening.

By contrast the present invention is limited to either amines or amine oxides which together with the selected acid or acidic salt are substantially water soluble, without a cationic or nonionic surfactant being required in the case of the amines to achieve solution and thickening, and in the case of the amine oxides, without the use of a cationic, nonionic or anionic surfactant, particulary an alkyl sulphate to achieve solution and thickening. It is also to be noted that in GB2071688 it is stated that neither of the amine, amine oxide, cationic surfactant or nonionic surfactant alone with an aqueous solution of an inorganic acid or acid salt will cause thickening.

It will also be appreciated that the aforementioned US 4,021,377 (Borchert et al) does not disclose, nor does it suggest that thickening will occur in compositions envisaged by the present invention without recourse to heating the amine with citric acid to form various reaction products. The present inventor believes that the disclosure in this US patent that the reaction products of citric acid and an amine are viscous in solution was merely an observation by the inventors, and perhaps not unexpected in view of the high concentration of reactants employed. In fact, there is no disclosure in this US patent that the inventors are aware that levels of amines as low as those preferred and exemplified in the present invention will form thickened compositions with acid or acidic salt solutions. The real thrust of this patent is a method of producing a concentrated solution of desired reaction products which happen in this high concentration to be viscous.

In order to demonstrate this, the present inventor produced aqueous solutions containing 5% w/w citric acid anhydrous and 2% w/w mono-, di- or tri-ethanolamine. No thickening was noted in any of these solutions.

Similarly, in US 3,786,091 (Bolsing), it is taught that it is necessary to obtain the reaction products between the selected amine and phosphoric acid by heating them together to produce a paste.

Thus, Bolsing in the simplest embodiment of his invention disperses the selected amine in water, heats the dispersion to between 40° C and 100° C and then adds to it at least a neutralising amount of phosphoric acid, preheated to between 40° C and 120° C. Stirring is continued until the temperature falls to between 5° C and 25° C and the resultant composition is a paste consisting of the reaction products between phosphoric acid and selected amine. Bolsing also discloses that other acids such as sulphuric, hydrochloric, tartaric, oxalic, hydrofluoric and nitric may be used as an additive to a base paste of his invention. He further discloses that other amines may also be used as additives.

The present invention may be distinguished over Bolsing when it is considered that the amines of the Bolsing invention must be derivatives of substituted or unsubstituted hydrocarbons having 8-24 carbon atoms, the selected amine must be reacted by heating with phosphoric acid to achieve viscosity and there is no hint or suggestion that acids other than phosphoric acid are operative. Additionally, with respect to acidic salts, it is noted that Bolsing refers to ammonium chloride as an auxilliary.

In contrast, the present invention teaches that thickening can be achieved with a range of acids and acidic salts, no heating is required to obtain thickening and the present inventor believes that amines additional to those of Bolsing are operative.

It is preferred that in the above formulae I or II, either of the groups R or R_3 contains at least six carbon atoms. More preferably, either of the groups R or R_3 contains from 8 to 24 carbon atoms. Most preferably either of the groups R or R_3 contains from 8 to 24 carbon atoms in an unsubstituted alkyl or alkenyl group.

Preferably, the groups R_1 and R_2 are independently a hydrogen atom or a lower unsubstituted alkyl group, where lower refers to groups containing 1 to 4 carbon atoms or a substituted alkyl group. More preferably the groups R_1 and R_2 are independently a hydrogen atom or a lower unsubstituted alkyl group. Most preferably, the groups R_1 and R_2 are independently a hydrogen atom or a methyl group.

Preferably, the groups R_4 and R_5 are independently a lower unsubstituted alkyl group, where lower refers to groups containing 1 to 4 carbon atoms or a substituted alkyl group. More preferably, the groups R_4 and R_5 are independently a lower substituted or unsubstituted alkyl group. Most preferably the groups R_4 and R_5 are independently a methyl, or hydroxyethyl, or hydroxy propyl group.

Preferred thickening agents of the present invention that are primary amines include Farmin O (Farmin is a registered trade mark of Kao Soap Co.) or Genamin OL-100D (Genamin is a registered trade mark of Hoechst), both of which are mainly oleylamine and Farmin T or Genamin TA100D, both of which are tallow fatty amine distilled. These thickening agents are able to thicken organic acids including formic, acetic, DL lactic, adipic, glycollic, malonic, succinic, pentetic, ascorbic, chloroacetic, citric and propionic acids. In some cases a small addition of a strong ionic salt such as sodium chloride is required to achieve adequate composition viscosity in the preferred concentration range of thickening agent. Naturally, increasing the concentration of thickening agent will increase viscosity in many cases. However, because of the relatively low cost of such salts, it is preferred to use a mixture of thickening agent and strong ionic salt to achieve the desired viscosity. However, it must also be considered that the addition of extra thickening agent may increase the pH and thereby decrease the efficiency of a composition.

Preferred thickening agents of the present invention that are tertiary amines include Genamin SO302D (dimethyl soya bean oil fatty amine distilled) and Genamin TA302D (dimethyl tallow fatty amine distilled). These amines are able to thicken organic acids including citric acid, L tartaric acid, formic acid, DL malic acid, acetic acid, DL lactic acid, adipic acid, maleic acid, ethylenediaminetetraacetic acid, glycollic, malonic, succinic and propionic acid and inorganic acids including sulfamic acid, phosphoric acid, boric, hydrofluoric and sulphuric acid. Generally, for reasons outlined above, these amines require the addition of a strong ionic salt, such as sodium chloride in order to achieve adequate composition viscosity in the preferred concentration range of thickening agent.

Preferred thickening agents of the present invention that are tertiary amines able to thicken acidic salts include Genamin TA302D and Genamin SO302D. Genamin TA302D is able to thicken aqueous solutions of monosodium citrate, and potassium hydrogen tartrate with the addition of a strong ionic salt such as sodium chloride. Genamin SO302D is able to thicken aqueous solutions of aluminium sulphate, sodium hydrogen sulphate, sodium dihydrogen orthophosphate, disodium ethylenediaminetetraacetate and aluminium potassium sulphate with a small addition of a strong ionic salt such as sodium chloride required in some cases; the sodium chloride being required to achieve adequate composition viscosity as previously described.

Preferred thickening agents of the present invention that are primary amines able to thicken acidic salts include farmin O, genamin OL-100D, Farmin T and Genamin TA-100D. These amines are able to thicken aqueous solutions of aluminium acetate.

Other amines considered by the present inventor to be within the scope of this invention include:
Farmin DMON (Dimethyl oleylamine),
Kao-DBA (dimethyl benzylamine);
N-lauryl morpholine;
N-Coco morpholine;
N-cetylmorpholine; and
Onamin 1416 (N-alkyl C_{14}-C_{16} dimethylamine)
Genamin 14R302D (tetradecyl dimethylamine distilled);
Genamin 16R302D (hexadecyl dimethylamine distilled);

Genamin 14R100D tetradecylamine distilled);
Genamin 16R100D (hexadecylamine distilled);
The following amines obtainable from KenoGard-
Amine 2MOL (dimethyloleylamine)
Amine 28 (dioctylamine)
Amine 210 (didecylamine)
Amine M28 (methyldioctylamine) and
Amine M210 (methyldidecylamine).

It is to be noted that the abovementioned preferred amines are in fact mixtures of a number of amines with one amine being predominant. The present inventor believes that the predominant amine may function to solubilize the minor amines in compositions of the present invention.

For example, Farmin O is predominantly oleylamine having an approximate alkyl content of 6% C_{14}, 13% C_{16} and 81% C_{18}, whilst Genamin SO302D has an approximate average chain length distribution of 2% C_{14}, 15% C_{16} and 83% C_{18} and Genamin TA302D has an approximate average chain length distribution of 5% C_{14}, 30% C_{16} and 65% C_{18}.

Preferred thickening agents of the present invention that are amine oxides include Aromox T/12 (bis[2-hydroxyethyl]tallow amine oxide) and Ammonyx MCO (mixture of myristyl and cetyl dimethyl amine oxides). Aromox is a trade mark of Armour Hess and Ammonyx is a trade mark of Onyx Chemicals Co. Aromox T/12 is able to thicken citric, phosphoric and sulphuric acids.

An example of a composition containing Ammonyx MCO was prepared to contain:
Ammonyx MCO (30% active) 6.67%
Sulphuric acid 3.83% w/w
Sodium chloride 0.7% w/w
Water 88.8% w/w

It was observed that whilst the viscosity was not determined, it appeared to be thick and viscous. Futhermore, it is to be noted that whilst Ammonyx MCO water soluble, its viscosity is water thin, even in a 6.67% aqueous solution additionally containing solely 2% sodium chloride.

As in the case of the amines of the invention, the preferred amine oxides falling within the scope of this invention are mixtures of amine oxides. Thus, Aromox T/12 has an average chain length distribution of 1% C_{12}, 3% C_{14}, 27% C_{16}, 24% C_{18}, 1% C_{14} (unsat), 4% C_{16} (unsat) 39% C_{18} (unsat), 1% C_{18} (double unsat). Similarly, the amine oxides of the invention, may require a small addition of a strong ionic salt to achieve adequate composition viscosity, as previously described.

Other amine oxides considered by the present inventor to be within the scope of this invention include:
bis (2-hydroxy ethyl) soya bean oil amine oxide;
dimethyl tallow amine oxide;
dimethyl oleyl amine oxide;
dimethyl soya bean oil amine oxide;
bis (2-hydroxy ethyl) oleyl amine oxide.

Additionally, amines or amine oxides of the invention may be generally derived from natural or synthetic sources of tallow, soya bean oil, oleic acid, palmitic acid, myristic acid, linoleic acid, linolenic acid, ricinoleic acid or hexadecanoic acid.

Generally the acids to which the present invention is directed include inorganic acids such as sulphuric hydrofluoric, boric, sulphamic and phosphoric acids and the organic acids Formic, acetic, DL lactic, propionic, citric, DL malic, L tartaric, adipic, maleic and ethylenediaminetetraacetic acid, malonic, glycollic, succinic, ascorbic, pentetic and chloroacetic acids.

The acidic salts to which the present invention is directed include the acid salts of inorganic or organic acids such as monosodium citrate, sodium hydrogen sulphate, sodium dihydrogen orthophosphate, disodium ethylenediaminetetraacetate, aluminium acetate and potassium hydrogen tartrate, aluminium sulphate and aluminium potassium sulphate.

The concentration of acid or acidic salt may be varied over a wide range depending on the end use of the composition. In some cases, particularly where a strong acid such as hydrofluoric acid is used and a near neutral product is required, the concentration of acid or acidic salt may be as low as 0.01% w/w.

In other cases, the concentration of acid or acidic salt may be in excess of 90%.

Generally, the concentration of acid or acidic salt will lie in the range of from 0.1 to 30% w/w.

In use, generally the thickening agent will be present in a concentration in the composition of from 0.1 to 10% w/w. Preferably, the concentration in the composition will lie in the range of from 0.4 to 5.0% w/w.

In order to achieve a desired viscosity in the composition, the concentration of the thickening agent may be varied appropriately. However, in some cases, it has been found that it is not possible to achieve sufficient composition viscosity for some applications. In such cases, the addition of a salt which has high ionic strength has been found to enhance the viscosity of these compositions. In most cases however, the concentration of thickening agent and high ionic strength salt will be optimized in order to produce a cost effective composition of the desired viscosity. Generally, the ionic salts will be selected from alkali metal halides or sulphates and ammonium halides or sulphates. Suitable such salts include sodium chloride, sodium sulphate, potassium sulphate, potassium chloride, ammonium chloride and the like.

Alternatively, the present inventor believes that certain long chain quaternary ammonium compounds may achieve similar thickening to the aforementioned salts. An example is Arquad 16-50 which is hexadecyltrimethyl ammonium chloride or Arquad S-50 which is a mixture of octadecanyl and octadecadienyl trimethyl ammonium chloride. Arquad is a trade mark of Armour Hess Chemicals.

It has further been found that in some cases whilst the composition is thick, clear and stable at room temperature, in order to achieve a satisfactory upper and lower cloud point for a composition, it is necessary to add another ingredient such as salt with a strong ionic effect of the type mentioned above, a cationic, nonionic or amphoteric surfactant or a solvent miscible with the composition, for example ethanol, isopropanol butyl Icinol and the like (Icionol is a trade mark of ICI) and Dowanol DPM (dipropyleneglycol methylether. Dowanol is a trade mark of Dow Chemicals). Such an addition of salt, surfactant or solvent insures that a composition will remain stable under hot and cold weather conditions.

A variety of other ingredients may be added to compositions of the invention depending on their end use. Thus, germicides, surfactants including anionic, nonionic, cationic and amphoteric, sequestering agents, corrosion inhibitors, perfumes and colouring agents may be added.

A principal advantage of the present invention is that an aqueous acid or acidic salt solution may be readily and easily thickened. Generally the steps of obtaining such thickened compositions will be - (a) add an appropriate amount of acid or acidic salt to water and stir to dissolve, (b) add a thickening agent of the present invention to the solution and stir until dissolved and (c) added other ingredients if required, stirring to dissolve.

It will be appreciated that since the thickening agent of the present invention is defined to be soluble in the selected acidic salt or acid solution, and as it will generally be easily wet, the step (b) above will be relatively rapid unlike many of the prior art thickening agents, which whilst they may be soluble are frequently difficult to wet.

Other advantages of the thickening agents of the present invention are that they are relatively inexpensive and in use produce smooth, homogeneous immediate thickening. Furthermore, thickened compositions are stable with respect to viscosity. For example, the present inventor has found that a citric acid composition thickened with Farmin O had no substantial change in viscosity when stored at room temperature for 12 months.

A still further advantage is that the present inventor has found that the compositions of the invention have some surfactant and corrosion inhibition properties. The former finding means that water immiscible substances such as fragrances may be directly solubilized in a composition of the invention without requiring the addition of emulsifiers or auxilliary solvents, and in compositions in which the surface active properties are required, potentially less or no additional surfactant would be required.

The present inventor has also found that if only sufficient of an acid or an acidic salt is present to just dissolve a thickening agent of the present invention, then a composition of near neutral pH may be obtained. Thus, Farmin O may be used to thicken lactic acid at a pH of 6.5. The advantage of this finding is that it may be used in aqueous liquid cleaners in general.

The present inventor has further found that an acid or acidic salt which is usually considered to be water insoluble at room temperature may be brought into solution through the use of a thickening agent of the present invention, with thickening occurring. The viscosity may be increased through the use of a strong ionic salt such as sodium chloride. To prepare such compositions, the acid is dispersed in the water and the thickening agent added with mixing. It is observed that as the acid and thickener go into solution, the solution increases in viscosity.

Preferred compositions of this type include ethylenediaminetetraacetic acid with Genamin S0302D as the thickening agent, potassium hydrogen tartrate with Genamin TA302D as thickening agent and pentetic acid with Farmin O as thickening agent.

Hereinafter are a number of examples, 1 to 60, of the present invention, together with comparative examples 1A and 1B, in which the viscosity, in centipoise, of each was determined using a Brookfield RVT viscometer using a spindle and speed as appropriate at 25°C. Note that the thickening agent is asterixed in each case.

All of these examples (except Nos. 27, 46 and 51) were produced by bringing the acid or acidic salt into solution, adding the thickening agent and mixing until dissolved, and then adding the other ingredients with mixing until dissolved.

Examples 27, 46 and 51 were prepared by dispersing the acid or acid salt in water, adding the thickening agent and mixing until solution occurred, followed by sodium chloride (if required) until a satisfactory viscosity was achieved.

Note that all examples were prepared under normal laboratory conditions.

Example 1

	% w/w
Citric Acid Anhydrous	5.0
* Farmin 0	1.8
Water	93.2
Viscosity (Spindle No. 2, speed 20 rpm, at 25°C)	670 cps
pH	2.2

Comparative Example 1A

Water Viscosity	Spindle 1	Speed 20 rpm :	3.5 cps
		Speed 50 rpm :	6.5 cps
	Spindle 2	Speed 20 rpm :	0 cps
		Speed 50 rpm :	5.5 cps

Example 1B

Aqueous 5% w/w Citric Acid Anhydrous solution

Viscosity Spindle 2	Speed 20 rpm :	0 cps
	Speed 50 rpm :	5.5 cps

Example 2

	% w/w
Citric Acid Anhydrous	5.0
* Farmin 0	2.0
Vantoc CL (Benzalkonium Chloride BP 50% w/v - Vantoc is a trade mark of ICI)	2.2
Sodium Chloride	0.7
Perfume	0.2
Dye	0.005
Water	89.9
Viscosity (Spindle No. 1, speed 50 rpm, at 25°C)	54 cps
pH	2.3

Example 3

	% w/w
DL-Lactic Acid 88%	5.0
* Farmin 0	2.0
Sodium Chloride	0.3
Water	92.7
Viscosity (Spindle No. 2, speed 20 rpm, at 25°C)	820 cps
pH	2.9

Example 4

	% w/w
DL-Lactic Acid 88%	5.0
* Farmin 0	2.0
Vantoc CL (Benzalkonium Chloride BP 50% w/v - Vantoc is a trade mark of ICI)	0.4
Sodium Chloride	0.35
Perfume	0.2
Dye	0.005
Water	92.05
Viscosity (Spindle No. 2, speed 20 rpm, at 25°C)	530 cps
pH	2.9

Example 5

	% w/w
DL-Lactic Acid 88%	0.85
* Farmin 0	2.0
Sodium Chloride	0.1
Water	97.05
Viscosity (Spindle No. 2, speed 20 rpm, at 25°C)	740 cps
pH	6.5

Example 6

		% w/w
	Formic Acid 88%	4.1
*	Farmin 0	2.0
	Sodium Chloride	0.05
	Water	93.85
	Viscosity (Spindle No. 1, speed 50 rpm, at 25°C)	58 cps
	pH	2.5

Example 7

		% w/w
	Formic Acid 88%	4.1
*	Genamin TA100D	2.0
	Sodium Chloride	0.05
	Water	93.85
	Viscosity (Spindle No. 1, speed 50 rpm, at 25°C)	30 cps
	pH	2.45

Example 8

		% w/w
	Acetic Acid (Glacial)	4.7
*	Farmin 0	2.0
	Sodium Chloride	0.25
	Water	93.05
	Viscosity (Spindle No. 2, speed 50 rpm, at 25°C)	160 cps
	pH	3.6

Example 9

		% w/w
	Acetic Acid (Glacial)	4.7
*	Farmin 0	2.0
	Vantoc CL (Benzalkonium Chloride BP 50% w/v - Vantoc is a trade mark of ICI	0.4
	Sodium Chloride	0.35
	Perfume	0.2
	Dye	0.005
	Water	92.35
	Viscosity (Spindle No. 2, speed 50 rpm, at 25°C)	180 cps
	pH	3.6

Example 10

		% w/w
	Acetic Acid (Glacial)	4.7
*	Genamin TA100D	2.0
	Sodium Chloride	0.3
	Water	93.0
	Viscosity (Spindle No. 2, speed 20 rpm, at 25°C)	660 cps
	pH	3.6

Example 11

		% w/w
	Propionic Acid	5.8
*	Farmin 0	2.0
	Sodium Chloride	0.3
	Water	91.9
	Viscosity (Spindle No. 1, speed 50 rpm, at 25°C)	58 cps
	pH	3.7

Example 12

		% w/w
	Citric Acid Anhydrous	5.0
*	Genamin SO302D	2.0
	Sodium Chloride	2.0
	Perfume	0.2
	Water	90.8
	Viscosity (Spindle No. 2, speed 50 rpm, at 25°C)	220 cps
	pH	2.35

Example 13

		% w/w
	Citric Acid Anhydrous	5.0
*	Genamin TA302D	2.0
	Sodium Chloride	2.0
	Perfume	0.2
	Water	90.8
	Viscosity (Spindle No. 2, speed 50 rpm, at 25°C)	240 cps
	pH	2.35

Example 14

		% w/w
	L-Tartaric Acid	5.9
*	Genamin SO302D	2.0
	Sodium Chloride	1.4
	Perfume	0.2
	Dye	0.005
	Water	90.5
	Viscosity (Spindle No. 2, speed 20 rpm, at 25°C)	625 cps
	pH	2.15

Example 15

	% w/w
L-Tartaric Acid	5.9
* Genamin TA302D	2.0
Sodium Chloride	1.4
Perfume	0.2
Water	90.5
Viscosity (Spindle No. 2, speed 20 rpm, at 25^{o}C)	1065 cps
pH	2.1

Example 16

	% w/w
Formic Acid 88%	4.1
* Genamin SO302D	2.0
Sodium Chloride	1.3
Dye	0.005
Water	92.6
Viscosity (Spindle No. 2, speed 50 rpm, at 25^{o}C)	160 cps
pH	2.4

Example 17

	% w/w
Formic Acid 88%	4.1
* Genamin TA302D	2.0
Sodium Chloride	1.6
Water	92.3
Viscosity (Spindle No. 2, speed 20 rpm, at 25^{o}C)	500 cps
pH	2.5

Example 18

	% w/w
DL-Malic Acid	5.2
* Genamin SO302D	2.0
Sodium Chloride	1.6
Dye	0.005
Water	91.2
Viscosity (Spindle No. 1, speed 20 rpm, at 25°C)	97 cps
pH	2.45

Example 19

	% w/w
DL-Lactic Acid 88%	5.0
* Genamin 16R302D	2.0
Sodium Chloride	2.0
Perfume	0.2
Dye	0.005
Water	88.8
Viscosity (Spindle No. 1, speed 20 rpm, at 25°C)	100 cps
pH	2.75

Example 20

	% w/w
Sulphamic Acid	7.6
* Genamin SO302D	2.0
Sodium Chloride	1.1
Water	89.3
Viscosity (Spindle No. 1, speed 50 rpm, at 25°C)	77 cps
pH	0.8

Example 21

	% w/w
Sulphamic Acid	7.6
* Genamin TA302D	2.0
Sodium Chloride	1.7
Water	88.7
Viscosity (Spindle No. 2, speed 20 rpm, at 25°C)	390 cps
pH	0.9

Example 22

	% w/w
Phosphoric Acid 85%	5.9
* Genamin SO302D	2.0
Sodium Chloride	1.1
Water	91.0
Viscosity (Spindle No. 2, speed 50 rpm, at 25°C)	170 cps
pH	1.35

Example 23

	% w/w
Phosphoric Acid 85%	5.9
* Genamin TA302D	2.0
Sodium Chloride	1.5
Water	90.6
Viscosity (Spindle No. 2, speed 20 rpm, at 25°C)	395 cps
pH	1.35

Example 24

	% w/w
Sulphuric Acid conc.	3.83
* Genamin SO302D	2.0
Water	94.17
Viscosity (Spindle No. 2, speed 20 rpm, at 25°C)	890 cps
pH	0.85

Example 25

	% w/w
Sulphuric Acid conc.	3.83
* Genamin TA302D	2.0
Water	94.2
Viscosity (Spindle No. 2, speed 20 rpm, at 25°C)	375 cps
pH	0.9

Example 26

	% w/w
Monosodium Citrate	8.35
* Genamin TA302D	2.0
Sodium Chloride	2.0
Water	87.65
Viscosity (Spindle No. 2, speed 20 rpm, at 25°C)	430 cps
pH	3.75

Example 27

	% w/w
Ethylenediaminetetraacetic Acid	0.8
* Genamin SO302D	2.0
Sodium Chloride	1.7
Water	95.5
Viscosity (Spindle No. 2, speed 20 rpm, at 25°C)	730 cps
pH	5.65

Example 28

	% w/w
$Al_2 (SO_4)_3.16H_2O$	6.7
* Genamin SO302D	2.0
Sodium Chloride	0.3
Water	91.0
Viscosity (Spindle No. 2, speed 20 rpm, at 25°C)	390 cps
pH	3.65

Example 29

	% w/w
$AlK(SO_4)_2.12H_2O$	10.0
* Genamin SO302D	2.0
Sodium Chloride	0.1
Water	87.9
Viscosity (Spindle No. 2, speed 50 rpm, at 25°C)	240 cps
pH	3.75

Example 30

	% w/w
Sodium Hydrogen Sulphate	9.5
* Genamin SO302D	2.0
Water	88.5
Viscosity (Spindle No. 2, speed 20 rpm, at 25°C)	1500 cps
pH	0.9

Example 31

	% w/w
Sodium Dihydrogen Orthophosphate Dihydrate	12.0
* Genamin SO302D	2.0
Water	86.0
Viscosity (Spindle No. 2, speed 20 rpm, at 25°C)	585 cps
pH	5.2

Example 32

	% w/w
Adipic Acid	1.0
* Genamin SO302D	2.0
Sodium Chloride	2.0
Water	95.0
Viscosity (Spindle No. 2, speed 50 rpm, at 25°C)	255 cps
pH	4.55

Example 33

		% w/w
	Adipic Acid	1.4
*	Farmin O	2.0
	Water	96.6
	Viscosity (Spindle No. 2, speed 5 rpm, at 25°C)	4095 cps
	pH	3.95

Example 34

		% w/w
	Maleic Acid	1.0
*	Genamin SO302D	2.0
	Sodium Chloride	0.5
	Water	96.5
	Viscosity (Spindle No. 1, speed 20 rpm, at 25°C)	113 cps
	pH	2.6

Example 35

		% w/w
	Disodium Ethylenediaminetetraacetate	6.6
*	Genamin SO302D	2.0
	Sodium Chloride	1.7
	Water	89.7
	Viscosity (Spindle No. 2, speed 20 rpm, at 25°C)	785 cps
	pH	5.8

Example 36

	% w/w
DL-Lactic Acid 88%	8.0
* Genamin TA100D	2.0
Sodium Chloride	0.6
Water	89.4
Viscosity (Spindle No. 2, speed 20 rpm, at 25°C)	1255 cps
pH	2.7

Example 37

	% w/w
Formic Acid 88%	4.1
* Farmin O	2.0
Vantoc CL (Benzalkonium Chloride BP 50% w/v - Vantoc is a trade mark of ICI	0.4
Sodium Chloride	0.15
Perfume	0.2
Dye	0.005
Water	93.15
Viscosity (Spindle No. 1, speed 50 rpm, at 25°C)	89 cps
pH	2.5

Example 38

	% w/w
Formic Acid 88%	5.5
* Farmin O	2.0
Vantoc CL (Benzalkonium Chloride BP 50% w/v - Vantoc is a trade mark of ICI	0.4
Sodium Chloride	0.2
Perfume	0.2
Dye	0.005
Water	91.7
Viscosity (Spindle No. 2, speed 20 rpm, at 25°C)	450 cps
pH	2.05

Example 39

		% w/w
	Glycollic Acid 70%	8.5
*	Farmin O	2.0
	Sodium Chloride	0.2
	Water	89.3
	Viscosity (Spindle No. 2, speed 20 rpm, at 25°C)	660 cps
	pH	2.5

Example 40

		% w/w
	Glycollic Acid 70%	8.5
*	Genamin SO 302D	2.0
	Sodium Chloride	1.8
	Water	87.7
	Viscosity (Spindle No. 2, speed 50 rpm, at 25°C)	290 cps
	pH	2.3

Example 41

		% w/w
	Malonic Acid	4.0
*	Farmin O	2.0
	Water	94.0
	Viscosity (Spindle No.2, speed 50 rpm, at 25°C)	185 cps
	pH	2.0

Example 42

		% w/w
	Malonic Acid	4.0
*	Genamin SO 302D	2.0
	Sodium Chloride	1.6
	Water	92.4
	Viscosity (Spindle No. 1, speed 50 rpm, at 25°C)	69 cps
	pH	1.9

Example 43

		% w/w
	Succinic Acid	4.6
*	Farmin O	2.0
	Sodium Chloride	0.1
	Water	93.3
	Viscosity (Spindle No. 2, speed 50 rpm, at 25°C)	230 cps
	pH	3.1

Example 44

		% w/w
	Succinic Acid	4.6
*	Genamin SO 302D	2.0
	Sodium Chloride	2.4
	Water	91.0
	Viscosity (Spindle No. 1, speed 50 rpm, at 25°C)	105 cps
	pH	3.1

Example 45

		% w/w
	L(+)-Ascorbic Acid	13.75
*	Farmin O	2.0
	Sodium Chloride	0.5
	Water	83.75
	Viscosity (Spindle No. 2, speed 20 rpm, at 25°C)	705 cps
	pH	2.9

Example 46

		% w/w
	D.T.P.A.(Pentetic Acid)	1.3
*	Farmin O	2.0
	Water	96.7
	Viscosity (Spindle No. 2, speed 20 rpm, at 25°C)	1185 cps
	pH	3.2

Example 47

	% w/w
Chloroacetic Acid	8.6
* Farmin O	2.0
Water	89.4
Viscosity (Spindle No. 1, speed 50 rpm, at 25°C)	96 cps
pH	1.7

Example 48

	% w/w
Hydrofluoric Acid 50%	3.1
* Genamin SO 302D	2.0
Sodium Chloride	0.6
Water	94.3
Viscosity (Spindle No. 2, speed 50 rpm, at 25°C)	370 cps
pH	1.2

Example 49

	% w/w
Boric Acid	5.0
* Genamin SO 302D	2.0
Sodium Chloride	1.4
Water	91.6
Viscosity (Spindle No. 1, speed 20 rpm, at 25°C)	280 cps
pH	6.2

Example 50

	% w/w
Aluminium Acetate	5.3
* Farmin O	2.0
Water	92.7
Viscosity (Spindle No. 2, speed 20 rpm, at 25°C)	1055 cps
pH	5.2

Example 51

		% w/w
	Potassium Hydrogen Tartrate	1.1
*	Genamin TA 302D	2.0
	Sodium Chloride	0.7
	Water	96.2
	Viscosity (Spindle No. 1, speed 50 rpm, at 25°C)	78 cps
	pH	6.3

Example 52

		% w/w
	Phosphoric Acid 85%	5.9
*	Aromox T/12	4.0
	Sodium Chloride	1.0
	Water	89.1
	Viscosity (Spindle No. 2, speed 20 rpm, at 25°C)	395 cps
	pH	1.5

Example 53

		% w/w
	Sulphuric Acid conc.	8.0
*	Aromox T/12	4.0
	Water	88.0
	Viscosity (Spindle No. 2, speed 20 rpm, at 25°C)	380 cps
	pH	0.7

Example 54

		% w/w
	Citric Acid Anhydrous	5.0
*	Aromox T/12	4.0
	Sodium Chloride	2.0
	Water	89.0
	Viscosity (Spindle No. 1, speed 20 rpm, at 25°C)	160 cps
	pH	2.5

Example 55

	% w/w
Sulphuric Acid Conc.	3.83
* Ammonyx MCO (30% active)	6.67
Sodium Chloride	0.60
Water	88.9
Viscosity (Spindle No. 1, speed 20 rpm, at 25°C) pH	180 cps

Example 56

	% w/w
Sulphuric Acid conc.	3.83
* Genamin 14R302D	1.00
* Genamin 16R302D	1.00
Sodium Chloride	3.00
Water	91.17
Viscosity (Spindle No. 1, speed 20 rpm, at 25°C) pH	212 cps

Example 57

	% w/w
Sulphuric Acid conc.	7.7
* Genamin 16R302D	2.0
Water	90.3
Viscosity (Spindle No. 2, speed 20 rpm, at 25°C) pH	556 cps

Example 58

	% w/w
Hydrochloric acid 30% technical	9.5
* Genamin 14R302D	2.0
Sodium Chloride	3.0
Water	85.5

Viscosity (Spindle No. 1, speed 50 rpm, at 25°C) pH	105 cps

Example 59

	% w/w
Hydrochloric acid 30% technical	53.0
* Genamin TA302D	2.0
Water	45.0
Viscosity (Spindle No. 2, speed 50 rpm, at 25°C pH	380 cps

Example 60

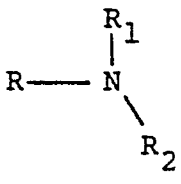
	% w/w
Hydrdochloric acid 30% technical	9.5
* Ammonyx MCO	6.67
Water	83.83
Viscosity reasonably thick at 25°C pH	

It is to be noted that the viscosity of Example 1, when compared with the viscosity of water (1A) and 5% w/w citric acid (1B), is substantially greater. A comparison with an aqueous solution of the thickening agent in this case was not possible as the thickening agent is water insoluble.

The examples 1 to 60 disclosed herein may be used for example as toilet bowl cleaners, metal cleaners and brighteners and the like as well as applications such as gel batteries

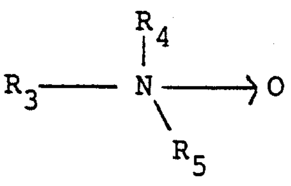
Claims

1. A thickened aqueous composition comprising at least one acid of acidic salt, a thickening agent which is a compound of the formula:



$R-N(R_1)(R_2)$

or



$R_3-N(R_4)(R_5)\rightarrow O$

(I)

(II)

in which R, R_3 is a substituted or unsubstituted alkyl, aryl, alkaryl, aralkyl or alkenyl group, R_1 is hydrogen, a substituted or unsubstituted alkyl, aryl, alkaryl, aralkyl or alkenyl group, R_2 is hydrogen, a substituted or unsubstituted alkyl, aryl, alkaryl, aralkyl or alkenyl group, R_4 is a substituted or unsubstituted alkyl, aryl, or alkaryl, aralkyl or alkenyl group, R_5 is a substituted or unsubstituted alkyl, aryl, alkaryl, aralkyl or alkenyl group, or R_1 and R_2 or R_4 and R_5 when taken together comprise a substituted or unsubstituted heterocyclic ring, provided that if either R, R_1 or R_2 is an alkyl or alkenyl group derived from a fatty acid obtained from a natural oil or fat or an equivalent synthetic fatty acid, or is an alkaryl group containing from 8 to 12 carbon atoms in the alkyl moiety, then the other substituents are not respectively of the

formulae: $[A]_x$ - H and $[A]_y$ - H where A is either ethoxy or propoxy and X, y are independently 1, 2 or 3, and optionally a strong ionic salt, the thickening agent and the acid or acidic salt being together substantially water soluble, and
wherein
the thickened aqueous composition has a viscosity of not less than 30 centipoise at 25° C when mesured with a Brookfield RVT viscometer at 50 rpm using a No. 1 spindle.

2. A composition as claimed in claim 1 wherein the thickening agent is water insoluble.

3. A composition as claimed in claim 1 or claim 2 wherein either of the groups R or R_3 contains at least six carbon atoms, preferably from eight to twenty four carbon atoms.

4. A composition as claimed in any one of claims 1 to 3, wherein the group R or R_3 is an unsubstituted alkyl or alkenyl group.

5. A composition as claimed in claim 4 wherein R or R_3 is derived from either a natural or synthetic source of tallow, soya bean oil, oleic acid, palmitic or myristic acid.

6. A composition as in claim 4 or claim 5 wherein R or R_3 is derived from either a natural or synthetic source of linolenic, ricinoleic, linoleic or hexadecanoic acid.

7. A composition as claimed in any one of claims 1 to 6, wherein the groups R_1 and R_2 are independently a hydrogen atom, a lower unsubstituted alkyl group containing one to four carbon atoms, preferably methyl, or a substituted alkyl group.

8. A composition as claimed in any one of claims 1 to 6 wherein the groups R_4 and R_5 are independently a lower unsubstituted alkyl group containing one to four carbon atoms or a substituted alkyl group.

9. A composition as claimed in claim 8, wherein the groups R_4 and R_5 are independently a methyl, hydroxyethyl or hydroxypropyl group.

10. A composition as claimed in any one of claims 1 to 13 wherein the thickening agent is a mixture of compounds of the formula I or a mixture of compounds of the formula II.

11. A composition as claimed in any one of claims 1 to 10 wherein the acid is phosphoric, sulphuric, boric, sulphamic, tartaric, citric, lactic, formic, acetic, glycollic, pentetic, ethylenediaminetetraacetic, propionic, malic, adipic, maleic, malonic, succinic, hydrofluoric, ascorbic or chloroacetic acid.

12. A composition as claimed in any one of claims 1 to 10, wherein the acidic salt is monosodium citrate, sodium hydrogen sulphate, sodium dihydrogen orthophosphate, disodium ethylenediaminetetraacetate, aluminium potassium sulphate, aluminium acetate, potassium hydrogen tartrate or aluminium sulphate.

13. A composition as claimed in any one of claims 1 to 16 wherein the concentration of thickening agent is in the range of from 0.1 to 10% w/w, preferably 0.4 to 5.0% w/w.

14. A composition as claimed in any one of claims 1 to 18 wherein the concentration of acid or acidic salt is not less than 0.01% w/w preferably 0.1 to 30% w/w.

15. A composition claimed as in any one of claims 1 to 14 additionally including a perfume, dye, sequestering agent, surfactant or bactericide.

16. A composition as claimed in any one of claims 1 to 15 wherein the strong ionic salt is an alkali metal halide, an alkali metal sulphate, an ammonium halide ammonium sulphate or a long chain quaternary ammonium compound.

17. A composition as claimed in any one of claims 1 to 16 further including a compound effective in adjusting the upper and/or lower cloud point of the composition, preferably a strong ionic salt anionic surfactant, cationic surfactant, nonionic surfactant, amphoteric surfactant, a solvent miscible with the composition, or a mixture thereof.

18. A composition as claimed in claim 19 wherein the solvent is ethanol, isopropanol butoxyethanol or dipropylene glycol methylether.

19. A method of forming a composition as claimed in any one of claims 1 to 18 comprising dissolving in water (a) at least one acid or acidic salt, (b) a thickening agent which is as defined in claim 1, and optionally (c) a strong ionic salt, the thickening agent and the acid or acidic salts being together substantially water soluble, in amounts sufficient to produce a viscosity of not less than 30 centipoise at 25° C when measured with a Brookfield RVT viscometer at 50 rpm using a No. 1 spindle.