

12

EUROPEAN PATENT APPLICATION

21 Application number: **89309173.6**

51 Int. Cl.⁵: **C11D 3/37**

22 Date of filing: **11.09.89**

30 Priority: **12.09.88 GB 8821282**

43 Date of publication of application:
21.03.90 Bulletin 90/12

84 Designated Contracting States:
CH DE ES FR GB IT LI NL SE

71 Applicant: **UNILEVER PLC**
Unilever House Blackfriars P.O. Box 68
London EC4P 4BQ(GB)
84 **GB**

Applicant: **UNILEVER NV**
Burgemeester s'Jacobplein 1 P.O. Box 760
NL-3000 DK Rotterdam(NL)
84 **CH DE ES FR IT LI NL SE**

72 Inventor: **Garvey, Michael Joseph**
"The Hollies" Nigel Road
Heswall Wirral Merseyside L60 1XU(GB)
Inventor: **Griffiths, Ian Charles**
24 Quarry Avenue
Bebington Wirral Merseyside L63 3HS(GB)

74 Representative: **Joppe, Hermina L. P. et al**
Unilever N.V. Patent Division P.O. Box 137
NL-3130 AC Vlaardingen(NL)

54 **Liquid cleaning products.**

57 A liquid cleaning composition comprises solid particles dispersed in a liquid solvent phase, which phase comprises a liquid polyalkoxylated material, the composition further comprising polyvinylpyrrolidone, or a derivative thereof, having a viscosity average molecular weight of less than 30,000 and being dissolved in said liquid solvent phase. The polymer inhibits network formation which would otherwise lead to viscosity increase on storage.

EP 0 359 491 A2

LIQUID CLEANING PRODUCTS

The present invention is concerned with liquid cleaning compositions of the kind comprising solid particles, such as detergency builders, bleaches, abrasives and mixtures thereof, dispersed in a liquid solvent phase, which phase comprises a liquid polyalkoxylated material.

European Patent Specification EP-A-266 199 (Unilever) claims and discloses a range of deflocculants for stabilising such suspensions. These deflocculants are believed to act by inhibiting aggregation of the individual particles so that they do not combine to form larger flocs which could sediment more rapidly. Some of the deflocculants described in the latter reference also inhibit network-formation by the particles in the longer term. This phenomenon eventually manifests itself in "setting" of the composition. That effect is sometimes referred to as "Ostwald ripening".

Network formation by the particles is generally undesirable because it affects the rheology of the product during storage in a variable and somewhat unpredictable manner. Ideally, the ultimate rheology should be determined solely at the time of manufacture, and governed by the chosen ingredients and manner of processing.

Such network formation can occur when sufficiently small particles are present, less than 10μ particle diameter, but mainly when less than 1μ , especially less than 0.1μ . This may be achieved by use of particles of functional ingredients having a size distribution such that at least some are below the required threshold, for example by milling them such that the volume average particle size is below 10μ , as disclosed in patent specification EP-A-30,096 (ICI). Alternatively, the small particles may be added in the form of an auxiliary dispersant comprising a highly voluminous metal oxide or metalloid oxide, such as silica, for example as described in British patent specifications GB 1,205,711 (Unilever) and GB 1,270,040 (Unilever). Best known amongst these small-particle silica-type materials are those sold under the trade name "Aerosil". The problems of network formation can be particularly acute when such auxiliary dispersants are used.

We have now found that whether or not an auxiliary dispersant is used, such network formation can be inhibited by incorporating an effective amount of polyvinylpyrrolidone, or a derivative thereof, said polymer material having a specific molecular weight.

Thus, according to the invention there is provided a substantially non-aqueous liquid cleaning composition comprising solid particles dispersed in a liquid solvent phase, which phase comprises a liquid polyalkoxylated material, characterised in that the composition further comprises a network inhibiting amount of vinylpyrrolidone polymer, or a derivative thereof, said polymer having a viscosity average molecular weight of less than 30,000 and being dissolved in said liquid solvent phase.

Without wishing to be bound by any theory or explanation, the applicants believe that the polymer material fulfils this function by adsorption onto the surfaces of the particles. For polymer molecules to be associated with the surfaces, they must be in equilibrium with at least some of the polymer which is in solution in the liquid solvent phase. Higher molecular weight polymers are less weight efficient, requiring a higher total concentration for saturation of the particle surfaces. Thus, we observe that a viscosity average molecular weight of less than 30,000 is required, although the best results are obtained with viscosity average molecular weights no greater than 24,000, most preferably no greater than 15,000.

The amount of polymer material required will depend in part on the other components of the composition, in particular on the type(s) and volume fraction of the dispersed solids. However, the molecular weight of the polymer material is of importance also. For consumer preferred flow behaviour, it is usually required that the viscosity of the product is no higher than 2.5 Pas, most preferably no greater than 1 Pas when measured at a shear rate of $21s^{-1}$. Network inhibition by an effective amount of the polymer materials should prevent the product viscosity from rising to unacceptable levels during storage. If an insufficient amount of polymer material is used though, it can result in a rapid viscosity increase. If this is observed, more must be added to achieve the desired effect. However, if too much is added, the amount of polymer dissolved in the liquid solvent phase will itself unnecessarily raise the viscosity. The higher the molecular weight of a given amount of the polymer, the greater the resultant viscosity. As one exceeds the upper molecular weight limit of 30,000, one finds that the amount of polymer at which the viscosity of the liquid solvent phase begins to be undesirable, is significantly reduced. In other words, the usable range of polymer level contracts as one exceeds the upper molecular weight limit.

Thus for example, in a formulation containing 2.5% w/w Aerosil 380 and when the viscosity average molecular weight of the polymer material is 10,000, typically a polymer level of 0.1% by weight will lead to a viscosity increase whereas amounts of around 0.5% by weight will exhibit optimal network formation inhibition, whilst above these levels, viscosity rises again until it becomes unnecessarily higher at above 1%

by weight of polymer material. It must be appreciated that these figures are only guidelines and the exact amount of given polymer material of a given molecular weight in order to achieve the desired effect will also vary according to the type(s) and amount(s) of other ingredients in the composition. In practice, the level of polymer material is determined by gradual progressive addition of that material to the system of choice and monitoring the viscosity profile described above, or sedimentation behaviour as described later.

Although the polymer material exhibits the unexpected advantage hereinbefore described, it can also endow additional benefits in the wash which are already known for such polymers when used in detergent compositions in general. Thus, US patent 3,000,830 (Fong et al) describes use of polyvinylpyrrolidone as a soil suspending agent and GB patent specification 1,348,212 (Procter & Gamble) discloses use of polyvinylpyrrolidone and certain derivatives thereof for prevention of dye transfer. We are also aware of European patent specification EP-A-256343 (Mira Lanza) which refers to the use of PVP with a molecular weight of 30,000 as a suspending agent in non-aqueous liquids.

Although polyvinylpyrrolidones are readily commercially available, in the light of the present teaching, the man skilled in the art will now appreciate that derivatives thereof with minor structural variations may be substituted therefor with expectation of achieving the same effect, provided that any such derivative is soluble in the liquid solvent phase. For example, such derivatives may be co-polymers containing minor amounts of other monomer units. Such derivatives may be any of those described in said GB 1,348,212, the text of which is incorporated herein by reference.

There is a wide range of possible ways of expressing polymer molecular weight, varying according to the particular assay used and how the average is calculated (e.g. number average, weight average etc.). However, the term 'viscosity average molecular weight' when used in respect of polyvinylpyrrolidones (or soluble derivatives thereof) will readily be understood by those skilled in the art and is widely used by manufacturers to characterise such polymer products.

The liquid solvent phase must contain at least some of a liquid polyalkoxylated material and must be such that the polymer material is soluble therein, although it is permissible for a portion of the polymer material to be present as dispersed solid. The polyalkoxylated liquids are chosen in particular for their ability to dissolve the polymer material although co-solvents may also be present, provided that the polymer is soluble in the resultant mixture. In the context of the present invention, a polyalkoxylated material is any which has a molecule which contains two or more alkoxy groups, whether the same or different, bonded directly to one another. All references to liquids refer to materials which are liquid at 25° C at atmospheric pressure.

It is particularly preferred for a major amount, e.g. 50% by weight or greater, of the liquid solvent phase to consist of one or more liquid polyalkoxylated materials.

Especially preferred are liquid polyalkoxylated nonionic surfactants such as are disclosed in our aforementioned EP-A-266,199, relevant parts of which are incorporated herein by reference. Usually, these will be chosen from liquids which are the condensation products of fatty alcohols with lower (C₁₋₄) alkylene oxides, especially ethylene oxide and/or propylene oxides. Other suitable polyalkoxylated liquids are poly-lower (C₁₋₄) alkylene glycols, especially liquid polyethylene glycols and liquid polypropylene glycols. For example, the polyethylene glycols may be chosen from those which are liquid and have molecular weights in the range of from 200 to 600. Also suitable are alkylene glycol mono- or di-alkyl ethers. Such mono-alkyl ethers are disclosed in British patent specification GB 2,169,613 (Colgate). Typical such di-alkyl ethers are diethylene glycol di-ethyl or di-butyl ether (di-ethyl and di-butyl Carbitol, respectively), most preferably diethylene glycol dimethyl ether (diglyme). The polymer material is insoluble in the latter liquid but when the diglyme is mixed with a polyalkoxylated nonionic surfactant liquid or a liquid polyalkylene glycol, especially a polyethylene glycol, then the polymer can be dissolved. For example, the polymer can be dissolved in mixtures of diglyme and polyethylene glycol, molecular weight 200, in weight ratios from at least 1:3 to 3:1.

Where non-polyalkoxylated co-solvents are also included, these may be selected from any co-solvent which is miscible with the liquid polyalkoxylated materials yet does not cause insolubility of the polymer material to the extent that the network inhibition effect is lost. Suitable co-solvents are disclosed in said EP-A-266,199.

All compositions according to the present invention are liquid cleaning products. They may be formulated in a very wide range of specific forms, according to the intended use. They may be formulated as cleaners for hard surfaces (with or without abrasive) or as agents for warewashing (cleaning of dishes, cutlery etc) either by hand or mechanical means, as well as in the form of specialised cleaning products, such as for surgical apparatus or artificial dentures. They may also be formulated as agents for washing and/or conditioning of fabrics. When additional ingredients are selected to adapt the basic formulation for the intended purpose, these will be chosen to be compatible therewith, ie. so as not to destroy the required network inhibiting effect.

In the case of hard-surface cleaning, the compositions may be formulated as main cleaning agents, or pre-treatment products to be sprayed or wiped on prior to removal, eg. by wiping off or as part of a main cleaning operation.

In the case of warewashing, the compositions may also be the main cleaning agent or a pre-treatment product, eg. applied by spray or used for soaking utensils in an aqueous solution and/or suspension thereof.

Those products which are formulated for the cleaning and/or conditioning of fabrics constitute an especially preferred form of the present invention because in that role, there is a very great need to be able to incorporate substantial amounts of various kinds of solids. These compositions may for example, be of the kind used for pre-treatment of fabrics (eg. for pot stain removal) with the composition neat or diluted, before they are rinsed and/or subjected to a main wash. The compositions may also be formulated as main wash products, being dissolved and/or dispersed in the water with which the fabrics are contacted. In that case, the composition may be the sole cleaning agent or an adjunct to another wash product. Within the context of the present invention, the term 'cleaning product' also embraces compositions of the kind used as fabric conditioners (including fabric softeners) which are only added in the rinse water (sometimes referred to as 'rinse conditioners').

Thus, the compositions will contain at least one agent which promotes the cleaning and/or conditioning of the article(s) in question, selected according to the intended application. Usually, this agent will be selected from surfactants, enzymes, bleaches, microbiocides, (for fabrics) fabric softening agents and (in the case of hard surface cleaning) abrasives. Of course in many cases, more than one of these agents will be present, as well as other ingredients commonly used in the relevant product form.

The compositions will be substantially free from agents which are detrimental to the article(s) to be treated. For example, they will be substantially free from pigments or dyes, although of course they may contain small amounts of those dyes (colourants) of the kind often used to impart a pleasing colour to liquid cleaning products, as well as fluorescers, bluing agents and the like.

All ingredients before incorporation will either be liquid, in which case, in the composition they will constitute all or part of the liquid solvent phase, or they will be solids, in which case, in the composition they will either be dispersed as deflocculated particles in the liquid solvent phase. Thus as used herein, the term "solids" is to be construed as referring to materials in the solid phase which are added to the composition and are dispersed therein in solid form, those solids which dissolve in the solvent and those in the liquid phase which solidify (undergo a phase change) in the composition, wherein they are then dispersed.

Thus, where surfactants are solids, they will usually be dissolved or dispersed in the liquid solvent phase. Where they are liquids, they will usually constitute all or part of the liquid solvent phase. However, in some cases the surfactants may undergo a phase change in the composition. In general, they may be chosen from any of the classes, sub-classes and specific materials described in 'Surface Active Agents' Vol. I, by Schwartz & Perry, Interscience 1949 and 'Surface Active Agents' Vol. II by Schwartz, Perry & Berch (Interscience 1958), in the current edition of "McCutcheon's Emulsifiers & Detergents" published by the McCutcheon division of Manufacturing Confectioners Company or in 'Tensid-Taschenbuch', H. Stache, 2nd Edn., Carl Hanser Verlag, München & Wien, 1981.

Nonionic detergent surfactants, both liquid and solid, are well-known in the art. They normally consist of a water-solubilizing polyalkoxyethylene or a mono- or di-alkanolamide group in chemical combination with an organic hydrophobic group derived, for example, from alkylphenols in which the alkyl group contains from about 6 to about 12 carbon atoms, dialkylphenols in which each alkyl group contains from 6 to 12 carbon atoms, primary, secondary or tertiary aliphatic alcohols (or alkyl-capped derivatives thereof), preferably having from 8 to 20 carbon atoms, monocarboxylic acids having from 10 to about 24 carbon atoms in the alkyl group and polyoxypropylenes. Also common are fatty acid mono- and dialkanolamides in which the alkyl group of the fatty acid radical contains from 10 to about 20 carbon atoms and the alkyl group having from 1 to 3 carbon atoms. In any of the mono- and di- alkanolamide derivatives, optionally, there may be a polyoxyalkylene moiety joining the latter groups and the hydrophobic part of the molecule. In all polyalkoxyethylene containing surfactants, the polyalkoxyethylene moiety preferably consists of from 2 to 20 groups of ethylene oxide or of ethylene oxide and propylene oxide groups. Amongst the latter class, particularly preferred are those described in European patent specification EP-A-225,654 (Unilever), especially for use as all or part of the solvent. Also preferred are those ethoxylated nonionics which are the condensation products of fatty alcohols with from 9 to 15 carbon atoms condensed with from 3 to 11 moles of ethylene oxide. Examples of these are the condensation products of C₁₁₋₁₃ alcohols with (say) 3 or 7 moles of ethylene oxide. These may be used as the sole nonionic surfactants or in combination with those of the described in the last-mentioned European specification, especially as all or part of the liquid solvent phase.

Another class of suitable nonionics comprise the alkyl polysaccharides

(polyglycosides/oligosaccharides) such as described in any of specifications US 3,640,998; US 3,346,558; US 4,223,129; EP-A-92,355; EP-A-99,183; EP-A-70,074, '75, '76, '77; EP-A-75,994, '95, '96.

Mixtures of different nonionic detergent surfactants may also be used, provided the mixture is liquid at room temperature. Mixtures of nonionic detergent surfactants with other detergent surfactants such as anionic, cationic or ampholytic detergent surfactants and soaps may also be used. If such mixtures are used, the mixture must be liquid at room temperature.

Examples of suitable anionic detergent surfactants are alkali metal, ammonium or alkylolamine salts of alkylbenzene sulphonates having from 10 to 18 carbon atoms in the alkyl group, alkyl and alkylether sulphates having from 10 to 24 carbon atoms in the alkyl group, the alkylether sulphates having from 1 to 5 ethylene oxide groups, olefin sulphonates prepared by sulphonation of C₁₀-C₂₄ alpha-olefins and subsequent neutralization and hydrolysis of the sulphonation reaction product.

Other surfactants which may be used include alkali metal soaps of a fatty acid, preferably one containing 12 to 18 carbon atoms. Typical such acids are oleic acid, ricinoleic acid and fatty acids derived from castor oil, rapeseed oil, groundnut oil, coconut oil, palmkernel oil or mixtures thereof. The sodium or potassium soaps of these acids can be used. As well as fulfilling the role of surfactants, soaps can act as detergency builders or fabric conditioners, other examples of which will be described in more detail hereinbelow. It can also be remarked that the oils mentioned in this paragraph may themselves constitute part of the solvent, whilst the corresponding low molecular weight fatty acids (triglycerides) can be dispersed as solids or function as structurants.

Yet again, it is also possible to utilise cationic, zwitterionic and amphoteric surfactants such as referred to in the general surfactant texts referred to hereinbefore. Examples of cationic detergent surfactants are aliphatic or aromatic alkyl-di(alkyl) ammonium halides and examples of soaps are the alkali metal salts of C₁₂-C₂₄ fatty acids. Ampholytic detergent surfactants are e.g. the sulphobetaines. Combinations of surfactants from within the same, or from different classes may be employed to advantage for optimising structuring and/or cleaning performance.

The compositions according to the present invention preferably also contain one or more other functional ingredients, for example selected from other detergency builders, bleaches or bleach systems, and (for hard surface cleaners) abrasives.

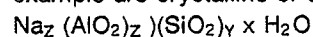
Detergency builders are those materials which counteract the effects of calcium, or other ion, water hardness, either by precipitation or by an ion sequestering effect. They comprise both inorganic and organic builders. They may also be sub-divided into the phosphorus-containing and non-phosphorus types.

In general, the inorganic builders comprise the various phosphate-, carbonate-, silicate-, borate- and aluminosilicate-type materials, particularly the alkali-metal salt forms. Mixtures of these may also be used.

Examples of phosphorus-containing inorganic builders when present include the water-soluble salts, especially alkali metal pyrophosphates, orthophosphates, polyphosphates and phosphonates. Specific examples of inorganic phosphate builders include sodium and potassium phosphates and hexametaphosphates, as well as sodium and potassium triphosphate.

Examples of non-phosphorus-containing inorganic builders, when present, include water-soluble alkali metal carbonates, bicarbonates, borates, silicates, metasilicates, and crystalline and amorphous aluminosilicates. Specific examples include sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonates, silicates and zeolites.

The aluminosilicates are an especially preferred class of non-phosphorus inorganic builders. These for example are crystalline or amorphous materials having the general formula:



wherein Z and Y are integers of at least 6, the molar ratio of Z to Y is in the range from 1.0 to 0.5, and x is an integer from 6 to 189 such that the moisture content is from about 4% to about 20% by weight (termed herein, 'partially hydrated'). This water content provides the best rheological properties in the liquid. Above this level (e.g. from about 19% to about 28% by weight water content), the water level can lead to network formation. Below this level (e.g. from 0 to about 6% by weight water content), trapped gas in pores of the material can be displaced which causes gassing and tends to lead to a viscosity increase also. The preferred range of aluminosilicate is from about 12% to about 30% on an anhydrous basis. The aluminosilicate preferably has a particle size of from 0.1 to 100 microns, ideally between 0.1 to 10 microns and a calcium ion exchange capacity of at least 200 mg calcium carbonate/g.

Examples of organic builders include the alkali metal, ammonium and substituted ammonium, citrates, succinates, malonates, fatty acid sulphonates, carboxymethoxy succinates, ammonium polyacetates, carboxylates, polycarboxylates, aminopolycarboxylates, polyacetyl carboxylates and polyhydroxysulphonates. Specific examples include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, melitic acid, benzene polycarboxylic

acids and citric acid. Other examples are organic phosphonate type sequestering agents such as those sold by Monsanto under the tradename of the Dequest range and alkanedihydroxy phosphonates.

Other suitable organic builders include the higher molecular weight polymers and co-polymers known to have builder properties, for example appropriate polyacrylic acid, polymaleic acid and polyacrylic/polymaleic acid co-polymers and their salts, such as those sold by BASF under the Sokalan Trade Mark.

Suitable bleaches include the halogen, particularly chlorine bleaches such as are provided in the form of alkalimetal hypochlorites, eg. hypochlorites. In the application of fabrics washing, the oxygen bleaches are preferred, for example in the form of an inorganic persalt, preferably with an precursor, or as a peroxy acid compound.

In the case of the inorganic persalt bleaches, the precursor makes the bleaching more effective at lower temperatures, ie. in the range from ambient temperature to about 60 °C, so that such bleach systems are commonly known as low-temperature bleach systems and are well known in the art. The inorganic persalt such as sodium perborate, both the monohydrate and the tetrahydrate, acts to release active oxygen in solution, and the precursor is usually an organic compound having one or more reactive acyl residues, which cause the formation of peracids, the latter providing for a more effective bleaching action at lower temperatures than the peroxybleach compound alone. The ratio by weight of the peroxybleach compound to the precursor is from about 15:1 to about 2:1, preferably from about 10:1 to about 3.5:1. Whilst the amount of the bleach system, ie. peroxybleach compound and precursor, may be varied between 5% and about 35% by weight of the total liquid, it is preferred to use from about 6% to about 30% of the ingredients forming the bleach system. Thus, the preferred level of the peroxybleach compound in the composition is between about 5.5% and about 27% by weight, while the preferred level of the precursor is between about 0.5% and about 40%, most preferably between about 1% and about 5% by weight.

Typical examples of the suitable peroxybleach compounds are alkalimetal perborates, both tetrahydrates and monohydrates, alkali metal percarbonates, persulfates and perphosphates, of which sodium perborate is preferred.

Precursors for peroxybleach compounds have been amply described in the literature, including in British patent specifications 836,988, 855,735, 907,356, 907,358, 907,950, 1,003,310 and 1,246,339, US patent specifications 3,332,882, and 4,128,494, Canadian patent specification 844,481 and South African patent specification 68/6,344.

The exact mode of action of such precursors is not known, but it is believed that peracids are formed by reaction of the precursors with the inorganic peroxy compound, which peracids then liberate active-oxygen by decomposition.

They are generally compounds which contain N-acyl or O-acyl residues in the molecule and which exert their activating action on the peroxy compounds on contact with these in the washing liquor. Cationic peracid bleach precursors such as those described in United States patent specifications US 4,751,015 and US 4,397,757 (Lever Bros.) can be included.

When the composition contains abrasives for hard surface cleaning (ie. is a liquid abrasive cleaner), these will inevitably be incorporated as particulate solids. They may be those of the kind which are water insoluble, for example calcite. Suitable materials of this kind are disclosed in the patent specifications EP-A-50,887; EP-A-80,221; EP-A-140,452; EP-A-214,540 and EP 9,942 (all Unilever) which relate to such abrasives when suspended in aqueous media. Water soluble abrasives may also be used.

While the present invention is particularly beneficial for those compositions which contain finely divided silica or other finely divided metal or metalloid oxides as referred to in British patent specifications GB 1,205,711 and GB 1,270,040, the compositions may alternatively or additionally contain other auxiliary dispersants such as fine particulate chain-structure clay as described in European specification EP-A-34,387 (Procter). They may also contain one or more of the deflocculants disclosed in EP-A-266,199, for example dodecyl benzene sulphononic acid (added in the free acid form) or lecithin.

The compositions of the invention optionally may also contain one or more minor ingredients such as fabric conditioning agents, enzymes, perfumes (including deoperfumes), micro-biocides, colouring agents, viscosity modifiers, fluorescers, soil-suspending agents (anti-redeposition agents), corrosion inhibitors, enzyme stabilizing agents, and lather depressants.

The compositions are substantially non-aqueous, ie. they contain little or no free water, preferably no more than 5%, preferably less than 3%, especially less than 1% by weight of the total composition. It has been found that the higher the water content, the more likely it is for the viscosity to be too high, or even for setting to occur.

Since the objective of a non-aqueous liquid will generally be to enable the formulator to avoid the negative influence of water on the components, e.g. causing incompatibility of functional ingredients, it is

clearly necessary to avoid the accidental or deliberate addition of water to the product at any stage in its life. For this reason, special precautions are necessary in manufacturing procedures and pack designs for use by the consumer.

Thus during manufacture, it is preferred that all raw materials should be dry and (in the case of hydratable salts) in a low hydration state, eg. anhydrous phosphate builder, sodium perborate monohydrate and dry calcite abrasive, where these are employed in the composition. In a preferred process, the dry, substantially anhydrous solids are blended with the solvent in a dry vessel. In order to minimise the rate of sedimentation of the solids, this blend is passed through a grinding mill or a combination of mills, eg. a colloid mill, a corundum disc mill, a horizontal or vertical agitated ball mill, to achieve a particle size of 0.1 to 100 microns, preferably 0.5 to 50 microns, ideally 1 to 10 microns. A preferred combination of such mills is a colloid mill followed by a horizontal ball mill since these can be operated under the conditions required to provide a narrow size distribution in the final product. Of course particulate material already having the desired particle size need not be subjected to this procedure and if desired, can be incorporated during a later stage of processing.

During this milling procedure, the energy input results in a temperature rise in the product and the liberation of air entrapped in or between the particles of the solid ingredients. It is therefore highly desirable to mix any heat sensitive ingredients into the product after the milling stage and a subsequent cooling step. It may also be desirable to de-aerate the product before addition of these (usually minor) ingredients and optionally, at any other stage of the process. Typical ingredients which might be added at this stage are perfumes and enzymes, but might also include highly temperature sensitive bleach components or volatile solvent components which may be desirable in the final composition. However, it is especially preferred that volatile material be introduced after any step of de-aeration. Suitable equipment for cooling (eg. heat exchangers) and de-aeration will be known to those skilled in the art.

It follows that all equipment used in this process should be completely dry, special care being taken after any cleaning operations. The same is true for subsequent storage and packing equipment.

The present invention will now be illustrated by way of the following Examples.

Example 1

To demonstrate determination of suitable amounts of polymer material according to the viscosity profile, model systems were formulated with Aerosil 380 finely divided silica auxiliary dispersant in liquid nonionic as Dobanol 91/6T, a C₉-₁₁ fatty alcohol alkoxylated with an average of 6 moles of ethylene oxide per molecule (ex Shell). In some compositions zeolite was included as an additional dispersed solid. Polymer materials were polyvinyl pyrrolidone, viscosity average molecular weights 2,500 (PVP 2.5K) and 10,000 (PVP 10K).

Composition	1	2	3	4	5	6	7
Aerosil	1.25	1.25	1.25	1.25	2.5	2.5	2.5
Zeolite	12.0	12.0	12.0	12.0	-	-	-
PVP 2.5K	-	0.5	-	-	-	-	-
PVP 10K	-	-	0.2	1.0	0.1	0.5	1.0
Nonionic	balance						

In reference composition 1 the polymer was omitted, whilst in composition 5, the polymer was found to be insufficient and particle aggregation appeared to be progressive leading to thickening, increasing on storage. In compositions 2, 3, 6 and 7 lack of particle aggregation was evident by visual inspection but composition 4 showed some evidence of a viscosity increase due to the use of too much polymer.

Example 2: Fully formulated composition	
	wt %
Dobanol 91/6T (1)	37.35
Glycerol tri-acetate	5.0
Aerosil 380 (2)	1.25
PVP (3)	1.0
STP (4)	30.0
Sodium carbonate 0aq	4.0
Na Perborate monohydrate	15.0
EDTA (5)	0.15
SCMC (6)	1.0
TAED (7)	4.0
Dequest 2041	0.1
Fluorescer (Tinopal DMS-X)	0.3
Tylose MH20	0.5
Silicone DB100	0.25
Savinase 8.0 SL	0.6

(1) (2) (3) : as Example 1.

(4) Sodium tripolyphosphate

(5) Ethylene diamine tetraacetic acid

(6) Sodium carboxymethylcellulose

(7) Tetraacetyl ethylenediamine

Example 3

A 51% by weight dispersion of zeolite (having a water content of 21.5% by weight and a particle size of approximately 4 microns) in Dobanol 91-6T was prepared in a Silverson mixer. Equal weights (15g) of this dispersion and solutions of PVP (having a molecular weight of 2.5K, 10K, 24K and 40K) in Dobanol 91-6T were mixed overnight on a bottle roller to give a range of samples containing 25.5% by weight zeolite and from 0 to 5% PVP.

Approximately 10cm³ of each sample was transferred to 10cm³ measuring cylinders and left to stand at a temperature of 31± 1° C. Sediment volumes and supernatant clarity were monitored at regular intervals over a period of 40 days.

The sediment volume results after 40 days were as follows.

5
10
15
20
25
30

Molecular Weight	PVP Concentration	Sediment Volume
	(%)	(%)
2,500	0.05	44
	0.1	44
	0.25	42
	0.5	42
	1.0	42
	2.5	41
10,000	5.0	41
	0.05	42
	0.1	42
	0.25	39
	0.5	31
	1.0	30
24,000	2.5	30
	5.0	30
	0.05	43
	0.1	41
	0.25	29
	0.5	30
40,000	1.0	29
	2.5	29
	5.0	30
	0.05	43
	0.1	36
	0.25	30
	0.5	30
	1.0	29
	2.5	30
	5.0	32

35

The samples using PVP with a molecular weight of 40K were measurably more viscous than the other samples.

The results show that for PVP with a molecular weight of 10K and greater, there is a noticeable decrease in sediment volume, at concentrations in the region of 0.5%, indicating that a reduction in the particle-particle attraction energy has occurred. This is believed to be due to the adsorption of the polymer with subsequent steric stabilisation of the particles inhibiting network formation. With PVP of molecular weight 2.5K little change in sediment volume is observed up to 5% polymer, indicating that this polymer gives rise to a weaker steric stabilisation.

The reduction in particle attraction is in the order $2.5K \ll 10K < 24K = 40K$ and illustrates the lack of benefit to be obtained from increasing the molecular weight above 24K.

Claims

1. A substantially non-aqueous liquid cleaning composition comprising solid particles dispersed in a liquid solvent phase, which phase comprises a liquid polyalkoxylated material, characterised in that the composition further comprises a network inhibiting amount of vinylpyrrolidone polymer, or a derivative thereof, said polymer having a viscosity average molecular weight of less than 30,000 and being dissolved in said liquid solvent phase.

2. A composition according to claim 1, wherein the viscosity average molecular weight of the polymer is no greater than 24,000.

3. A composition according to claim 1, wherein the viscosity average molecular weight of the polymer is no greater than 15,000.

4. A composition according to claim 1, wherein the liquid polyalkoxylated material comprises a liquid nonionic surfactant.

5. A composition according to claim 1, wherein the liquid polyalkoxylated material comprises an alkylene glycol mono-or di-alkyl ether.

5 6. A composition according to claim 1, wherein the liquid polyalkoxylated material comprises a liquid polyalkylene glycol.

7. A composition according to claim 1, wherein the liquid polyalkoxylated material comprises diglyme and a polyethylene glycol in a weight ratio of from 1:3 to 3:1.

10 8. A composition according to claim 1, wherein the solid particles have a particle size of less than 100 microns.

9. A composition according to claim 1, wherein the solid particles are selected from particles of metal or metalloid oxides, detergency builders, bleaches, abrasives and mixtures thereof.

15

20

25

30

35

40

45

50

55