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<p>(54) Title: DETERGENT COMPOSITION</p>		
<p>(57) Abstract</p>		
<p>Liquid detergent composition comprising a polymeric hydrotrope. The polymer has at least one of the following effects, i.e. dispersion improvement, dissolution improvement and dispensing improvement to (at least partially) overcome gelling problems, in particular at low water levels. Preferably, the composition further comprises electrolyte material. The invention further relates to a surfactant containing composition with polymeric hydrotrope and to a method of preparing a non-aqueous detergent composition, to a method of applying a composition and to a method of mixing a composition with water.</p>		

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DETERGENT COMPOSITIONTechnical Field

The present invention relates to compositions which  
5 comprise polymer material and to a method of preparing such  
compositions.

Background & Prior Art

Detergent compositions may be aqueous or non-aqueous, both  
10 either in solid or in liquid form. Non-aqueous liquid  
detergent compositions are known in the art and have been  
described in quite a number of patent publications, e.g. in  
US-A-4,316,812, US-A-4,874,537 and EP-A-0,484,095.

Generally, the free water content of non-aqueous liquid  
15 detergent compositions is less than 5% by weight,  
preferably less than 3% by weight, more preferably less  
than 2% by weight, most preferably substantially nil. Non-  
aqueous liquid detergent compositions provide a way of  
concentrating liquid detergents without giving in on  
20 washing performance.

Non-aqueous liquid detergent compositions normally comprise  
a non-aqueous liquid phase having incorporated therein as  
dispersion, solution or combination thereof, the usual  
25 detergent components and adjuncts depending on the purpose  
of use, primarily surfactants and builders.

The non-aqueous liquid phase often comprises a nonionic  
surfactant as major component, which apart from acting as  
30 carrier liquid for the other detergent components, usually  
and preferably also has detergent-active properties,  
thereby acting wholly or in part as the surfactant  
ingredient.

35 One weakness of non-aqueous liquid detergent compositions  
is that on dilution with water, they may tend to suffer

from gelling and the ingredients tend to stick together. As a consequence thereof, the product may disperse only slowly in water and this may have a negative influence on the cleaning performance of the product, e.g. the product will  
5 not uniformly and timely dissolve in the washing liquor. This is for example true with liquid phases comprising a nonionic surfactant, such as mixtures of C13-C15 alcohols with an average of 3 ethoxy groups and C13-C15 alcohols with an average of 7 ethoxy groups and liquid phases as  
10 described in GB-A-1,462,134, WO-A-91/12313, WO-A-91/14765 and EP-A-0,510,762 and more in particular for liquids comprising a dispersed solid particulate phase.

Such problems have for example been described in GB-A-  
15 2,169,613 (Colgate) wherein alkylene glycol mono alkyl ethers are disclosed as anti-gelling agent. GB-A-2,168,995 (Colgate) describes acid-terminated nonionics and GB-A-2,177,716 (Colgate) dicarboxylic acids as gel-inhibition agents. Other examples of anti-gelling compounds, such as  
20 lower aliphatic alcohols, glycols and polyethyleneglycol, are described in EP-A-413,616 (Colgate). Our co-pending PCT Application No. EP/94/01289 (Unilever) describes the use of an ester material to overcome gelling problems.

25 Indeed, it has been found that these solvent materials may be beneficial in at least partially overcoming the gelling problem of non-aqueous liquid detergent compositions. However, we have found that these materials are only effective to overcome gelling caused at relatively high  
30 water levels, whereas they are less effective or even ineffective in overcoming relatively low water level gelling problems, e.g. at water levels in which 5 to 50% by weight of water is added to the product.

35 Therefore, there still exists a gelling problem of non-aqueous liquid detergent compositions at relatively low

water levels, say water levels of 5 to 50% by weight of the composition. Additionally, gelling problems of non-aqueous liquid detergent compositions at relatively high water levels, say water levels of 70 to 250% by weight of the  
5 composition, can still occur.

Gelling problem of non-aqueous liquids are not only noticeable for non-aqueous liquid containing a non-aqueous phase, but also, and in particular, when solid dispersed  
10 particles are present.

Further, dispersion problems of non-aqueous liquid detergent compositions may occur upon dilution with water. Low dispersion may for example lead to high concentrations  
15 of product on the cloth that may have negative effects on the cloth's quality.

A further problem related to the use of non-aqueous liquid compositions is dissolution. Slow dissolution of the  
20 concentrated composition may result in liberation of the components to the wash liquor only at a late stage during the washing process, at which point they may be less effective.

25 Another problem that is in particular important in the industrial area is the dispensing problem of non-aqueous liquids, i.e. the blocking of pipes and valves of the dosing system for non-aqueous liquid detergent compositions. This problem has e.g. been described in EP-A-  
30 480,490 (Unilever).

It is an object of the present invention to improve at least one of the problems related to gelling, dispersion, dissolution and/or dispensing of non-aqueous liquids.

We have found that one or more of the above problems may also occur in composition comprising from 10 to 90% by weight of surfactant material. The compositions are preferably non-aqueous (either solid or preferably liquid).

5

We have further found that applying compositions to a washing machine may lead to one or more of the above problems. The compositions are preferably non-aqueous (either solid or preferably liquid).

10

We have further found that mixing a composition with water may lead to one or more of the above problems. The compositions are preferably non-aqueous (either solid or preferably liquid).

15

Surprisingly, we have found that the above mentioned problems of gelling, dispersion, dissolution and/or dispensing may at least partially be overcome by including a particular polymeric material.

20

Non-aqueous liquids comprising polymeric material have for example been described in EP-A-510,762 (Unilever) that discloses non-aqueous liquids comprising a polymer material comprising at least one group capable of association with  
25 the solid phase and at least one group capable of extending from the solid phase. The polymer is amongst other incorporated to lower the viscosity and the clear layer separation.

30 WO 94/01524 (Unilever) discloses non-aqueous liquids comprising a polymeric material with a group that exhibits self association to reduce viscosity and the clear layer formation of the liquids.

35 WO 94/12611 (Unilever) discloses non-aqueous liquids comprising dry particulate solubilised biopolymer material

to improve the dispersion of the liquid. Preferred biopolymers are polysaccharides and polypeptides.

EP-A-413,616 (Colgate) discloses non-aqueous liquid  
5 detergent compositions comprising nonionic surfactants, solid particles and a polymer derived from  $\alpha,\beta$ -mono-ethylenically unsaturated carboxy-containing monomers.

EP-A-359,491 (Unilever) and EP-A-359,492 (Unilever)  
10 disclose non-aqueous liquids comprising respectively low and high molecular weight vinyl pyrrolidone polymers.

EP-A-28,849 (Unilever) discloses non-aqueous liquids comprising a stabilising polymer that is an at least  
15 partially hydrolysed copolymer of maleic anhydride with ethylene or vinylmethylether.

GB-A-2,228,944 (Unilever) discloses non-aqueous liquids comprising polymeric materials that may comprise acryl  
20 amide monomers.

#### Statement of the invention

The present invention provides a non-aqueous liquid detergent composition comprising a non-aqueous liquid  
25 phase, wherein the composition comprises a polymeric hydrotrope comprising hydrophillic and hydrophobic monomers.

Preferably, the non-aqueous liquids according to the  
30 invention comprise an electrolyte material. Preferably, liquid composition of the present invention further comprise at least one ingredient selected from abrasives, bleaches, bleach catalysts, bleach precursors, corrosion inhibitors, dispersants, enzymes, fabric softening agents,  
35 microbiocides and mixtures thereof. Preferably, these ingredients are included at levels of from 0.01 to 90% by

weight of the composition. Preferably, the non-aqueous liquids according to the invention comprise solid dispersed particles which are more preferably selected from bleaches, builders, abrasives, dispersants, enzymes, solid  
5 surfactants, fluorescers, enzymes, bleach precursors, bleach catalysts, colorants, pigments, opacifying agents and mixtures thereof.

The present invention further provides a composition  
10 comprising from 10 to 90% by weight of surfactant material and further comprising a polymeric hydrotrope.

The invention further provides a method of preparing a non-aqueous liquid detergent composition comprising a non-  
15 aqueous phase and a polymeric hydrotrope, wherein the polymeric hydrotrope is added to the non-aqueous phase in a form comprising 25% or less by weight of water.

The invention further provides a method of applying a  
20 composition by mixing the composition with a polymeric hydrotrope, whereafter the composition with the polymer is applied to a washing machine. Preferably, the composition comprises surfactant material and more preferably nonionic surfactant material. Preferably, the composition is non-  
25 aqueous (either solid or preferably liquid).

The invention further provides a method of mixing a composition with water, wherein the composition is prepared by mixing a surfactant with a polymeric hydrotrope,  
30 whereafter the composition is mixed with water. Preferably, the composition comprises surfactant material and more preferably nonionic surfactant material. Preferably, the composition is non-aqueous (either solid or preferably liquid). Preferably the composition is mixed with water in  
35 a washing machine.

### Description of the Invention

It has been found that non-aqueous liquids comprising the polymeric hydrotrope show reduced gelling characteristics upon dilution, improved dispersion, dissolution and/or  
5 dispensing.

It has further been found that the use of the polymeric hydrotrope in non-aqueous liquids according to the invention may have certain advantages compared with use of  
10 conventional hydrotropes, including low foaming properties, good surfactant solubilising characteristics, chemical stability, ease of handling, cost effective, substantially free of nitrosamines commonly associated with compositions using nitrogen-based hydrotropes or solubilisers, such as  
15 amine oxides.

Further, use of the polymer hydrotrope has been found to lead to reduced gelling, improved dispersion, dissolution and/or dispensing of compositions comprising high  
20 surfactant levels.

Mixing the polymeric hydrotrope in a composition has been found to be advantageous as to reduced gelling characteristics upon dilution, improved dispersion,  
25 dissolution and/or dispensing when applying the composition to a washing machine.

Mixing a surfactant-composition with a polymeric hydrotrope leads to reduced gelling characteristics upon dilution,  
30 improved dispersion, dissolution and/or dispensing when mixing the composition with water.

### Polymeric Hydrotrope

The polymeric hydrotrope may be a homopolymer or a copolymer, in block and/or random form. Preferably, the polymer comprises hydrophillic and hydrophobic monomers.

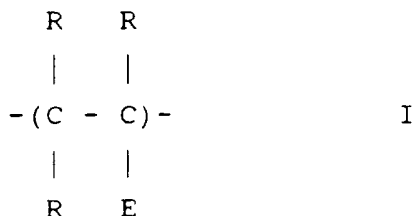
5 The hydrophillic monomers are sufficiently water soluble. They preferably have a water solubility at ambient temperature and at a pH of 3.0 to 12.5 (preferably 7.0) of more than 1 g/l, more preferably more than 5g/l, most preferred more than 10g/l.

10

The hydrophobic monomers have a low water solubility. Preferably less than 1 g/l, more preferred less than 0.5 g/l, most preferred less than 0.1 g/l of the hydrophobic monomer will dissolve in water at ambient temperature and a  
 15 pH of 3.0 to 12.5, preferably 7.0.

Hydrophillic monomers are preferably selected from monomers of formula I:

20



25

wherein:

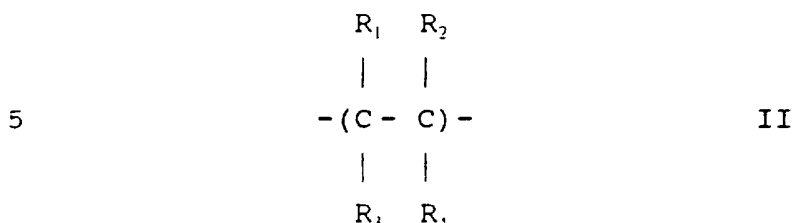
E is a hydrophillic functional groups, preferably selected from (C1-8 alk(en)yl/aryl) carboxylate, (C1-8 alk(en)yl/aryl)sulphonate, sulphate, amide and  
 30 pyrolidon;

R is independently selected from H, a lower (C<sub>1</sub>-C<sub>8</sub>) alk(en)yl group and a hydrophillic functional group.

35

Preferably, E is carboxylic and R is H, (C1-8) lower alkyl or carboxylic.

Hydrophobic monomers are preferably selected from monomers of formula II:



wherein:

10  $R_{1,2}$  are independently selected from H, C3-C20 alk(en)yl, O-C<sub>1-10</sub> alkyl, (substituted) aryl, carboxylate or sulphonate esterified with C1-C10 alk(en)yl, C1-C10 alk(en)yl esters of sulphate and two R groups forming a ring structure (e.g. cyclohexene).

15

Preferably, at least 1 R is not H and, more preferably,  $R_1$  is styrene and  $R_{2,3}$  represent an H.

Preferably, the molar ratio between the hydrophillic and 20 the hydrophobic monomers in the polymer is from 5:1 to 1:5, preferably 3:1 to 1:3, more preferably 2:1 to 1:2.

The hydrophillic monomer is preferably selected from acrylic acid and substituted acrylic acids (eg. methacrylic 25 acid, maleic acid and half-ester thereof) crotonic and itaconic acids and other alkene carboxylic acids and their derivatives, carboxylated styrene, sulphonated styrene, ethylene sulphonic acid, and certain nitrogen-based monomers (eg. acrylamide, vinyl pyrrolidone) and mixtures 30 of such hydrophillic monomers.

The hydrophobic monomer is preferably selected from the group: styrene and substituted styrenes (eg. alpha-methyl styrene), alpha-olefins (eg. C<sub>12</sub>-alpha-olefin), vinyl ethers 35 (eg. butyl vinyl ether), allyl ethers (eg. butyl allyl

ether), unsaturated hydrocarbons (eg. ethylene, propylene, cyclohexene) and dienes (eg. 1,6 hexadiene), divinyl benzene, cyclohexadiene, esters of acrylic and substituted acrylic acids (eg. butyl acrylate, ethyl acrylate, methyl methacrylate), esters of other ethylenically unsaturated carboxylic acids (eg. of itaconic acid, crotonic acid), esters of ethylenically unsaturated sulphonic acids (eg. alkyl styrene sulphonates), alkyl and aryl vinyl sulphonates and sulphates, alkyl and aryl allyl sulphonates and sulphates.

Such hydrophobic moieties may also be introduced into the polymer by chain transfer agents and initiators (eg. mercaptans such as dodecyl mercaptans) and peroxides and azo initiators, eg. dilauryl peroxide, AIBN (azo-isobutyro-nitrile). Mixtures of hydrophobic monomers may also be used. A single monomer with both hydrophilic and hydrophobic properties may also be used.

One preferred polymer comprises acrylic acid and styrene, possibly with minor amounts of dodecylmercaptan (DDM). Acrylic acid is preferably present in an amount in the range 50-80% by wt, the styrene is preferably present in an amount in the range 20-50 % by weight and DDM is preferably present in an amount up to about 1% by weight, eg. 0.1-1% by weight.

A particularly preferred polymer comprises 50.81 wt% acrylic acid, 48.93 wt% styrene, 0.26 wt% DDM, with a molecular weight of about 1,000 and substantially no cross-linking. This polymer is found to be very versatile and to have a wide range of uses and applications.

Another preferred polymer comprises 54 wt% methacrylic acid and 46% styrene, with a molecular weight of about 100,000 and substantially no cross-linking. Such a polymer is found

to be hypochlorite-stable and to be an effective thickener in hypochlorite bleach.

For most applications the polymer is preferably  
5 substantially non cross-linked, although a degree of cross-linking can be tolerated.

The polymer typically has a molecular weight of between about 1,000 and 1,000,000. For many purposes polymers with  
10 molecular weights at the bottom end of the range are preferred, as these generally make better hydrotropes. For example, a polymer with a molecular weight of about 1000 is found to be very versatile and useful in a wide range of applications. Polymers with higher molecular weights, eg.  
15 about 100,000, also function well as hydrotropes and may additionally perform a thickening function which may be desirable in certain applications, eg. production of thickened compositions.

20 Preferably, the molecular weight of polymers according to the invention is at least 500, more preferably at least 750 and preferably at most 10,000, more preferably at most 5,000, most preferably at most 3,000, e.g. 1,000.

25 Suitable polymers can be readily made in conventional manner, eg. by emulsion or solution polymerisation, and are preferably in the form of low viscosity non-aqueous solutions or powders.

30 The polymer is present in an appropriate amount to achieve desired results, such as particular desired composition properties, and suitable amounts can be readily determined by experiment. Typically amounts in the range 0.1 to 15% by wt as active material are suitable, preferably 0.5 to 10%  
35 by wt.

Electrolyte material

Preferably, electrolyte material is incorporated in compositions according to the invention.

5 For the purpose of this invention electrolyte material is defined as material that dissociates at least for 10% by weight of the total amount of electrolyte upon dilution of 1g in 100ml of water at 25°C. The electrolyte material may include builder, bleach or other materials.

10

Preferably, the electrolyte material according to the invention is ionisable and water soluble. More preferably, the electrolyte material is an alkaline material, i.e. the salt form of the electrolyte has a pH in water at 25°C  
15 and 1 atm of higher than 7, preferably 7.5 or higher, more preferably 8.0 or higher.

In particular it is preferred that the electrolyte material is selected from salts (e.g. alkali metal) organic and  
20 mineral acids. Examples of such electrolyte material are phosphates (e.g. STP), silicates (eg. metasilicates, disilicates), hypochlorites, carbonates (e.g. bicarbonates and percarbonates), hydroxides, halides (e.g. chloride), sulphates (e.g. sulphate), sequestrants (e.g. ethylene-  
25 diamine-tetracetic acid and sodium nitrilotriacetate), citrates and borates (e.g. perborates). Equally, the corresponding acids can be used, as these generally turn into the effective salt form in the non-aqueous liquid product itself or immediately upon dilution in the wash  
30 solution.

Electrolyte is typically present in an amount of at least 0.5%, preferably 1.0%, more preferably 2% and preferably at most 60%, more preferably at most 50% by weight of the  
35 composition.

#### Non-Aqueous Liquid Phase

Composition of the present invention may comprise surfactant material, non-surfactant material, solvent material and other liquid material such as deflocculant  
5 material.

Compositions of the invention may comprise from 10 to 90% by weight of a non-aqueous liquid phase. Preferably the level of the liquid phase is at most 75%, or at most 70%  
10 and preferably, at least 20%, more preferably at least 30%.

Non-aqueous liquids to which the hydrotrope may be added contain a non-aqueous phase comprising a single surfactant or a mixture of surfactants selected from a wide range,  
15 including the following.

#### Surfactants

Detergent compositions according to the invention may  
20 comprise anionic, nonionic, cationic, amphoteric and/or zwitterionic surfactant material, preferably in levels of from 10 to 90% by weight of the composition.

Typical blends of surfactants include a nonionic and/or  
25 non-alkoxylated anionic and/or alkoxylated anionic surfactant. Cationic, zwitterionic and amphoteric surfactants may also be present in minor amounts as desired. These and other surfactants are described in "Surface Active Agents" Vol I, by Schwartz & Perry,  
30 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,  
35 2nd Edn., Carl Hanser Verlag, Munchen & Wien.

Compositions often and preferably comprise a liquid nonionic surfactant as major component. Nonionic detergent surfactants are well-known in the art. They normally consist of a water-solubilising polyalkoxylene (preferably  
5 from 3-10 ethoxy and/or propoxy groups) or a mono- or di-alkanolamide group in chemical combination with an organic hydrophobic group derived from, for example, fatty alcohols with from 9 to 15 carbon atoms (optionally branched, e.g. methyl branched), alkylphenols (preferably  
10 from 12 to 20 carbon atoms) in which the alkyl group contains from about 6 to about 12 carbon atoms, dialkylphenols in which each alkyl group contains from 6 to 2 carbon atoms, primary, secondary or tertiary aliphatic alcohols (or alkyl-capped derivatives thereof),  
15 monocarboxylic acids having from 10 to about 24 carbon atoms in the alkyl group and polyoxypropylenes.

Fatty acid mono- and dialkanolamides in which the alkyl group of the fatty acid radical contains from 10 to about  
20 20 carbon atoms and the alkyloyl group having from 1 to 3 carbon atoms are also common. In any of the mono- and dialkanolamide derivatives, optionally, there may be a polyoxyalkylene moiety joining the latter groups and the hydrophobic part of the molecule.

25

In all polyalkoxylene containing surfactants, the polyalkoxylene moiety usually consists of an average of from 2 to 20 groups of ethylene oxide, propylene oxide groups or mixtures thereof. The latter class includes those  
30 described in European Patent Specification EP-A-0,225,654, especially for use as all or part of the liquid phase.

Especially preferred are those ethoxylated nonionics which are condensation products of fatty alcohols with from 9 to  
35 15 carbon atoms condensed with 3 to 7 moles of ethylene oxide. Examples of those are the condensation products of

C11-13 alcohols with 3 or 7 moles of ethylene oxide. These may be used as the sole nonionic surfactant or in combination with those described in EP-A-0,225,654.

Suitable examples of such nonionics are Vista 1012-6.2, 5 which is a C<sub>10-12</sub> alcohol ethoxylated with on average 6.2 ethoxy groups, and Dobanol 25-3, which is a C<sub>10-15</sub> alcohol ethoxylated with on average 3 ethoxy groups.

Another class of suitable nonionics include the alkyl 10 saccharides (polyglycosides/oligosaccharides) and, in particular those described in the following patent specifications, US-A-3,640,998; US-A-3,346,558; US-A-4,223,129; EP-A-0,092,355; EP-A-0,099,183; EP-A-0,070,074; EP-A-0,070,075; EP-A-0,070,075; EP-A-0,070,076; 15 EP-A-0,070,077; EP-A-0,075,994; EP-A-0,075,995 and EP-A-0,075,996.

Mixtures of different nonionic detergent surfactants may also be used. Mixtures of nonionic detergent surfactants 20 with other detergent surfactants such as anionic, cationic or ampholytic surfactants and soaps may also be used.

Preferably, the level of nonionic surfactant is from 10 to 90% by weight of the composition, more preferably from 20 25 to 70% by weight of the composition and, most preferably, from 35 to 50% by weight of the composition.

#### Solvent Material

Solvent material may be included in compositions according 30 to the present invention and in particular materials as disclosed in our co-pending PCT application EP/94/01289, i.e. an ester of a C<sub>1-6</sub> carboxylic acid and/or poly-carboxylic acid and an alcohol selected from dihydric alcohols, ether alcohols and sterically hindered alcohols. 35 Preferably, the ester is present in amounts of from 0.01 to 50% by weight of the composition. A suitable ester material

is propyleneglycoldiacetate. Other examples are disclosed in GB-A-2,169,613, GB-A-2,177,716 and EP-A-413,616 (Colgate).

#### 5 Other Liquid Material

Other liquid material which may be present in the liquid phase include liquid bleach precursors such as for example glyceroltriacetate, solvent material, for example ethanol and dodecanol, and deflocculant material such as described  
10 in EP-A-0,266,199.

The level of liquid precursors is preferably 0 to 20% by weight, more preferably 0 to 10% by weight. The level of solvents, other than nonionic surfactants, is preferably  
15 from 0 to 20% by weight, more preferably 0 to 10%.

In principle, any material may be used as a deflocculant provided it fulfils the deflocculation test described in European Patent Specification EP-A-0,266,199 (Unilever).  
20 The capability of a substance to act as a deflocculant will partly depend on the solids/liquid phase combination. However, especially preferred are acids.

Deflocculants are preferably selected from Bronsted acids  
25 and Lewis acids. Examples thereof are transition metals, anhydrides, organic acids, inorganic mineral acids and salts,  $C_x-C_{20}$  fatty acids and salts,  $C_1-C_{10}$  alkanolic acids, substituted anhydrous alkali-metal aluminosilicate, alkyl, alkenyl aryl, aralkyl and aralkenyl sulphonic or carboxylic  
30 acids and salts and halogenated derivatives thereof, zwitterionic surfactants, anionic surfactants of the formula R-L-A-Y, as defined in EP-A-0,266,199, and compounds having an acidic -P-OH group. Preferably, deflocculants in the acid form are used.

Deflocculant material, if included, may be present at levels of from 0 to 15%, preferably at least 0.01 and most preferably at least 1% by weight. For most purposes, the amount of deflocculant material will be from 2 to 12 % by 5 weight, preferably 4 to 10% by weight based on the final composition.

#### Solid Particles

Composition according to the invention may be isotropic 10 (i.e. may not contain solid particles) or they may comprise solid (dispersed) particles in which case the solid phases may include one or more components selected from abrasives, bleaches, bleach catalysts, colorants, bleach precursors, builders, dispersants, enzymes, fluorescers, opacifying 15 agents, pigments, solid surfactants and mixtures thereof.

Preferably, compositions according to the invention contain from 0 to 90% (or even up to 95 or up to 100% in case of a solid composition) by weight of a solid phase. Preferably, 20 the level of the solid phase is at least 10%, more preferably at least 20%. Preferably, at most 80%, more preferably at most 70%, in particular at most 60%.

Usually (at least part of) the particle size of the solid 25 phase in terms of  $D(3,2)$  will be less than 500, preferably not more than  $250\mu\text{m}$ , more preferably not more than  $100\mu\text{m}$ . Preferably, the particle size is at least  $0.1\mu\text{m}$ .  $D(3,2)$  refers to average particle diameter, which is an average surface weighted, volume/weight mean diameter.

30

#### Bleach system

Optionally compositions of the present invention may comprise a bleach system. Suitable bleaches for inclusion in the detergent compositions of the invention include 35 halogen, particularly chlorine bleaches, such as are provided in the form of alkali-metal hypohalites (e.g.

hypochlorites), as well as peroxygen bleach. When the compositions of the invention are to be used for fabric washing, peroxygen bleaches are preferred, for example, in the form of an inorganic peroxybleach, optionally in  
5 combination with one or more bleach activators.

Typical examples of suitable peroxy bleach are alkali-metal perborates, both tetrahydrates and monohydrates, alkali metal percarbonates, persulphates, persilicates,  
10 perphosphates and peracids. Perborate and percarbonate are preferred, in particular in the sodium form.

#### Activators

Compositions according to the invention comprise preferably  
15 additionally to the peroxygen bleach, a bleach activator, which makes the bleach more effective at lower temperatures, i.e. in the range from ambient temperature to about 60°C. Bleach activators may be selected from bleach precursors, bleach catalysts and mixtures thereof.

20

Peroxygen bleach such as sodium perborate, both the monohydrate and the tetrahydrate, acts to release active oxygen in solution, and the precursor which is usually an organic compound having one or more reactive acyl residues  
25 which causes the formation of peroxy acids; the latter providing for more effective bleaching action at lower temperatures than the peroxybleach compound alone.

Precursors according to the invention include compounds  
30 with N- and O-acyl groups. Suitable classes include anhydrides, esters, imides and acylated derivatives of imidazoles and oximes, and examples of useful materials within these classes are disclosed in GB-A-1,586,789, GB-A-0,836,988, GB-A-0,864,798, GB-A-1,147,871, GB-A-2,143,231  
35 and GB-A-0,855,735 and GB-A-1,246,338. Specific O-acetylated precursor compounds include 2,3,3-tri-methyl

hexanoyl oxybenzene sulfonates, benzyl oxybenzene sulfonates and penta acetyl glucose. Particularly preferred precursor compounds are the N-,N,N1N1 tetra acetylated compounds of which tetra acetyl methylene diamine (TAMD),  
5 tetraacetyl ethylene diamine (TAED) and tetraacetyl hexylene diamine (TAHD) are preferred examples. The ratio of the peroxybleach to the precursor is from 20:1 to about 1:1. The preferred level of the peroxybleach compound in the composition is from 0 to 30% by weight. The preferred  
10 level of precursor is from 0 to 20% by weight of the composition.

Inclusion of bleach catalysts and, in particular, transition metal catalysts may also be advantageous. Such  
15 catalysts, optionally together with stabilisers, as hereinafter defined, can be used to activate peroxide compounds to make them more suitable for use for bleaching at lower temperatures, e.g. from 20 to 60°C. As stated above, such catalysts may be incorporated in the form of a  
20 particulate product according to the invention. Such catalysts, which only need be present in such detergent composition in small amounts such as from 0.005 to 5% by weight of the composition.

25 Bleach catalysts may include those based on metal ion delivered by simple salts such as Cu(II) sulphate. Preferred bleach catalysts are based on transition metal coordination complexes as has been described and defined in EP-A-0,458,397, EP-A-0,458,398, EP-A-0,522,817, EP-A-  
30 0,544,440, EP-A-0,544,490, EP-A-0,549,272, EP-A-0,549,271, EP-A-0,544,491, US-A-5,194,416, WO 93/25562, WO 94/00439, and WO 94/05422. These references are incorporated in the present application by reference.

35 Other compounds that may be used in compositions according to the present invention are oxygen transfer agents as

described and defined in EP-A-446,981, EP-A-453,003 and EP-A-446,982. These references are incorporated in the present application by reference.

5 It may also be desirable to include in the compositions a stabiliser for the bleach or bleach system, for example hydroxyethylidene-1,1-diphosphonic acid, ethylene diamine tetramethylene phosphonate and diethylene triamine pentamethylene phosphonate or other appropriate organic  
10 phosphonates or salts thereof, such as the Dequest® range of materials.

#### Builders

The detergency builders are those materials which  
15 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, the latter being preferred when  
20 environmental considerations are important.

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

Examples of phosphorus-containing builders are the water-soluble salts, especially alkali metal pyrophosphates, orthophosphates, polyphosphates and  
30 phosphonates. Examples of non-phosphorus-containing inorganic builders are water-soluble alkali metal carbonates, bicarbonates, borates, silicates, metasilicates, and crystalline and amorphous aluminosilicates.

Examples of organic builders include the alkali metal, ammonium and substituted ammonium, citrates, succinates, malonates, fatty acid sulphonates, carboxymethoxy succinates, ammonium polyacetates, carboxylates, 5 polycarboxylates, aminopolycarboxylates, polyacetyl carboxylates and polyhydroxysulphonates. Specific examples include salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, melitic acid, benzene polycarboxylic acids and citric acid.

10

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 15 co-polymers and their salts, such as those sold by BASF under the Sokalan<sup>®</sup> Trade Mark. Polyacrylates or their derivatives may also be useful for their anti-ashing properties.

20 Preferably, the level of builder materials is from 5 to 50% by weight of the composition, more preferably 10 to 40%, most preferably 15 to 35%.

#### Dispersants

25 The physical stability of non-aqueous liquid detergent compositions can be improved and/or setting problems can be minimised, if dispersants are used.

For the purpose of the present invention, a dispersant 30 material is a material, of which the main purpose is to stabilise the composition. Preferably, the dispersant is selected from hydrophobically modified dispersant materials, metal oxides as defined in EP-A-515,435 incorporated herein by reference (preferably having a bulk 35 density of 200 to 1000 g/l), finely divided clay material, aluminium tri-stearate and mixtures thereof.

A preferred material is hydrophobically modified (HM) silica containing dispersants are used as described and defined in EP-A-515,418 incorporated herein by reference.

5 Other Optional Ingredients

Other ingredients comprise those remaining ingredients which may be used in detergent compositions, such as fabric conditioning agents, abrasive material, enzymes, enzyme stabilising agents (if necessary), fluorescers, perfumes  
10 (including deoperfumes), micro-biocides, soil-suspending agents (anti-redeposition agent), corrosion inhibitors, and lather depressants.

Amongst the fabric conditioning agents which may be used,  
15 either in fabric washing liquids or in rinse conditioners, are fabric softening materials such as fabric softening clays, quaternary ammonium salts, imidazolinium salts, fatty amines and cellulases.

20 Abrasive are particularly preferred for incorporation in hard surface cleaners (liquid abrasive cleaners).

Enzymes which can be used in compositions according to the present invention include proteolytic enzymes (protease),  
25 amylolytic enzymes (amylase), lipolytic enzymes (lipases) and cellulolytic enzymes (cellulase). The preferred level of enzyme materials is from 0.01 to 5% by weight of the composition.

30 The total amount of the fluorescent agent or agents used in a composition is generally from 0.02 to 2% by weight.

When it is desired to include anti-redeposition agents in the liquid detergent compositions, the amount thereof is  
35 normally from about 0.1% to about 5% by weight, preferably

from about 0.2% to about 2.5% by weight of the total composition.

#### Product Form

5 Compositions according to the present invention 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)  
10 either by hand or mechanical means, as well as in the form of specialised cleaning products, such as for surgical apparatus or artificial dentures.

Preferably compositions of the invention are formulated as  
15 agents for washing and/or conditioning of fabrics and then the compositions 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,  
20 enzymes, bleaches, builders, buffers, 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.

25

For the washing of fabrics, preferably an aqueous liquor containing 0.1 to 10 %, more preferably 0.2 to 2%, of the non-aqueous detergent composition of the invention is used.

#### 30 Processing

During manufacture, it is preferred that all equipment and raw materials should be dry and (in the case of hydratable salts) in a low hydration state, e.g. anhydrous phosphate builder, sodium perborate monohydrate and dry calcite  
35 abrasive, where these are employed in the composition. In a preferred process for preparing non-aqueous liquids, the

dry, substantially anhydrous solids are blended with the liquid phase in a dry vessel. If deflocculant materials are used, these should preferably -at least partly- be mixed with the liquid phase, prior to the addition of the solids.

5 This blend is passed through a grinding mill or a combination of mills to achieve a  $D(3,2)$  particle size of between 0.1 to 100 microns. A preferred combination of such mills is a colloid mill followed by a horizontal ball mill. Of course particulate material already having the desired

10 particle size need not be subjected to this procedure.

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

15 ingredients. It is therefore highly desirable to mix any heat sensitive ingredients such as perfumes, enzymes and bleach components, 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

20 minor) ingredients and optionally, at any other stage of the process.

The present invention further relates to a method of preparing a non-aqueous detergent composition comprising a

25 polymeric hydrotrope, wherein the polymeric hydrotrope is added to the composition in a form comprising 25% or less by weight of water, preferably less 20% or less, more preferably 15% or less, most preferably 10% or less, in particular substantially non-aqueous.

30

Preferably, in case of a non-aqueous liquid, the non-aqueous phase further comprises ingredients selected from abrasives, bleaches, bleach catalysts, bleach precursors, corrosion inhibitors, dispersants, enzymes, fabric

35 softening agents, microbiocides, soil-suspending agents,

solid surfactants and mixtures thereof and preferably at a level of from 0.01 to 90% by weight of the composition.

The polymeric hydrotrope can either be added as solid particles that are freeze-dried (less than 5% by weight of water), or spray-dried (5-15% water) or, preferably, in the form of a non-aqueous solution or dispersion, e.g. in non-ionic surfactant material or in a solvent material.

10 The following examples are intended to further illustrate and describe the invention and are not intended to limit the invention in any way.

EXAMPLESExample 1 - gelling test

10ml product was magnetically stirred, water was added and  
5 the viscosity visually determined.

## Example 1.1 - Soda

Two compositions (A and 1) were prepared with 10g Vista  
1012-62 and Dobanol 25-3 (weight ratio 55/45) mixed with 2g  
10 soda. The nonionic of composition 4 additionally contained  
2% of Narlex H100 polymer (PPE 1269, a Acrylic  
Acid/Styrene/DDM polymer, ex National Starch Chemical  
Company), hereafter the Narlex polymer. Composition 1  
showed less gelling in the gelling test than composition A.

15

## Example 1.2 - STP

Two compositions (B and 2) were prepared with 10g Vista  
1012-62 and Dobanol 25-3 (weight ratio 55/45) mixed with 2g  
STP. The nonionic of composition 2 additionally contained  
20 2% of the Narlex polymer. Composition 2 showed less gelling  
in the gelling test than composition B.

## Example 1.3 - SMS

Two compositions (C and 3) were prepared with 10g Vista  
25 1012-62 and Dobanol 25-3 (weight ratio 55/45) mixed with 2g  
SMS. The nonionic of composition 3 additionally contained  
2% of the Narlex polymer. Composition 3 showed less gelling  
in the gelling test than composition C.

## 30 Example 1.4 - Percarbonate

Two compositions (D and 4) were prepared with 10g Vista  
1012-62 and Dobanol 25-3 (weight ratio 55/45) mixed with 2g  
percarbonate. The nonionic in composition 4 additionally  
contained 2% of the Narlex polymer. Composition 4 showed  
35 less gelling in the gelling test than composition D.

Example 1.5 - Soda/Percarbonate

Four compositions (E and 5-7) were prepared with 10g Vista 1012-62 and Dobanol 25-3 (weight ratio 55/45) mixed with 2g soda (compositions E and 5) or 2g percarbonate (composition 5 6 and 7). Composition 7 additionally contained 1g soda.

Compositions 5-7 all contained 2% of the Narlex polymer of Example 1.1. Composition 7 showed the lowest gelling, followed by composition 5, followed by composition 6 and composition E showed the worst gelling behaviour.

10

Example 1.6 - Soda/STP

Four compositions (8-11) were prepared with 10g Vista 1012-62 and Dobanol 25-3 (weight ratio 55/45) mixed with 2g soda and 2% of the Narlex polymer. Compositions 8-10 all

15 contained 1g soda. Composition 9 further contained 2g STP.

Composition 10 further contained 0.5g Sodium citrate.

Composition 11 contained 2g STP. All compositions showed low gelling behaviour.

20

Example 1.7 - Soda & Vista 1012-5.5

Two compositions (F and 12) were prepared containing 10g Vista 1012-5.5 and 2g soda. Composition 12 additionally contained 2% of the Narlex polymer of Example 1.1 and had

25 far lower gelling behaviour than composition F.

Example 1.8 - Soda & Dobanol 25-3

Two compositions (G and 13) were prepared containing 10g Dobanol 25-3 and 2g soda. Composition 13 additionally

30 contained 4% of the Narlex polymer and had far lower gelling behaviour than composition F (that showed lump formation).

Example 1.9 - Polymeric hydrotrope without salts

35 Four compositions were prepared (H and 14-16) were prepared with Vista 1012-62 with 0, 1, 2 and 4% of the Narlex

polymer, respectively. Composition 16 showed the lowest viscosity, followed by composition 15, followed by composition 14. Composition H had the highest viscosity in the gelling test.

5

Comparative Example 1.10 - SXS

Two compositions (I and J) were prepared with Vista 1012-62 and Dobanol 25-3 (40/60 weight ratio) and 2g soda.

Composition J additionally contained 6% Eltesel SXS 40.

10 Both compositions showed the same high gelling behaviour.

Example 1.11 - STP

Composition 2 was prepared without polymer (K) and with 1% of the Narlex polymer of Example 1.1 (17). Composition 17

15 showed very low gelling compared with composition K.

Example 1.12 - Sodium citrate & Dobanol 25-3

Two compositions (L and 18) were prepared with 10g Dobanol 25-3 mixed with 2g Sodium citrate. The nonionic of

20 composition 18 additionally contained 2% of the Narlex polymer. Composition 18 showed less gelling in the gelling test than composition L.

Example 1.13 - Magnesium Sulphate & Dobanol 25-3

25 Two compositions (M and 19) were prepared with 10g Dobanol 25-3 mixed with 2g Magnesium Sulphate. The nonionic of composition 19 additionally contained 2% of the Narlex polymer. Composition 19 showed less gelling in the gelling test than composition M.

30

Example 1.12 - Sodium EDTA & Dobanol 25-3

Two compositions (N and 20) were prepared with 10g Dobanol 25-3 mixed with 2g Sodium EDTA. The nonionic of composition 20 additionally contained 2% of the Narlex polymer.

35 Composition 20 showed less gelling in the gelling test than composition N.

Example 2 - dissolution test

The following compositions were made by adding the ingredients in the order listed. After colloid milling, the compositions were ball-milled after addition of 5 perborate/metasilicate. The resulting compositions have a D(3,2) particle size of from 1-15 $\mu$ m.

<u>Composition 21</u>		<u>(in % by weight)</u>
	Nonionic mix 1)	46.4
10	LAS acid	7.0
	Sodium Carbonate	21.0
	Calcium Carbonate	7.0
	Hydrophobed silica	4.2
	Minors	1.7
15	Perborate	12.2

1) Vista 1012-6.2 and Dobanol 25-3 in 55/45 weight ratio

<u>Composition 22</u>		<u>(in % by weight)</u>
20	Nonionic mix 1)	40.0
	LAS acid	3.1
	Minors	10.9
	Sodium metasilicate	46.0

25

<u>Composition 23</u>		<u>(in % by weight)</u>
	Nonionic mix 1)	39.8
	Sodium carbonate	18.0
	LAS acid	6.0
30	Calcium carbonate	6.0
	Hydrophobed silica	4.0
	Sodium perborate	10.5
	Solvent	10.0
	Minors	5.7

35

Dissolution test

1 gram of product was put in a 100ml beaker that was put in a large 3 liter beaker filled with 2.5 litre water of 20°C and magnetically stirred at 350 rpm. The conductivity (in 5 %) of the water was determined over time.

## Example 2.1

Three compositions (O, 24 and 25) were prepared according to composition 21 with respectively 0, 1 and 2% of the 10 Narlex polymer. Composition 25 showed the best dissolution followed by composition 24.

## Example 2.2

Three compositions (P, 26 and 27) were prepared according 15 to composition 22 with respectively 0, 1 and 2% of the Narlex polymer. Composition 27 showed the best dissolution followed by composition 26.

## Example 2.3

20 Composition 23 was prepared and 25% by weight of water was added, whereafter the composition was stirred homogeneously. The composition was prepared without polymer (Q) and with 1% of the Narlex polymer of Example 1.1 (Composition 28). Both compositions were tested in the 25 above dissolution test. After 4 minutes, 83% of Composition 28 was dissolved, whereas only 47% of composition Q was dissolved.

30 Example 3 - Dispersion test

1 gram of product (a spot of about 4 cm diameter) was put on a standard CSG test cloth. The cloth was wetted and mounted on a sample jar that was put in a 3 litre beaker containing 2.5 liters of water of 20°C. About 3 cm above 35 the cloth a six blade stirrer (12 cm diameter) was placed

that stirred with 70rpm. The time for complete dispersion of the product from the test cloth was determined.

#### Example 3.1

5 Composition 21 was prepared without polymer (R), with 1% Narlex polymer (29) and with 2% of the Narlex polymer (30). Composition R was dispersed after 37 minutes, whereas composition 29 was dispersed after 23 minutes and composition 30 after 13 minutes.

10

#### Example 3.2

Composition 21 with 10% additional nonionic mix was prepared without polymer (S) and with 1% of Narlex polymer (31). Composition S was dispersed after 35 minutes, whereas  
15 composition 31 was dispersed after 16 minutes.

#### Example 3.3

Composition 23 was prepared without polymer (T) and with 1% Narlex polymer (32). Composition T was dispersed after 29  
20 minutes, whereas composition 32 was dispersed after 22 minutes.

#### Example 4 - Dispensing test

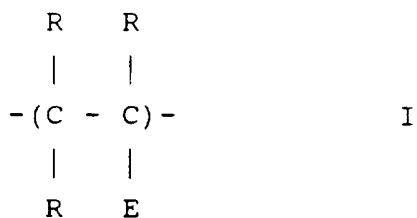
25 Composition 22 was prepared without polymer (U) and with 1% additional Narlex polymer (33). Composition 33 dispenses better in a system involving three-way valve as disclosed in the figure of EP-A-480,490 than composition U.

CLAIMS

1. Non-aqueous liquid detergent composition comprising a non-aqueous liquid phase, wherein the composition comprises  
 5 a polymeric hydrotrope comprising hydrophillic and hydrophobic monomers.

2. Composition according to claim 1, wherein the hydrophillic monomers is of formula I:

10



15

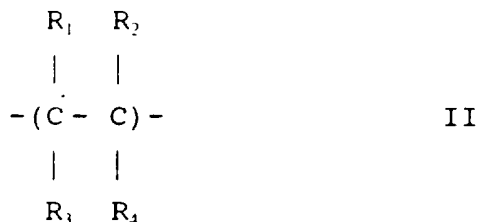
wherein:

E is a hydrophillic functional groups, preferably selected from (alkyl/aryl)carboxylic, (alkyl/aryl)sulphonate,  
 20 sulphate, amide and pyrrolidone;

R is independently selected from H, a lower (C<sub>1</sub>-C<sub>8</sub>) alk(en)yl group and a hydrophillic functional group; and

hydrophobic monomers selected from monomers of formula II:

25



30

wherein:

R<sub>1,4</sub> are independently selected from H, C<sub>3</sub>-C<sub>20</sub> alk(en)yl, O-C<sub>1,10</sub> alkyl, (substituted) aryl, a carboxylic or sulphonic  
 35 acid group that is esterified with C<sub>1</sub>-C<sub>10</sub> alk(en)yl, C<sub>1</sub>-C<sub>10</sub>

alk(en)yl esters of sulphate and two R groups forming a ring structure (e.g. cyclohexene).

3. Composition according to claims 1-2, wherein the  
5 hydrophillic monomer is selected from acrylic acid, substituted acrylic acid, crotonic and itaconic acids and other alkene carboxylic acids and their derivatives, carboxylated styrene, sulphonated styrene, ethylene  
10 sulphonic acid, acrylamide, vinyl pyrrolidone and mixtures of such hydrophillic monomers.

4. Composition according to claims 1-3, wherein the  
hydrophobic monomer is selected from styrene and  
substituted styrenes alpha-olefins, vinyl ethers, allyl  
15 ethers, unsaturated hydrocarbons, dienes, divinyl benzene, cyclohexadiene, esters of acrylic and substituted acrylic acids, esters of other ethylenically unsaturated carboxylic acids, esters of ethylenically unsaturated sulphonic acids, alkyl and aryl vinyl sulphonates and sulphates, alkyl and  
20 aryl allyl sulphonates and sulphates.

5. Composition according to claims 1-4, wherein the composition further comprises an electrolyte material.

25 6. Composition according to claims 1-5, further comprising solid dispersed particles.

7. Composition comprising from 10 to 90% by weight of surfactant material and further comprising a polymeric  
30 hydrotrope.

8. Method of preparing a non-aqueous detergent composition comprising a polymeric hydrotrope, wherein the polymeric hydrotrope is added to the composition in a form comprising  
35 25% or less by weight of water.

9. Method of applying a composition, by mixing the composition with a polymeric hydrotrope, whereafter the composition with the polymer is applied to a washing machine.

5

10. Method of mixing a composition with water, wherein the composition is prepared by mixing a surfactant with a polymeric hydrotrope, whereafter the composition is mixed with water.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 95/04723

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 6 C11D17/00 C11D3/37

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 6 C11D

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)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 534 298 (HENKEL KGAA. ) 31 March 1993 see page 5, line 49 - line 54 see claims 1-4,12 ---	1-7
X	EP,A,0 381 261 (UNILEVER NV. ) 8 August 1990 see page 4, line 21 - line 46 see claims 1-7 ---	1-7
X	EP,A,0 510 580 (NATIONAL STARCH AND CHEMICAL INVESTMENT HOLDING CORP. ) 28 October 1992 see the whole document --- -/--	1-4,7

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  <b>13 March 1996</b>	Date of mailing of the international search report  <b>27.03.1996</b>
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Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Authorized officer  <b>Serbetsoglou, A</b>
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INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 95/04723

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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 Intern: al Application No  
 PCT/EP 95/04723

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