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

(54) **Title:** DETERGENT COMPOSITIONS

(57) **Abstract:** AbstractThe invention relates to the use of a water-soluble random copolymer of vinyl pyrrolidone and vinyl acetate in a laundry detergent composition to improve the oily soil detergency of the composition. The copolymer preferably contains from 50 to 70 mole% of vinyl pyrrolidone monomer units and from 30 to 50 mole% of vinyl acetate units. The copolymer is suitably used in amounts of from 0.5 to 3 wt%, preferably from 1 to 2 wt%. Preferably the detergent composition contains a sulphonate anionic detergent such as linear alkylbenzene sulphonate.

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DETERGENT COMPOSITIONSTECHNICAL FIELD

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The present invention relates to laundry detergent compositions containing certain vinyl pyrrolidone copolymers. The compositions exhibit improved detergency on oily soils as well as reduced soil redeposition during the wash.

10

BACKGROUND AND PRIOR ART

Polyvinyl pyrrolidone and some related polymers are known ingredients of laundry detergent compositions, providing the benefit of reduced dye transfer between fabrics in a mixed load.

15

Laundry detergent compositions containing polyvinyl pyrrolidone as a dye transfer inhibitor are disclosed, for example, in WO 92 18597A, WO 94 03567A, WO 95 03390A, WO 95 17496A, WO 95 27028A and WO 95 34627A (Procter & Gamble), and WO 94 06354A, WO 94 24249A and WO 97 03166A (Henkel).

25

GB 1 354 498 (Unilever) discloses laundry detergent compositions containing vinyl pyrrolidone/vinyl acetate copolymers as antiredeposition agents. During the wash, the polymers effectively prevent or reduce redeposition onto washed fabrics of soil suspended in the wash liquor. Polyvinyl pyrrolidone itself is stated to be ineffective.

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DE 2 165 898A (Henkel) also discloses the antiredeposition benefits of these copolymers.

It has now been discovered that vinyl pyrrolidone/vinyl
5 alcohol copolymers are also effective to enhance oily soil detergency, especially in detergent compositions containing anionic surfactants, more especially alkylbenzene sulphonate.

10 DEFINITION OF THE INVENTION

The present invention provides a the use of a water-soluble random copolymer of vinyl pyrrolidone and vinyl acetate in a laundry detergent composition comprising an organic
15 surfactant and optionally a detergency builder to improve the oily soil detergency of the composition.

The random vinyl pyrrolidone/vinyl acetate polymer

20 The random copolymer of vinyl pyrrolidone/vinyl acetate used in accordance with the present invention will be referred to hereinafter for convenience as a PVP/PA copolymer.

The PVP/PA copolymer preferably contains not more than
25 30 mole% of vinyl acetate (VA) monomer units. Copolymers containing higher proportions of VA units are less water-soluble and therefore less preferred. More preferably the copolymer contains not more than 50 mole% of VA units.

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Most preferably, the copolymer contains from 50 to 70 mole% of vinyl pyrrolidone (VP) monomer units and from 30 to 50 mole% of VA units.

- 5 The copolymer preferably has a molecular weight within the range of from 10 000 to 100 000, more preferably from 25 000 to 75 000.

A wide selection of PVP/PA copolymers is available from
 10 International Speciality Products (ISP). These are supplied as solutions (clear viscous liquids) in ethanol, isopropanol or water, or as solid (white powder). Some examples are shown in the table below.

Grade	Solvent or form	Mole ratio VP:VA	Approximate molecular weight
E-335	Ethanol	30:70	28 800
E-535		50:50	36 700
E-635		60:40	38 200
E-735		70:30	56 700
I-335	Isopropanol	35:65	12 700
I-535		50:50	19 500
I-735		70:30	22 300
W-735	Water	70:30	27 300
S-630	Solid	60:40	51 000

15

The solutions have a solids content of approximately 50 wt%.

PVP/PA copolymers are also available from BASF as the Luviskol (Trade Mark) VA series.

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Luviskol VA	Solvent or form	Mole ratio VP:VA
28E	Ethanol	20:80
37E		30:70
55E		50:50
64E		60:40
28I	Isopropanol	20:80
37I		30:70
55I		50:50
64I		60:40
64W	Water	60:40
73W		70:30
64 powder	Solid	60:40

These polymers are marketed as film-formers for cosmetic and personal products, and for use in hair styling formulations
5 such as mousses, gels and setting lotions.

The laundry detergent composition

In a laundry detergent composition in accordance with the
10 invention, the polymer is present in an amount sufficient to enhance oily soil detergency. Suitably the polymer is present in an amount of from 0.5 to 3 wt%, preferably from 1 to 2 wt%.

15 The detergent composition may suitably comprise:

- (a) from 5 to 60 wt%, preferably from 10 to 40 wt%, of organic surfactant,

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- (b) optionally from 5 to 80 wt%, preferably from 10 to 60 wt%, of detergency builder,
(c) from 0.5 to 3 wt%, preferably from 1 to 2 wt%, of the random copolymer of vinyl pyrrolidone and vinyl acetate,
5 (d) optionally other detergent ingredients to 100 wt%.

The organic surfactant

The detergent composition in accordance with the invention
10 may contain any organic surfactants (detergent-active compounds) suitable for incorporation into laundry detergent compositions.

Detergent-active compounds (surfactants) may be chosen from
15 soap and non-soap anionic, cationic, nonionic, amphoteric and zwitterionic detergent-active compounds, and mixtures thereof. Many suitable detergent-active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes
20 I and II, by Schwartz, Perry and Berch. The preferred detergent-active compounds that can be used are soaps and synthetic non-soap anionic and nonionic compounds. The total amount of surfactant present is suitably within the range of from 5 to 60 wt%, preferably from 5 to 40 wt%.

25

Anionic surfactants are well-known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly linear alkylbenzene sulphonates having an alkyl chain length of C₈-C₁₅; primary and secondary
30 alkylsulphates, particularly C₈-C₂₀ primary alkyl sulphates;

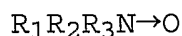
- 6 -

alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

- 5 Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C₈-C₂₀ aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C₁₀-C₁₅ primary and secondary aliphatic
- 10 alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).
- 15 Cationic surfactants that may be used include quaternary ammonium salts of the general formula $R_1R_2R_3R_4N^+ X^-$ wherein the R groups are long or short hydrocarbyl chains, typically alkyl, hydroxyalkyl or ethoxylated alkyl groups, and X is a solubilising anion (for example, compounds in which R₁ is a
- 20 C₈-C₂₂ alkyl group, preferably a C₈-C₁₀ or C₁₂-C₁₄ alkyl group, R₂ is a methyl group, and R₃ and R₄, which may be the same or different, are methyl or hydroxyethyl groups); and cationic esters (for example, choline esters).
- 25 Amphoteric surfactants and/or zwitterionic surfactants may also be present.

Preferred amphoteric surfactants are amine oxides. These are materials of the general formula

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wherein R_1 is typically a C_8 - C_{18} alkyl group, for example,
5 C_{12} - C_{14} alkyl, and R_2 and R_3 , which may be the same or
different, are C_1 - C_3 alkyl or hydroxyalkyl groups, for
example, methyl groups. The most preferred amine oxide is
coco dimethylamine oxide.

10 Preferred zwitterionic surfactants are betaines, and
especially amidobetaines.

Preferred betaines are C_8 - C_{18} alkyl amidoalkylbetaines, for
example, coco amidopropyl betaine (CAPB).

15

According to a preferred embodiment of the invention, the
composition comprises a sulphonate anionic surfactant.
According to an especially preferred embodiment, the
sulphonate anionic surfactant comprises linear alkylbenzene
20 sulphonate (LAS).

An especially favourable interaction between LAS and the
PVP/VA copolymer has been observed, giving improved primary
detergency on difficult oily soils such as dirty motor oil.
25 Without being bound by theory, it is postulated that the
this benefit may be attributed to a reduction in the
critical micelle concentration (CMC) of the LAS.

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The known benefit of reduced redeposition of soil onto the washload during the wash (sometimes referred to as secondary detergency) is also observed.

- 5 Preferably, the compositions contains from 3 to 30 wt%, more preferably from 10 to 25 wt%, of LAS.

The optional detergency builder

- 10 Preferably, the detergent compositions in accordance with the invention also contain one or more detergency builders. The total amount of detergency builder in the compositions may suitably range from 5 to 80 wt%, preferably from 10 to 60 wt%.

- 15 Preferred builders are alkali metal aluminosilicates, more especially crystalline alkali metal aluminosilicates (zeolites), preferably in sodium salt form.

- 20 Zeolite builders may suitably be present in a total amount of from 5 to 60 wt%, preferably from 10 to 50 wt%.

The zeolites may be supplemented by other inorganic builders, for example, amorphous aluminosilicates, or layered silicates such as SKS-6 ex Clariant.

25

- The zeolites may be supplemented by organic builders, for example, polycarboxylate polymers such as polyacrylates and acrylic/maleic copolymers; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-,
30 di- and trisuccinates, carboxymethyloxysuccinates, carboxymethyloxymalonates, dipicolinates,

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hydroxyethyliminodiacetates, alkyl- and alkenylmalonates and succinates; and sulphonated fatty acid salts.

Alternatively, the compositions in accordance with the
5 invention may contain phosphate builders, for example, sodium tripolyphosphate.

Especially preferred organic builders are citrates, suitably used in amounts of from 1 to 30 wt%, preferably from 2 to 15 wt%; and acrylic polymers, more especially
10 acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt%, preferably from 1 to 10 wt%. Builders, both inorganic and organic, are preferably present in alkali metal salt, especially sodium salt, form.

15 According to a preferred embodiment of the invention, the detergency builder, which is present in an amount of from 5 to 80 wt%, preferably from 10 to 60 wt%, is selected from sodium tripolyphosphate, zeolites, sodium carbonate and mixtures thereof.

20

Other detergent ingredients

Detergent compositions in accordance with the invention may also suitably contain a bleach system. Preferably this will
25 include a peroxy bleach compound, for example, an inorganic persalt or an organic peroxyacid, capable of yielding hydrogen peroxide in aqueous solution.

Preferred inorganic persalts are sodium perborate monohydrate and tetrahydrate, and sodium percarbonate, the
30 latter being especially preferred. The sodium percarbonate may have a protective coating against destabilisation by

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moisture. The peroxy bleach compound is suitably present in an amount of from 5 to 35 wt%, preferably from 10 to 25 wt%.

The peroxy bleach compound may be used in conjunction with a
5 bleach activator (bleach precursor) to improve bleaching action at low wash temperatures. The bleach precursor is suitably present in an amount of from 1 to 8 wt%, preferably from 2 to 5 wt%. Preferred bleach precursors are
10 peroxycarboxylic acid precursors, more especially peracetic acid precursors and peroxybenzoic acid precursors; and peroxycarbonic acid precursors. An especially preferred bleach precursor suitable for use in the present invention is N,N,N',N'-tetracetyl ethylenediamine (TAED).

15 A bleach stabiliser (heavy metal sequestrant) may also be present. Suitable bleach stabilisers include ethylenediamine tetraacetate (EDTA), diethylenetriamine pentaacetate (DTPA), ethylenediamine disuccinate (EDDS), and the polyphosphonates such as the Dequests (Trade Mark),
20 ethylenediamine tetramethylene phosphonate (EDTMP) and diethylenetriamine pentamethylene phosphate (DETPMP).

The compositions in accordance with the invention may contain alkali metal, preferably sodium, carbonate, in order
25 to increase detergency and ease processing. Sodium carbonate may suitably be present in amounts ranging from 1 to 60 wt%, preferably from 2 to 40 wt%.

As previously indicated, sodium silicate may also be present. The amount of sodium silicate may suitably range
30 from 0.1 to 5 wt%. Sodium silicate, as previously

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indicated, is preferably introduced via the second base granule.

Powder flow may be improved by the incorporation of a small amount of a powder structurant. Examples of powder structurants, some of which may play other roles in the formulation as previously indicated, include, for example, fatty acids (or fatty acid soaps), sugars, acrylate or acrylate/maleate polymers, sodium silicate, and dicarboxylic acids (for example, Sokalan (Trade Mark) DCS ex BASF). One preferred powder structurant is fatty acid soap, suitably present in an amount of from 1 to 5 wt%.

Other materials that may be present in detergent compositions in accordance with the invention include antiredeposition agents such as cellulosic polymers; soil release agents; anti-dye-transfer agents; fluorescers; inorganic salts such as sodium sulphate; enzymes (proteases, lipases, amylases, cellulases); dyes; coloured speckles; perfumes; and fabric conditioning compounds. This list is not intended to be exhaustive.

Product form and preparation

The compositions in accordance with the invention may be of any suitable physical form, for example, particulates (powders, granules, tablets), liquids, pastes, gels or bars. According to one especially preferred embodiment of the invention, the detergent composition is in particulate form.

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Powders of low to moderate bulk density may be prepared by spray-drying a slurry, and optionally postdosing (dry-mixing) further ingredients. "Concentrated" or "compact" powders may be prepared by mixing and granulating processes, for example, using a high-speed mixer/granulator, or other non-tower processes.

Tablets may be prepared by compacting powders, especially "concentrated" powders.

10

Also preferred are liquid detergent compositions, which may be prepared by admixing the essential and optional ingredients in any desired order to provide compositions containing the ingredients in the requisite concentrations.

15

Incorporation of the PVP/VA copolymer

The polymers may be incorporated at any suitable stage in the manufacture of the compositions in accordance with the invention. As previously indicated, the polymers are commercially available both in solution form and in solid form.

20

For example, in the manufacture of spray-dried particulate compositions, polymer in powder or solution (preferably aqueous) form may be incorporated in the slurry. For non-tower particulates, polymer powder or solution may be easily introduced into mixing and granulating apparatus, either alone or in admixture with other solid or liquid ingredients as appropriate.

30

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EXAMPLES

The invention is further illustrated by the following Examples, in which parts and percentages are by weight
5 unless otherwise stated.

EXAMPLES 1 to 16, COMPARATIVE EXAMPLES A and B

10 Detergency benefits on dirty motor oil using model wash
liquors

Wash liquors containing 1 g/litre or 2.5 g/litre of a notional detergent composition (the "product") containing linear alkylbenzene sulphonate (LAS) and sodium carbonate
15 were prepared to the following general formulation:

Ingredient	Weight% in "product"	Weight% in 1 g/l wash liquor	Weight% in 2.5 g/l wash liquor
Sodium LAS	14.82	0.1482	0.3705
Sodium carbonate	11.50	0.1150	0.2785
Polymer (see below)	0, 0.20 or 0.80	0, 0.0020 or 0.0080	0, 0.0050 or 0.0200
Water	Balance	Balance	Balance

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The polymers used, all commercial products from ISP provided as 40 wt% solutions, were as follows:

Example	Trade name	VP/VA mole ratio	Solvent
1, 2, 9, 10	E535	50:50	ethanol
3, 4, 11, 12	E735	70:30	ethanol
5, 6, 13, 14	I535	50:50	isopropanol
7, 8, 15, 16	I735	70:30	isopropanol

5

Detergency on white cotton cloth soiled with dirty motor oil was assessed using a high throughput small scale wash method. The wash was carried out in water of 20° (French) hardness (Ca:Mg 2:1), at a temperature of 20°C for 20 minutes.

10

Whiteness before and after the wash was determined using the technique of colour change by image analysis using a greyness scale. The results are analogous to reflectance changes at 460 nm as measured by a reflectance spectrophotometer and are expressed as ΔR and $\Delta \Delta R$.

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Results at 1 g/litre "product" concentration

Example	Polymer	Polymer level in "product"	ΔR	$\Delta\Delta R$
A	none	0	81.76	0
1	E535	0.2	84.53	+ 2.77
2	E535	0.8	83.78	+ 2.02
3	E735	0.2	83.86	+ 2.10
4	E735	0.8	85.05	+ 3.29
5	I535	0.2	82.99	+ 1.23
6	I535	0.8	83.16	+ 1.40
7	E735	0.2	84.90	+ 3.14
8	E735	0.8	84.66	+ 2.90

5 Results at 2.5 g/litre "product" concentration

Example	Polymer	Polymer level in "product"	ΔR	$\Delta\Delta R$
B	none	0	82.04	0
9	E535	0.2	84.53	+ 2.49
10	E535	0.8	82.51	+ 0.47
11	E735	0.2	83.69	+ 1.65
12	E735	0.8	84.65	+ 2.61
13	I535	0.2	83.59	+ 1.55
14	I535	0.8	82.38	+ 0.34
15	E735	0.2	84.99	+ 2.95
16	E735	0.8	84.58	+ 2.54

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EXAMPLE 17, COMPARATIVE EXAMPLE CAssessment of soil removal and whiteness for polymer in a detergent powder composition

5

A detergent powder composition was prepared to the following formulation:

Ingredient	Weight%
Sodium linear alkylbenzene sulphonate	9.31
Nonionic surfactant	3.58
Sodium tripolyphosphate	21.32
Sodium carbonate	12.97
Sodium hydroxide	1.95
Sodium carboxymethyl cellulose	0.62
Sodium silicate (r = 2.4)	5.18
Fluorescers	0.13
Zeolite	1.24
Sodium perborate tetrahydrate	15.00
Tetraacetyl ethylenediamine	3.80
Enzymes (protease, lipase, amylase)	2.27
Antifoam granule	2.00
Dequest 2047	0.50
Granular sodium tripolyphosphate	10.00
Perfume	0.65
Citric acid	2.75
Water to	100.00

10

Soil removal was determined using samples of woven white cotton cloth soiled with two different model oily soils coloured to increase visibility: soya bean oil coloured with violet dye, and mechanical grease mixed with carbon

15 black.

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The assessments were carried out in tergotometers at a wash temperature of 20-25°C in water of 19° French hardness (Ca:Mg 2:1) at a liquor to cloth ratio of 8:1. The wash regime was as follows: 10 minute soak, 15 minute wash, two 2 minute rinses. The product dosage for the soak and wash was 4.4 g/l.

In Example 17, the wash liquor for both soak and wash additionally included a 70:30 PVP/VA polymer (W735 ex ISP as described above). The amounts used were:

Soak: 0.20 g/l, equivalent to 4 wt% of the product

Wash: 0.05 g/l, equivalent to 1 wt% of the product

Example C was a control without polymer.

Soil removal was measured by whole spectrum reflectance spectrophotometry and expressed as soil removal index (SRI), which is defined as

$$\text{SRI} = 100 - \Delta E$$

where ΔE is the difference between reflectance before and after the wash. A difference of 0.6 percentage units is considered statistically significant.

The SRI results were as shown in the Table below.

Soil	Example C	Example 17
Soya bean oil with violet dye	84.07	84.69
Mechanical grease/carbon black	51.24	57.08

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CLAIMS

- 1 Use of a water-soluble random copolymer of vinyl
pyrrolidone and vinyl acetate in a laundry detergent
5 composition comprising an organic surfactant and optionally
a detergency builder to improve the oily soil detergency of
the composition.
- 2 Use as claimed in claim 1, characterised in that the
10 copolymer contains not more than 30 mole%, preferably not
more than 50 mole%, of vinyl acetate monomer units.
- 3 Use as claimed in claim 2, characterised in that the
copolymer contains from 50 to 70 mole% of vinyl pyrrolidone
15 monomer units and from 30 to 50 mole% of vinyl acetate
units.
- 4 Use as claimed in any preceding claim, characterised in
that the copolymer has a molecular weight within the range
20 of from 10 000 to 100 000, preferably from 25 000 to 75 000.
- 5 Use as claimed in any preceding claim, characterised in
that the laundry detergent composition contains from 0.5 to
3 wt%, preferably from 1 to 2 wt%, of the copolymer.

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6 Use as claimed in any preceding claim, characterised in that the laundry detergent composition comprises:

(a) from 5 to 60 wt%, preferably from 10 to 40 wt%, of organic surfactant,

5 (b) optionally from 5 to 80 wt%, preferably from 10 to 60 wt%, of detergency builder,

(c) from 0.5 to 3 wt%, preferably from 1 to 2 wt%, of the random copolymer of vinyl pyrrolidone and vinyl acetate,

(d) optionally other detergent ingredients to 100 wt%.

10

7 Use as claimed in any preceding claim, characterised in that the organic surfactant comprises a sulphonate anionic surfactant.

15 8 Use as claimed in claim 7, characterised in that the organic surfactant comprises linear alkylbenzene sulphonate.

9 Use as claimed in claim 8, characterised in that the laundry detergent composition contains from 3 to 30 wt%,
20 preferably from 10 to 25 wt%, of linear alkylbenzene sulphonate.

10 Use as claimed in any preceding claim, characterised in that the laundry detergent composition comprises from 5 to
25 80 wt%, preferably from 10 to 60 wt%, of detergency builder selected from sodium tripolyphosphate, zeolites, sodium carbonate and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International Publication No

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/37 C11D1/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 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)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 21 65 898 A (HENKEL & CIE GMBH) 5 July 1973 (1973-07-05) cited in the application the whole document ---	1-10
A	GB 1 354 498 A (UNILEVER LTD) 5 June 1974 (1974-06-05) cited in the application the whole document ---	1-10
A	GB 1 536 136 A (UNILEVER LTD) 20 December 1978 (1978-12-20) the whole document ---	1-10
A	EP 0 350 449 A (CIBA GEIGY AG) 10 January 1990 (1990-01-10) claims; examples ---	1-9
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☒ 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

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INTERNATIONAL SEARCH REPORT

International Application No.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 23591 A (UNILEVER) 3 July 1997 (1997-07-03) claims; examples ---	1,6-10
A	WO 95 13354 A (PROCTER & GAMBLE) 18 May 1995 (1995-05-18) claims; examples ---	1,6-10
A	WO 98 54394 A (BLACK ROBERT H) 3 December 1998 (1998-12-03) the whole document ---	1,6,10
A	WO 95 23840 A (PROCTER & GAMBLE) 8 September 1995 (1995-09-08) page 1, line 26 -page 3, line 2; claims; examples ---	1,6-10
A	EP 0 372 291 A (HENKEL KGAA) 13 June 1990 (1990-06-13) the whole document -----	1,6-10

INTERNATIONAL SEARCH REPORT

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International Application No

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