

NEW SULPHONATED POLYESTERS AND THEIR USE
AS ANTISOILING AGENTS IN DETERGENT COMPOSITIONS
FOR RINSING, SOFTENING AND THE TREATMENT OF TEXTILES

The present invention relates to new water-
5 dispersible or water-soluble sulphonated polyesters, to
a process for their preparation and to their use as
antisoiling and/or antiredeposition agent and
optionally detergent in detergent compositions, in
rinsing, softening or antisoiling ("finishing")
10 treatment compositions, for washing with or without
pretreatment, rinsing, softening or the antisoiling
treatment of textiles, especially those polyester-
based.

According to the invention these are water-
15 dispersible or water-soluble sulphonated polyesters
characterized in that they are capable of being
obtained by esterification and/or transesterification
and polycondensation of a monomer composition based:

- on an unsulphonated diacidic monomer (A)
20 consisting of at least one dicarboxylic acid or
anhydride chosen from terephthalic, isophthalic and
2,6-naphthalenedicarboxylic acids or anhydrides or
their diesters, in a quantity corresponding to a molar
ratio $(A)/(A)+(SA)$ of the order of 95/100 to 60/100,
25 preferably of the order of 93/100 to 65/100

- on a sulphonated diacidic monomer (SA)

consisting of at least one sulphonated aromatic or
sulphonated aliphatic dicarboxylic acid or anhydride,
or their diesters, in a quantity corresponding to a
molar ratio $(SA)/(A)+(SA)$ of the order of 5/100 to
5 40/100, preferably of the order of 7/100 to 35/100,
it being possible for up to 50 mol%, preferably up to
30 mol%, of the quantity of unsulphonated diacidic
monomer (A) and/or of sulphonated diacidic monomer (SA)
to be replaced with a hydroxylated diacidic monomer
10 (HA) consisting of at least one hydroxylated aromatic
or aliphatic dicarboxylic acid or anhydride or a
diester of the said hydroxylated aromatic or aliphatic
dicarboxylic acid

- and on a polyol monomer (P) consisting of
15 at least one polyol chosen from ethylene glycol,
propylene glycol, diethylene glycol, dipropylene
glycol, glycerol, 1,2,4-butanetriol and 1,2,3-
butanetriol, in a quantity corresponding to a ratio of
number of OH functional groups of the polyol monomer
20 (P)/number of COOH functional groups or functional
group equivalents of the diacidic monomers
(A)+(SA)+(HA) of the order of 1.05 to 4, preferably of
the order of 1.1 to 3.5 and very particularly of the
order of 1.8 to 3

25 in that the sulphonated diacidic monomer (SA) consists
of at least one sulphonated aromatic dicarboxylic acid
or anhydride or of a mixture of sulphonated aromatic

acids or anhydrides and of sulphonated aliphatic acids or anhydrides or their diesters when the polyol monomer (P) does not contain any polyol other than a glycol or when the hydroxylated diacidic monomer (HA) is absent

5 and in that the said sulphonated polyesters exhibit

- a number molecular mass lower than 20 000,
- a sulphur weight content of the order of 0.5 to 10 %, preferably of the order of 1.2 to 8 %
- and a hydroxyl functional group content, expressed as

10 OH equivalent/kg of polymer, higher than 0.2.

The hydroxyl functional group contents are estimated by proton NMR; the measurement is carried out in dimethyl sulphoxide.

The number molecular masses are measured by

15 gel permeation chromatography in dimethylacetamide containing 10^{-2} N of LiBr, at 25°C. The results are expressed as polystyrene equivalents.

The elementary unit considered in the definition of the mole of monomer (A), (SA) or (HA) is

20 the COOH functional group in the case of the diacids or the COOH functional group equivalent in the case of the anhydrides or of the diesters.

The unsulphonated diacidic monomer (A) preferably consists of 50 to 100 mol%, very

25 particularly of 70 to 90 mol%, of terephthalic acid or anhydride or of one of its lower (methyl, ethyl, propyl, isopropyl, butyl) diesters and of 0 to 50 mol%,

very particularly from 10 to 30 mol%, of isophthalic acid or anhydride and/or of 2,6-naphthalenedicarboxylic acid or anhydride or of one of their lower (methyl, ethyl, propyl, isopropyl, butyl) diesters; the
5 preferred diesters are methyl diesters.

In the unsulphonated diacidic monomer (A) there may additionally be present minor quantities of aromatic diacids other than those mentioned above, such as ortho-phthalic acid, anthracene, 1,8-naphthalene,
10 1,4-naphthalene and biphenyl dicarboxylic acids or aliphatic diacids such as adipic, glutaric, succinic, trimethyladipic, pimelic, azelaic, sebacic, suberic, itaconic and maleic acids, etc. in the form of acid, anhydride or lower (methyl, ethyl, propyl, isopropyl,
15 butyl) diesters.

The sulphonated diacidic monomer (SA) has at least one sulphonic acid group, preferably in the form of an alkali metal (preferably sodium) sulphonate, and two acidic functional groups or acidic functional group
20 equivalents (that is to say an anhydride functional group or two ester functional groups) attached to one or a number of aromatic rings, when aromatic dicarboxylic acids or anhydrides or their diesters are involved, or to the aliphatic chain when aliphatic
25 dicarboxylic acids or anhydrides or their diesters are involved.

Among the sulphonated diacidic monomers (SA), there may be mentioned aromatic sulphonated

dicarboxylic acids or anhydrides such as
sulphoisophthalic, sulphoterephthalic, sulpho-ortho-
phthalic acids or anhydrides, 4-sulpho-2,7-
naphthalenedicarboxylic acids or anhydrides, sulpho-
5 4,4'-bis(hydroxycarbonyl)diphenyl sulphones,
sulphodiphenyldicarboxylic acids or anhydrides, sulpho-
4,4'-bis(hydroxycarbonyl)diphenylmethanes, sulpho-5-
phenoxyisophthalic acids or anhydrides or their lower
(methyl, ethyl, propyl, isopropyl, butyl) diesters and
10 sulphonated aliphatic sulphonated dicarboxylic acids or
anhydrides such as sulphosuccinic acids or anhydrides
or their lower (methyl, ethyl, propyl, isopropyl,
butyl) diesters. The preferred sulphonated diacidic
monomers (SA) are sulphoisophthalic and sulphosuccinic
15 acids or anhydrides and their methyl diesters and very
particularly dimethyl 5-sodiooxysulphonylisophthalate.

The hydroxylated diacidic monomer (HA) has at
least one hydroxyl group attached to one or a number of
aromatic rings when it is an aromatic monomer or to the
20 aliphatic chain when it is an aliphatic monomer.

Among the hydroxylated diacidic monomers (HA)
there may be mentioned 5-hydroxyisophthalic, 4-
hydroxyisophthalic, 4-hydroxyphthalic, 2-
hydroxymethylsuccinic, hydroxymethylglutaric and
25 hydroxyglutaric acids or anhydrides etc., or their
lower (methyl, ethyl, propyl, isopropyl, butyl)
diesters.

The polyol monomer (P) preferably used is

monoethylene glycol and/or glycerol.

The said water-soluble and/or water-dispersible sulphonated polyesters can be obtained by the usual esterification and/or transesterification and polycondensation processes, for example by an esterification and/or transesterification reaction, in the presence of a catalyst of esterification/transesterification of the polyol monomer (P) with the various diacidic monomers, each diacid being in the acid or anhydride form or in the form of one of its diesters, and polycondensation of the polyol esters at reduced pressure in the presence of a polycondensation catalyst.

According to a preferred method of preparation the said water-soluble and/or water-dispersible sulphonated polyesters are obtained by carrying out the following successive stages:

- a stage of transesterification (interchange) between, on the one hand, the sulphonated diacidic monomer (SA) in diester form and from 50 to 100 mol%, very particularly from 30 to 90 mol%, of the total quantity of the unsulphonated diacidic monomer (A), in diester form, and, on the other hand, a quantity of polyol monomer (P) corresponding to a ratio of number of OH functional groups of the polyol monomer (P)/number of COOH functional group equivalents of the said monomers (A) and (SA) in the form of diesters of the order of 1.05 to 4, preferably of the order of 1.1

to 3.5 and very particularly of the order of 1.8 to 3.0

- an optional stage of esterification between the possible remaining quantity of the unsulphonated diacidic monomer (A), in diacid or anhydride form, and
5 a quantity of polyol monomer (P) corresponding to a ratio of number of OH functional groups of the polyol monomer (P)/number of COOH functional groups of the unsulphonated diacidic monomer (A) in diacid or anhydride form of the order of 1.05 to 4, preferably of
10 the order of 1.1 to 3.5 and very particularly of the order of 1.8 to 3.0

- a polycondensation stage.

The diesters of the unsulphonated (A) and sulphonated (SA) dicarboxylic acids used in the
15 transesterification (interchange) stage are preferably methyl diesters.

The interchange stage is performed at a temperature higher than or equal to 130°C, preferably of the order of 140 to 220°C and very particularly of
20 the order of 180 to 220°C; at this temperature the methanol formed (in the preferred case of the methyl diesters) is removed from the reaction mixture preferably by distillation. This interchange operation is preferably carried out in the presence of a metallic
25 transesterification catalyst, especially a metal carboxylate such as manganese acetate, zinc acetate, cobalt acetate or calcium acetate, or of an organic or inorganic titanate such as butyl titanate, 2,2'-

nitrilotriethyl titanate (or titanium aminotriethanolate) or calcium titanate. The preferred catalysts are organic titanates; they are used in quantities of the order of at least 0.001 % by weight, expressed as titanium, preferably of the order of 0.002 % to 0.02 % by weight of titanium relative to the weight of reactants present.

The duration of the interchange operation is from 1 to 4 hours; it is generally of the order of 2 to 3 hours.

When more than 90 % of the theoretical quantity of methanol has been distilled the excess polyol is removed by raising the temperature of the reaction mixture to 230°C.

The esterification operation is carried out by adding to the reaction mixture the remaining fraction of the unsulphonated diacidic monomer (A), in diacid form, and of the polyol monomer (P) suspended beforehand, at a temperature corresponding to that of the end of the interchange temperature; the addition period is of the order of 1 hour.

This esterification operation is carried out at a temperature of the order of 230 to 280°C, preferably of the order of 250 to 260°C, in the presence of a catalyst of the same type as that for transesterification; the preferred catalysts are organic titanates; they are used in quantities of the order of at least 0.001 % by weight expressed as

titanium, preferably of the order of 0.002 % to 0.02 %
by weight of titanium relative to the weight of
reactants introduced at the esterification stage; the
reaction takes place with removal of water, which is
5 drawn off from the reactor at the same time as the
excess polyol.

The polycondensation operation is preferably
carried out at a temperature of the order of 230 to
280°C, preferably of the order of 240 to 260°C, in
10 another reactor preheated to this temperature and
gradually evacuated to a pressure which may be up to
10 Pa; a pressure reduction to approximately
10 millibars lasts of the order of 40 minutes.

The polycondensation operation takes place
15 with removal of polyol molecules. This operation is
stopped when the drive torque of the stirrer shaft
shows a value equivalent to approximately 0.5 to
5 newton metres for a reaction mass temperature of
250°C and a stirring rate of 80 revolutions/minute of
20 an anchor-shaped rotor in a 7.5-litre reactor; the
torquemeter employed is of Kyowa type, the measurement
range of which is between 0 and 100 newton metres.

The vacuum is next broken with nitrogen and
the polymer is poured into an ingot mould; after
25 cooling, the polymer is ground.

The preferred sulphonated polyesters are
capable of being obtained from

- terephthalic acid (A1) in (preferably

methyl) diester form and isophthalic acid (A2) in the form of diacid or anhydride, or terephthalic acid (A1) in (preferably methyl) diester form and a hydroxylated terephthalic or hydroxylated isophthalic acid (HA) in the form of diacid or anhydride, optionally mixed with isophthalic acid (A2) in the form of diacid or anhydride, in an (A1)/(A1)+(A2), (A1)/(A1)+(HA) or (A1)/(A1)+(HA)+(A2) molar ratio of the order of 100/100 to 50/100, preferably of the order of 90/100 to 70/100 [as monomer (A) or monomers (A) and (HA)]

- sulphisophthalic acid in (preferably methyl) diester form [as monomer (SA)]

- monoethylene glycol and/or glycerol [as polyol monomer (P)].

They may be prepared according to the preferred process described above, by carrying out the following successive stages:

- a stage of transesterification (interchange) between, on the one hand, the (preferably methyl) diester of terephthalic acid (A1) and the (preferably methyl) diester of sulphisophthalic acid (SA) and, on the other hand, monoethylene glycol and/or glycerol (P), the ratio of number of OH functional groups of (P)/number of COOH functional group equivalents of (A1)+(SA) being of the order of 1.05 to 4, preferably of the order of 1.1 to 3.5, and very particularly of the order of 1.8 to 3

- a stage of esterification between

isophthalic acid (A2) and/or hydroxy(iso- or
tere)phthalic acid (HA) and, on the other hand,
monoethylene glycol and/or glycerol (P), the ratio of
number of OH functional groups of (P)/number of COOH
5 functional groups of (A2) +/-or (HA) being of the order
of 1.05 to 4, preferably of the order of 1.1 to 3.5 and
very particularly of the order of 1.8 to 3

- a polycondensation stage.

The sulphonated polyesters forming the
10 subject of the invention are very particularly
advantageous as antisoiling and/or antiredeposition
agents and optionally detergents in detergent
compositions, in rinsing, softening or antisoiling
("finishing") treatment compositions for washing with
15 or without pretreatment, rinsing, softening or
antisoiling treatment of textiles, especially
polyester-based.

A further subject of the present invention is
detergent compositions containing of the order of 0.01
20 to 10 %, preferably of the order of 0.1 % to 5 % and
very particularly of the order of 0.2 to 3 %, relative
to the weight of the said compositions, of the said
sulphonated polyesters forming the subject of the
invention.

25 Another subject of the invention consists of
the use, as antisoiling agents in detergent
compositions for washing textile articles based
especially on polyester fibres, of water-dispersible or

water-soluble sulphonated polyesters capable of being obtained by esterification and/or transesterification and polycondensation of a monomer composition based:

- on an unsulphonated diacidic monomer (A)
5 consisting of at least one dicarboxylic acid or anhydride chosen from terephthalic, isophthalic and 2,6-naphthalenedicarboxylic acids or anhydrides or their diesters, in a quantity corresponding to a molar ratio $(A)/(A)+(SA)$ of the order of 95/100 to 60/100,
10 preferably of the order of 93/100 to 65/100
- on a sulphonated diacidic monomer (SA)
consisting of at least one sulphonated aromatic or sulphonated aliphatic dicarboxylic acid or anhydride, or their diesters, in a quantity corresponding to a
15 molar ratio $(SA)/(A)+(SA)$ of the order of 5/100 to 40/100, preferably of the order of 7/100 to 35/100, it being possible for up to 50 mol%, preferably up to 30 mol%, of the quantity of unsulphonated diacidic monomer (A) and/or of sulphonated diacidic monomer (SA)
20 to be replaced with a hydroxylated diacidic monomer (HA) consisting of at least one hydroxylated aromatic or aliphatic dicarboxylic acid or anhydride or a diester of the said hydroxylated aromatic or aliphatic dicarboxylic acid
- and on a polyol monomer (P) consisting of
25 at least one polyol chosen from ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, glycerol, 1,2,4-butanetriol and 1,2,3-

butanetriol, in a quantity corresponding to a ratio of number of OH functional groups of the polyol monomer (P)/number of COOH functional groups or functional group equivalents of the diacidic monomers

- 5 (A)+(SA)+(HA) of the order of 1.05 to 4, preferably of the order of 1.1 to 3.5 and very particularly of the order of 1.8 to 3

the said sulphonated polyesters exhibiting

- a number molecular mass lower than 20 000,
- 10 - a sulphur weight content of the order of 0.5 to 10 %, preferably of the order of 1.2 to 8 %
- and a hydroxyl functional group content, expressed as OH equivalent/kg of polymer, higher than 0.2.

Examples of monomers (A), (SA), (HA) and (P)

- 15 have already been mentioned above; the operating conditions for preparation of the said sulphonated polyesters are those or equivalent to those also described above.

The detergent compositions for washing
20 textile articles, especially based on polyester fibres, which are particularly advantageous in respect of their ecotoxicological properties, are those containing:

- of the order of 0.01 to 10 % by weight, preferably of the order of 0.1 to 5 % by weight, very
25 particularly of the order of 0.2 to 3 % by weight of a water-dispersible or water-soluble sulphonated polyester antisoiling agent described above

- and of the order of 3 to 40 % by weight,

preferably of the order of 5 to 35 % by weight, of at least one anionic surface-active agent chosen from the sulphates of C_5 - C_{24} saturated aliphatic alcohols optionally condensed with approximately 0.5 to 30 moles of ethylene oxide, not more than 5 % by weight of the said detergent composition being capable of consisting of another type of anionic surface-active agent with less advantageous ecotoxicological properties, such as C_1 - C_{18} alkylbenzenesulphonates.

Among the sulphates of optionally ethoxylated alcohols which may be used there may be mentioned the sulphates of unethoxylated C_8 - C_{18} (preferably C_{10} - C_{15}) alcohols, the sulphates of C_5 - C_{13} (preferably C_{10} - C_{13}) fatty alcohols condensed with approximately 1 to 30 (preferably 1 to 10 moles) of ethylene oxide, and the sulphates of C_{14} - C_{20} (preferably C_{14} - C_{18}) fatty alcohols condensed with approximately 4 to 30 moles (preferably 4 to 10 moles) of ethylene oxide.

Other additives of the type of those described below may be present in the detergent compositions besides the said sulphonated polyesters of the invention.

- SURFACE-ACTIVE AGENTS, in quantities corresponding to approximately 3-40 % by weight relative to the detergent composition, surface-active agents such as anionic surface-active agents

- alkyl ester sulphonates of formula $R-CH(SO_3M)-COOR'$,

- where R denotes a C_8-C_{20} , preferably $C_{10}-C_{16}$ alkyl radical, R' a C_1-C_6 , preferably C_1-C_3 alkyl radical and M an alkali metal (sodium, potassium, lithium) cation, substituted or unsubstituted ammonium (methyl-,
- 5 dimethyl-, trimethyl-, tetramethylammonium, dimethylpiperidinium etc.) or one derived from an alkanolamine (monoethanolamine, diethanolamine, triethanolamine etc.). Very particularly, the methyl ester sulphonates in which the radical R is $C_{14}-C_{16}$ may
- 10 be mentioned;
- alkyl sulphates of formula $ROSO_3M$, where R denotes a C_5-C_{24} , preferably $C_{10}-C_{18}$ alkyl or hydroxyalkyl radical, M denotes a hydrogen atom or a cation with the same definition as above, and their ethoxylated (EO)

15 and/or propoxylated (PO) derivatives containing on average from 0.5 to 30, preferably from 0.5 to 10 EO and/or PO units;

 - alkylamide sulphates of formula $RCONHR'OSO_3M$, where R denotes a C_2-C_{22} , preferably C_6-C_{20} alkyl radical, R' a

20 C_2-C_3 alkyl radical, M denoting a hydrogen atom or a cation with the same definition as above, and their ethoxylated (EO) and/or propoxylated (PO) derivatives containing on average from 0.5 to 60 EO and/or PO units;

 - salts of C_8-C_{24} preferably $C_{14}-C_{20}$, saturated or

25 unsaturated fatty acids, C_9-C_{20} alkylbenzenesulphonates, primary or secondary C_8-C_{22} alkyl sulphonates, alkylglycerol sulphonates, the sulphonated

- polycarboxylic acids described in GB-A-1 082 179,
paraffin sulphonates, N-acyl-N-alkyltaurates, alkyl
phosphates, isethionates, alkylsuccinamates,
alkylsulphosuccinates, sulphosuccinate monoesters or
5 diesters, N-acylsarcosinates, alkylglycoside sulphates
and polyethoxycarboxylates
the cation being an alkali metal (sodium, potassium,
lithium), a substituted or unsubstituted ammonium
residue (methyl-, dimethyl-, trimethyl-,
10 tetramethylammonium, dimethylpiperidinium etc.) or one
derived from an alkanolamine (monoethanolamine,
diethanolamine, triethanolamine etc.);
nonionic surface-active agents
- polyoxyalkylenated (polyethoxyethylenated,
15 polyoxypropylenated, polyoxybutylenated) alkylphenols
in which the alkyl substituent is C₆-C₁₂ and containing
from 5 to 25 oxyalkylene units; the examples which may
be mentioned are Tritons X-45, X-114, X-100 or X-102,
marketed by Rohm & Haas Co.;
20 - glucosamide, glucamide, glycerolamide;
- polyoxyalkylenated C₈-C₂₂ aliphatic alcohols
containing from 1 to 25 oxyalkylene (oxyethylene,
oxypropylene) units; examples which may be mentioned
are Tergitol 15-S-9, Tergitol 24-L-6 NMW marketed by
25 Union Carbide Corp., Neodol 45-9, Neodol 23-65, Neodol
45-7, Neodol 45-4 marketed by Shell Chemical Co. and
Kyro EOB marketed by the Procter & Gamble Co.;
- the products resulting from the condensation of

ethylene oxide the compound resulting from the condensation of propylene oxide with propylene glycol, such as the Pluronics marketed by BASF;

- the products resulting from the condensation of
5 ethylene oxide the compound resulting from the condensation of propylene oxide with ethylenediamine, such as the Tetronics marketed by BASF;

- amine oxides such as (C₁₀-C₁₈ alkyl)dimethylamine
oxides and (C₈-C₂₂ alkoxy)ethyldihydroxyethylamine
10 oxides;

- the alkylpolyglycosides described in US-A-4 565 647;

- C₈-C₂₀ fatty acid amides

- ethoxylated fatty acids

- ethoxylated fatty amides

15 - ethoxylated amines

cationic surface-active agents

- alkyltrimethylammonium halides

amphoteric and zwitterionic surface-active agents

- alkyltrimethylbetaines,

20 alkylamidopropyltrimethylbetaines,

alkyltrimethylsulphobetaines, the products of

condensation of fatty acids and of protein hydrolysates

- alkylamphoacetates or alkylamphodiacetates in which
the alkyl group contains from 6 to 20 carbon atoms.

25 - ADJUVANTS IMPROVING THE PROPERTIES OF THE SURFACE-
ACTIVE AGENTS ("BUILDER" AGENTS), in quantities
corresponding to approximately 5-50 %, preferably to
approximately 5-30 % by weight for the liquid detergent

formulations or to approximately 10-80 %, preferably 15-50 % by weight for the powder detergent formulations, builder agents such as inorganic ("builder") adjuvants

- 5 - alkali metal, ammonium or alkanolamine polyphosphates (tripolyphosphates, pyrophosphates, orthophosphates, hexametaphosphates)
- tetraborates or borate precursors
- silicates, in particular those which have an $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of the order of 1.6/1 to 3.2/1 and the lamellar
10 silicates described in US-A-4 664 839
- alkali or alkaline-earth metal carbonates (bicarbonates, sesquicarbonates)
- cogranulates of hydrated alkali metal silicates and
15 of alkali metal (sodium or potassium) carbonates rich in silicon atoms in Q2 or Q3 form, described in EP-A-488 868
- crystalline or amorphous alkali metal (sodium, potassium) or ammonium aminosilicates such as zeolites
20 A, P, X etc.; zeolite A of particle size of the order of 0.1-10 micrometres is preferred

organic ("builder") adjuvants

- water-soluble polyphosphonates (ethane 1-hydroxy-1,1-diphosphonates, methylenediphosphonate salts etc.)
- 25 - water-soluble salts of carboxylic polymers or copolymers or their water-soluble salts such as
 - polycarboxylate ethers (oxydisuccinic acid and its salts, tartrate monosuccinic acid and its salts,

tartrate disuccinic acid and its salts

- hydroxypolycarboxylate ethers
- citric acid and its salts, mellitic acid,

succinic acid and their salts

- 5 - salts of polyacetic acids

(ethylenediaminetetraacetates, nitrilotriacetates,

N-(2-hydroxyethyl)nitrilodiacetates)

- (C₅-C₂₀ alkyl)succinic acids and their salts (2-dodecenylsuccinates, laurylsuccinates)

- 10 - carboxylic polyacetal esters

- polyaspartic acid, polyglutamic acid and their salts

- polyimides derived from the polycondensation of aspartic acid and/or of glutamic acid

- 15 - polycarboxymethylated derivatives of glutamic acid or of other amino acids;

- BLEACHING AGENTS, in quantities of approximately 0.1-20 %, preferably approximately 1-10 % by weight, optionally in combination with BLEACHING ACTIVATORS, in

- 20 quantities of approximately 0.1-60 %, preferably of approximately 0.5-40 % by weight, agents and activators such as

bleaching agents

- 25 - perborates such as sodium perborate monohydrate or tetrahydrate

- peroxygen compounds such as sodium carbonate peroxyhydrate, pyrophosphate peroxyhydrate, urea peroxyhydrate, sodium peroxide, sodium persulphate

preferably used in combination with a bleaching activator generating a carboxylic peroxyacid in situ in the washing medium; among these activators there may be mentioned tetraacetylenethylenediamine,

5 tetraacetylmethylenediamine, tetraacetylglycoluryl, sodium p-acetoxybenzene sulphonate, pentaacetylglucose, octaacetyllactose etc.

- percarboxylic acids and their salts (called "percarbonates") such as magnesium monoperoxyphthalate
10 hexahydrate, magnesium meta-chloroperbenzoate, 4-nonylamino-4-oxoperoxybutyric acid, 6-nonylamino-6-oxoperoxycaproic acid, diperoxydodecanedioic acid, the nonylamide of peroxysuccinic acid and decyldiperoxysuccinic acid.

15 These agents may be used in combination with at least one of the antisoiling or antiredeposition agents mentioned below.

 Mention may also be made of nonoxygenated bleaching agents acting by photoactivation in the
20 presence of oxygen, agents such as sulphonated aluminium and/or zinc phthalocyanines

- other ANTISOILING AGENTS, in quantities of approximately 0.01-10 %, preferably approximately 0.1-5 % and very particularly of the order of 0.2-3 % by
25 weight, agents such as

- cellulose derivatives such as cellulose hydroxyethers, methyl cellulose, ethyl cellulose, hydroxypropyl methyl cellulose, hydroxybutyl methyl

cellulose

- polyvinyl esters grafted onto polyalkylene backbones, such as polyvinyl acetates grafted onto polyoxyethylene backbones (EP-A-219 048)

5 - polyvinyl alcohols

- polyester copolymers based on ethylene terephthalate and/or propylene terephthalate and polyoxyethylene terephthalate units, with an ethylene terephthalate and/or propylene terephthalate (number of

10 units)/polyoxyethylene terephthalate (number of units) molar ratio of the order of 1/10 to 10/1, preferably of the order of 1/1 to 9/1, the polyoxyethylene terephthalates exhibiting polyoxyethylene units which have a molecular weight of the order of 300 to 5000,
15 preferably of the order of 600 to 5000 (US-A-3 959 230, US-A-3 893 929, US-A-4 116 896, US-A-4 702 857, and US-A-4 770 666);

- the sulphonated polyester oligomers obtained by sulphonation of an oligomer derived from from

20 ethoxylated allyl alcohol, from dimethyl terephthalate and from 1,2-propylene diol, containing from 1 to 4 sulphonated groups (US-A-4 968 451)

- polyester copolymers based on propylene terephthalate and polyoxyethylene terephthalate units and ending in

25 ethyl or methyl units (US-A-4 711 730) or polyester oligomers ending in alkylpolyethoxy groups (US-A-4 702 857) or sulphopolyethoxy (US-A-4 721 580) or sulphocaroyl (US-A-4 877 896) anionic groups

- other ANTIREDEPOSITION AGENTS in quantities of approximately 0.01-10 % by weight for a powder detergent composition, of approximately 0.01-5 % by weight for a liquid detergent composition, agents such
- 5 as
- ethoxylated monoamines or polyamines, ethoxylated amine polymers (US-A-4 597 898, EP-A-11 984)
 - carboxymethyl cellulose
 - sulphonated polyester oligomers obtained by

10 condensation of isophthalic acid, of dimethyl sulphosuccinate and of diethylene glycol (FR-A-2 236 926)

 - polyvinylpyrrolidones
 - CHELATING AGENTS for iron and for magnesium, in

15 quantities of the order of 0.1-10 %, preferably of the order of 0.1-3 % by weight, agents such as

 - aminocarboxylates such as ethylenediaminetetraacetates, hydroxyethyl ethylenediaminetriacetates, nitrilotriacetates

20 - aminophosphonates such as nitrilotris(methylenephosphonates)

 - polyfunctional aromatic compounds such as dihydroxydisulphobenzenes;
 - POLYMERIC DISPERSING AGENTS, in a quantity of the

25 order of 0.1-7 % by weight, to control the calcium and magnesium hardness, agents such as

 - the water-soluble salts of polycarboxylic acids of molecular mass of the order of 2000 to 100 000,

- obtained by polymerization or copolymerization of ethylenically unsaturated carboxylic acids such as acrylic acid, maleic acid or anhydride, fumaric acid, itaconic acid, aconitic acid, mesaconic acid,
- 5 citraconic acid or methylenemalononic acid, and very particularly the polyacrylates of molecular mass of the order of 2 000 to 10 000 (US-A-3 308 067) and copolymers of acrylic acid and of maleic anhydride of molecular mass of the order of 5 000 to 75 000
- 10 (EP-A-66 915)
- polyethylene glycols of molecular mass of the order of 1000 to 50 000;
 - FLUORESCENCE AGENTS (BRIGHTENERS), in a quantity of approximately 0.05-1.2 % by weight, agents such as
 - 15 stilbene derivatives, pyrazoline, coumarine, fumaric acid, cinnamic acid, azoles, methinecyanines, thiophenes etc. ("The production and application of fluorescent brightening agents" - M. Zahradnik, published by John Wiley & Sons, New York - 1982);
 - 20 - FOAM-SUPPRESSOR AGENTS, in quantities which may range up to 5 % by weight, agents such as
 - C₁₀-C₂₄ monocarboxylic fatty acids or their alkali metal, ammonium or alkanolamine salts, fatty acid triglycerides
 - 25 - aliphatic, alicyclic, aromatic or heterocyclic saturated or unsaturated hydrocarbons such as the paraffins and waxes
 - N-alkylaminotriazines

- monostearyl phosphates, monostearyl alcohol phosphates
- polyorganosiloxane oils or resins optionally combined with silica particles;
- 5 - SOFTENING AGENTS, in quantities of approximately 0.5-10 % by weight, agents such as clays;
- ENZYMES in a quantity which may range to 5 mg by weight, preferably of the order of 0.05-3 mg of active enzyme/g of detergent composition, enzymes such as
- 10 - proteases, amylases, lipases, cellulases, peroxydases (US-A-3 553 139, US-A-4 101 457, US-A-4 507 219, US-A-4 261 868;
- OTHER ADDITIVES such as
- alcohols (methanol, ethanol, propanol, isopropanol,
- 15 propanediol, ethylene glycol, glycerine)
- buffer agents
- perfumes
- pigments

The following examples are given by way of
20 illustration.

Example 1

Preparation of a sulphonated polyester

Into a 7.5-litre stainless steel reactor fitted with an anchor stirrer rotating at
25 80 revolutions/min, connected to a Kyowa torquemeter, a jacket for the circulation of a heat transfer fluid and a distillation column controlled by a solenoid valve, are introduced:

- 12.17 moles of dimethyl terephthalate (2363 g)
- 1.99 moles of sodium 5-dimethylsulphonate isophthalate (590 g)
- 5 - 40.16 moles of ethylene glycol (2493 g)
- 54 ppm (by weight) of titanium in the form of butyl orthotitanate.

The mixture is preheated to 130°C.

It is then heated to a temperature of 220°C
10 over approximately 130 minutes, to distil more than 90 % of the theoretical quantity of methanol.

The reaction mixture is next heated to 230°C over 30 minutes. When the reaction mass has reached 230°C the introduction of a suspension is commenced,
15 containing:

- 2.99 moles of isophthalic acid (497 g)
- 8.00 moles of ethylene glycol (497 g)

This introduction is carried out over a period of 60 minutes while the reaction mass is
20 maintained at 230°C.

Heating is then continued to bring the reaction mass to a temperature of 250°C over 60 minutes.

During the period of introduction of the
25 mixture of isophthalic acid and of ethylene glycol and the period of heating to 250°C a mixture of water and ethylene glycol is distilled without moving back.

The reaction mixture is next transferred into

an autoclave preheated to 250°C and then placed at reduced pressure to reach a value of 10 millibars in 38 minutes, which corresponds to a driving torque of 3 N m.

5 The reaction mass is then poured; after cooling a water-dispersible polyester is obtained exhibiting the following characteristics:

- number molecular mass = 10480
- sulphonate functional group content: 11.6 mol%
- 10 - OH functional group content: 0.48 eq./kg

Example 2

Preparation of a sulphonated polyester

The stages described in Example 1 are repeated under the same operating conditions, by using

- 15 - 7.99 moles of dimethyl
terephthalate (1551 g)
 - 5.38 moles of sodium 5-
dimethylsulphonateisophthalate (1594 g)
 - 37.5 moles of ethylene glycol (2325 g)
 - 20 - 54 ppm (by weight) of titanium in
the form of butyl orthotitanate (1.34 g)
- followed by the introduction at 230°C of a suspension of
- 2.00 moles of isophthalic acid (332.6 g)
 - 25 - 5.36 moles of ethylene glycol (332.8 g)

The reaction mass is poured when the drive torque is 3 N m, which corresponds in this case to a reduced pressure of 100 millibars.

A water-dispersible polyester is obtained, with the following characteristics:

- number molecular mass = 9100
- sulphonate functional group content: 35 mol%
- 5 - OH functional group content: 0.39 eq./kg.

Example 3

Preparation of a sulphonated polyester

The stages described in Example 1 are repeated under the same operating conditions, by using

- 10 - 9.04 moles of dimethyl terephthalate (1736 g)
- 1.46 moles of sodium 5-dimethylsulphonateisophthalate (433 g)
- 29.4 moles of ethylene glycol (1825 g)
- 15 - 54 ppm (by weight) of titanium in titanium aminotriethanolate form (1.34 g)

followed by the introduction at 230°C of a suspension of

- 2.40 moles of hydroxyisophthalic acid (400 g)
- 20 - 19.33 moles of ethylene glycol (1200 g)

The reaction mass is poured when the drive torque is 3 N m, which corresponds in this case to a reduced pressure of 13 millibars.

A water-dispersible polyester is obtained with the following characteristics:

- 25 - number-average molecular mass = 13310
- sulphonate functional group content: 11.3 mol%
- OH functional group content: 0.54 eq./kg.

Example 4

Preparation of a sulphonated polyester

The stages described in Example 1 are repeated under the same operating conditions, by using

- | | | |
|----|--|----------|
| 5 | - 12.17 moles of dimethyl
terephthalate | (2363 g) |
| | - 1.99 moles of sodium 5-
dimethylsulphonateisophthalate | (590 g) |
| | - 40.16 moles of ethylene glycol | (2493 g) |
| 10 | - 54 ppm (by weight) of titanium
in the form of butyl orthotitanate | |

followed by the introduction at 230°C of a suspension
of

- | | | |
|----|----------------------------------|---------|
| | - 2.99 moles of isophthalic acid | (497 g) |
| 15 | - 2.99 moles of glycerol | (275 g) |
| | - 5.01 moles of ethylene glycol | (261 g) |

The reaction mass is poured when the drive torque is 3 N m, which corresponds in this case to a reduced pressure of 13 millibars

- 20 A water-dispersible polyester is obtained
with the following characteristics:

- number-average molecular mass = 12130
- sulphonate functional group content: 11.6 mol%
- OH functional group content: 0.41 eq./kg

25 **Example 5**

Formulation of a washing machine detergent composition

Washing powder composition	parts by weight
1. Sodium carbonate	100
2. Sodium silicate	100
3. Sodium phosphate	100
4. Sodium borate	100
5. Sodium carbonate	100
6. Sodium carbonate	100
7. Sodium carbonate	100
8. Sodium carbonate	100
9. Sodium carbonate	100
10. Sodium carbonate	100
11. Sodium carbonate	100
12. Sodium carbonate	100
13. Sodium carbonate	100
14. Sodium carbonate	100
15. Sodium carbonate	100
16. Sodium carbonate	100
17. Sodium carbonate	100
18. Sodium carbonate	100
19. Sodium carbonate	100
20. Sodium carbonate	100
21. Sodium carbonate	100
22. Sodium carbonate	100
23. Sodium carbonate	100
24. Sodium carbonate	100
25. Sodium carbonate	100
26. Sodium carbonate	100
27. Sodium carbonate	100
28. Sodium carbonate	100
29. Sodium carbonate	100
30. Sodium carbonate	100
31. Sodium carbonate	100
32. Sodium carbonate	100
33. Sodium carbonate	100
34. Sodium carbonate	100
35. Sodium carbonate	100
36. Sodium carbonate	100
37. Sodium carbonate	100
38. Sodium carbonate	100
39. Sodium carbonate	100
40. Sodium carbonate	100
41. Sodium carbonate	100
42. Sodium carbonate	100
43. Sodium carbonate	100
44. Sodium carbonate	100
45. Sodium carbonate	100
46. Sodium carbonate	100
47. Sodium carbonate	100
48. Sodium carbonate	100
49. Sodium carbonate	100
50. Sodium carbonate	100
51. Sodium carbonate	100
52. Sodium carbonate	100
53. Sodium carbonate	100
54. Sodium carbonate	100
55. Sodium carbonate	100
56. Sodium carbonate	100
57. Sodium carbonate	100
58. Sodium carbonate	100
59. Sodium carbonate	100
60. Sodium carbonate	100
61. Sodium carbonate	100
62. Sodium carbonate	100
63. Sodium carbonate	100
64. Sodium carbonate	100
65. Sodium carbonate	100
66. Sodium carbonate	100
67. Sodium carbonate	100
68. Sodium carbonate	100
69. Sodium carbonate	100
70. Sodium carbonate	100
71. Sodium carbonate	100
72. Sodium carbonate	100
73. Sodium carbonate	100
74. Sodium carbonate	100
75. Sodium carbonate	100
76. Sodium carbonate	100
77. Sodium carbonate	100
78. Sodium carbonate	100
79. Sodium carbonate	100
80. Sodium carbonate	100
81. Sodium carbonate	100
82. Sodium carbonate	100
83. Sodium carbonate	100
84. Sodium carbonate	100
85. Sodium carbonate	100
86. Sodium carbonate	100
87. Sodium carbonate	100
88. Sodium carbonate	100
89. Sodium carbonate	100
90. Sodium carbonate	100
91. Sodium carbonate	100
92. Sodium carbonate	100
93. Sodium carbonate	100
94. Sodium carbonate	100
95. Sodium carbonate	100
96. Sodium carbonate	100
97. Sodium carbonate	100
98. Sodium carbonate	100
99. Sodium carbonate	100
100. Sodium carbonate	100

- zeolite 4A 25

	- light carbonate	15
	- R2A disilicate	5
	- Sokalan CP5 acrylic/maleic copolymer (BASF)	5
5	- Na sulphate	10.7
	- carboxymethyl cellulose	1
	- perborate monohydrate	15
	- tetraacetylenediamine	5
	- linear dodecylbenzenesulphonate	6
10	- Synperonic A3 (C ₁₂ -C ₁₅ fatty alcohol ethoxylated with 3 EO	3
	- Synperonic A9 (C ₁₂ -C ₁₅ fatty alcohol ethoxylated with 9 EO	9
	- Esperase 4.0T enzyme	0.3
15	- antisoiling agent.	

Example 6

ANTISOILING PROPERTIES

The antisoiling polymers tested are introduced into the detergent composition of Example 5 in a proportion of 1 % by weight of polymer active substance.

Test

Prewashing:

Polyester or polyester/cotton (65/35) squares 10 x 10 cm in size are prewashed in a Tergotometre for 20 minutes at 40°C with the washing powder formulation containing 1 % by weight of test polymer active

substance; the water employed has a hardness of 30°TH; the quantity of washing powder used is 5 g per 1 litre of water.

The fabric squares are then rinsed 3 times
5 for 5 minutes with cold water (14°C) and then dried by two passes under a glazing device.

Staining:

4 drops of engine sump oil are deposited on 6
of the prewashed squares and, in order to ensure the
10 fixing of the stain, the fabrics are placed in an oven at 60°C for 1 hour. To allow good reproducibility of the results the fabrics are washed within 24 hours.

Washing:

The washing is performed in the same
15 conditions as the prewashing (at 40°C for 20 minutes, with the aid of 5 g of washing powder containing 1 % of antisoiling polymer active substance per 1 litre of water of 30°TH, then 3 rinses for 5 minutes with cold water and 2 dryings under a glazing device).

20 Evaluation

The reflectance of the fabrics before and after washing is measured with the aid of the Dr. Lange/Luci 100 colorimeter.

The effectiveness of the test polymer as
25 antisoiling agent is assessed as the % of removal of the stains, calculated by the formula

$$E \text{ in } \% = 100 \times (R3-R2)/(R1-R2)$$

R1 denoting the reflectance of the unsoiled fabric
before washing

R2 denoting the reflectance of the soiled fabric before
washing

5 R3 denoting the reflectance of the soiled fabric after
washing.

The average of the % of the stain removal is
calculated for each test product.

The results obtained are given in Table 1
10 which follows.

	polymer	E in %
	-	10
	that of Example 1	63
	that of Example 2	80
15	that of Example 3	50
	Gerol PS 32*	13

* water-dispersible sulphonated polyester containing
11.62 mol% of sulphonate functional groups and with a
number-average molecular mass of 25000, marketed by
20 Rhône-Poulenc

Example 7

PRIMARY DETERGENCY PROPERTIES

The following test pieces of standard fabrics
manufactured by the CFT (Center for test materials)

- 25 - cotton sebum 10D
- polyester/cotton (65/35) sebum 20D
- polyester sebum 30D

test pieces 10 x 10 cm in size, are washed in a

Tergotometre for 20 minutes at 40°C with the above washing formulation to which 1 % by weight of polymer active substance is added; the water employed has a hardness of 30°TH.

5 The fabrics are then rinsed 3 times for 5 minutes and dried on a glazing device.

 The reflectance of the test pieces is measured with the aid of a Xenocolor (Dr Lange) reflectometer before washing and after washing and
10 drying, according to the "L", "a" and "b" system (scale from black to white, from green to red and from blue to yellow).

 The ΔE value is calculated for each type of fabric by obtaining the geometric sum of the colour
15 differences ΔL , Δa and Δb before and after washing on the soiled fabrics, that is

$$\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$$

 The results obtained appear in the following table

20	polymer	ΔE
	-	40
	that of Example 1	42
	that of Example 2	51.3
	that of Example 3	43.6
25	Gerol PS 32	46.2

Example 8

Formulation of a washing machine detergent composition

Composition of the washing powder		parts by weight
5	- zeolite 4A	25
	- light carbonate	15
	- disilicate R2A	5
	- Sokalan CP5 acrylic/maleic copolymer (BASF)	5
	- Na sulphate	5.7
10	- carboxymethyl cellulose	1
	- perborate monohydrate	15
	- tetraacetythylenediamine	5
	- ethoxylated lauryl ether sulphate (1 oxyethylene unit)	10
15	- Synperonic A3 (C ₁₂ -C ₁₅ fatty alcohol ethoxylated with 3 EO	3
	- Synperonic A9 (C ₁₂ -C ₁₅ fatty alcohol ethoxylated with 9 EO	9
	- Esperase 4.0T enzyme	0.3
20	- antisoiling polymer of Example 2	1

The test described in Example 6 is repeated; the average of the % stain removal E is 75 %.

Example 9

Formulation of a washing machine detergent composition

25	Composition of the washing powder	parts by weight
	- zeolite 4A	25
	- light carbonate	15
	- disilicate R2A	5

	- Sokalan CP5 acrylic/maleic copolymer (BASF)	5
	- Na sulphate	5.7
	- carboxymethyl cellulose	1
5	- perborate monohydrate	15
	- tetraacetylenediamine	5
	- ethoxylated lauryl ether sulphate (2 oxyethylene units)	10
10	- Synperonic A3 (C ₁₂ -C ₁₅ fatty alcohol ethoxylated with 3 EO	3
	- Synperonic A9 (C ₁₂ -C ₁₅ fatty alcohol ethoxylated with 9 EO	9
	- Esperase 4.0T enzyme	0.3
	- antisoiling polymer of Example 2	1

15 The test described in Example 6 is repeated;
the average of the % stain removal E is 71 %.

CLAIMS



1. Water-dispersible or water-soluble
sulphonated polyesters characterized in that they are
capable of being obtained by esterification and/or
5 transesterification and polycondensation of a monomer
composition based:
- on an unsulphonated diacidic monomer (A)
consisting of at least one dicarboxylic acid or
anhydride chosen from terephthalic, isophthalic and
10 2,6-naphthalenedicarboxylic acids or anhydrides or
their diesters, in a quantity corresponding to a molar
ratio $(A)/(A)+(SA)$ of the order of 95/100 to 60/100,
preferably of the order of 93/100 to 65/100
 - on a sulphonated diacidic monomer (SA)
15 consisting of at least one sulphonated aromatic or
sulphonated aliphatic dicarboxylic acid or anhydride,
or their diesters, in a quantity corresponding to a
molar ratio $(SA)/(A)+(SA)$ of the order of 5/100 to
40/100, preferably of the order of 7/100 to 35/100,
20 it being possible for up to 50 mol%, preferably up to
30 mol%, of the quantity of unsulphonated diacidic
monomer (A) and/or of sulphonated diacidic monomer (SA)
to be replaced with a hydroxylated diacidic monomer
(HA) consisting of at least one hydroxylated aromatic
25 or aliphatic dicarboxylic acid or anhydride or a
diester of the said hydroxylated aromatic or aliphatic
dicarboxylic acid
 - and on a polyol monomer (P) consisting of



at least one polyol chosen from ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, glycerol, 1,2,4-butanetriol and 1,2,3-butanetriol, in a quantity corresponding to a ratio of

5 number of OH functional groups of the polyol monomer (P)/number of COOH functional groups or functional group equivalents of the diacidic monomers (A)+(SA)+(HA) of the order of 1.05 to 4, preferably of the order of 1.1 to 3.5 and very particularly of the

10 order of 1.8 to 3

in that the sulphonated diacidic monomer (SA) consists of at least one sulphonated aromatic dicarboxylic acid or anhydride or of a mixture of sulphonated aromatic acids or anhydrides and of sulphonated aliphatic acids

15 or anhydrides or their diesters when the polyol monomer (P) does not contain any polyol other than a glycol or when the hydroxylated diacidic monomer (HA) is absent and in that the said sulphonated polyesters exhibit

- a number molecular mass lower than 20 000,
- 20 - a sulphur weight content of the order of 0.5 to 10 %, preferably of the order of 1.2 to 8 %
- and a hydroxyl functional group content, expressed as OH equivalent/kg of polymer, higher than 0.2.

2. Polyesters according to claim 1,

25 characterized in that the unsulphonated diacidic monomer (A) consists of 50 to 100 mol% of terephthalic acid or anhydride or of one of its lower diesters and of 0 to 50 % of isophthalic acid or anhydride and/or of



2,6-naphthalenedicarboxylic acid or anhydride or of one of their lower diesters.

3. Polyesters according to claim 1 or 2, characterized in that the sulphonated monomer (SA) is
5 chosen from sulphoisophthalic, sulphoterephthalic, sulpho-ortho-phthalic acids or anhydrides, 4-sulpho-2,7-naphthalenedicarboxylic acids or anhydrides, sulpho-4,4'-bis(hydroxycarbonyl)diphenyl sulphones, sulphodiphenyldicarboxylic acids or anhydrides, sulpho-
10 4,4'-bis(hydroxycarbonyl)diphenylmethanes, sulpho-5-phenoxyisophthalic acids or anhydrides, sulphosuccinic acids or anhydrides or their lower diesters.

4. Polyesters according to any one of claims 1 to 3, characterized in that the hydroxylated diacidic
15 monomer (HA) is chosen from 5-hydroxyisophthalic, 4-hydroxyisophthalic, 4-hydroxyphthalic, 2-hydroxymethylsuccinic, hydroxymethylglutaric and hydroxyglutaric acids or anhydrides or their lower diesters.

20 5. Polyesters according to any one of claims 1 to 4, characterized in that the polyol monomer (P) is monoethylene glycol and/or glycerol.

6. Polyesters according to any one of the preceding claims, characterized in that they are
25 capable of being obtained from

- terephthalic acid (A1) in (preferably methyl) diester form and isophthalic acid (A2) in the form of diacid or anhydride, or terephthalic acid (A1)



in (preferably methyl) diester form and a hydroxylated terephthalic or hydroxylated isophthalic acid (HA) in the form of diacid or anhydride, optionally mixed with isophthalic acid (A2) in the form of diacid or

5 anhydride, in an (A1)/(A1)+(A2), (A1)/(A1)+(HA) or (A1)/(A1)+(HA)+(A2) molar ratio of the order of 100/100 to 50/100, preferably of the order of 90/100 to 70/100

- sulphisophthalic acid in (preferably methyl) diester form

10 - monoethylene glycol and/or glycerol.

7. Process for the preparation of polyesters forming the subject of any one of the preceding claims, characterized in that the following successive stages are carried out:

15 - a stage of transesterification (interchange) between, on the one hand, the sulphonated diacidic monomer (SA) in diester form and from 50 to 100 mol%, very particularly from 30 to 90 mol%, of the total quantity of the unsulphonated diacidic monomer
20 (A), in diester form, and, on the other hand, a quantity of polyol monomer (P) corresponding to a ratio of number of OH functional groups of the polyol monomer (P)/number of COOH functional group equivalents of the said monomers (A) and (SA) in the form of diesters of
25 the order of 1.05 to 4, preferably of the order of 1.1 to 3.5 and very particularly of the order of 1.8 to 3.0
- an optional stage of esterification between the possible remaining quantity of the unsulphonated



diacidic monomer (A), in diacid or anhydride form, and
a quantity of polyol monomer (P) corresponding to a
ratio of number of OH functional groups of the polyol
monomer (P)/number of COOH functional groups of the
5 unsulphonated diacidic monomer (A) in diacid or
anhydride form of the order of 1.05 to 4, preferably of
the order of 1.1 to 3.5 and very particularly of the
order of 1.8 to 3.0

- a polycondensation stage

10 the polycondensation operation taking place with
removal of polyol molecules and being stopped when the
drive torque of the stirrer shaft shows a value
equivalent to approximately 0.5 to 5 newton metres at a
stirring rate of 80 revolutions/minute of an anchor-
15 shaped rotor in a 7.5-litre reactor and a reaction mass
temperature of 250°C.

8. Detergent compositions containing of the
order of 0.01 % to 10 % by weight of the polyesters
forming the subject of any one of claims 1 to 6,
20 relative to the weight of the said compositions.

9. Use, as antisoiling agents in detergent
compositions, of water-dispersible or water-soluble
sulphonated polyesters capable of being obtained by
esterification and/or transesterification and
25 polycondensation of a monomer composition based:

- on an unsulphonated diacidic monomer (A)
consisting of at least one dicarboxylic acid or
anhydride chosen from terephthalic, isophthalic and



2,6-naphthalenedicarboxylic acids or anhydrides or their diesters, in a quantity corresponding to a molar ratio $(A)/(A)+(SA)$ of the order of 95/100 to 60/100, preferably of the order of 93/100 to 65/100

- 5 - on a sulphonated diacidic monomer (SA) consisting of at least one sulphonated aromatic or sulphonated aliphatic dicarboxylic acid or anhydride, or their diesters, in a quantity corresponding to a molar ratio $(SA)/(A)+(SA)$ of the order of 5/100 to 10 40/100, preferably of the order of 7/100 to 35/100, it being possible for up to 50 mol%, preferably up to 30 mol%, of the quantity of unsulphonated diacidic monomer (A) and/or of sulphonated diacidic monomer (SA) to be replaced with a hydroxylated diacidic monomer 15 (HA) consisting of at least one hydroxylated aromatic or aliphatic dicarboxylic acid or anhydride or a diester of the said hydroxylated aromatic or aliphatic dicarboxylic acid

- and on a polyol monomer (P) consisting of 20 at least one polyol chosen from ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, glycerol, 1,2,4-butanetriol and 1,2,3-butanetriol, in a quantity corresponding to a ratio of number of OH functional groups of the polyol monomer 25 (P)/number of COOH functional groups or functional group equivalents of the diacidic monomers $(A)+(SA)+(HA)$ of the order of 1.05 to 4, preferably of the order of 1.1 to 3.5 and very particularly of the



order of 1.8 to 3

the said sulphonated polyesters exhibiting

- a number molecular mass lower than 20 000,

- a sulphur weight content of the order of 0.5 to 10 %,

5 preferably of the order of 1.2 to 8 %

- and a hydroxyl functional group content, expressed as OH equivalent/kg of polymer, higher than 0.2.

10. Use according to claim 9, characterized in that the unsulphonated diacidic monomer (A) consists of
10 50 to 100 mol% of terephthalic acid or anhydride or of one of its lower diesters and of 0 to 50 % of isophthalic acid or anhydride and/or of 2,6-naphthalenedicarboxylic acid or anhydride or of one of their lower diesters.

15 11. Use according to claim 9 or 10, characterized in that the sulphonated monomer (SA) is chosen from sulphisophthalic, sulphoterephthalic, sulpo-ortho-phthalic acids or anhydrides, 4-sulpho-2,7-naphthalenedicarboxylic acids or anhydrides, sulpo-
20 4,4'-bis(hydroxycarbonyl)diphenyl sulphones, sulphodiphenyldicarboxylic acids or anhydrides, sulpo-4,4'-bis(hydroxycarbonyl)diphenylmethanes, sulpo-5-phenoxyisophthalic acids or anhydrides, sulphosuccinic acids or anhydrides or their lower diesters.

25 12. Use according to any one of claims 9 to 11, characterized in that the hydroxylated diacidic monomer (HA) is chosen from 5-hydroxyisophthalic, 4-hydroxyisophthalic, 4-hydroxyphthalic,



2-hydroxymethylsuccinic, hydroxymethylglutaric and hydroxyglutaric acids or anhydrides or their lower diesters.

13. Use according to any one of claims 9 to 12,
5 characterized in that the polyol monomer (P) is monoethylene glycol and/or glycerol.

14. Use according to any one of claims 9 to 13,
characterized in that the said the said water-soluble or water-dispersible sulphonated polyesters are capable
10 of being obtained from

- terephthalic acid (A1) in (preferably methyl) diester form and isophthalic acid (A2) in the form of diacid or anhydride, or terephthalic acid (A1) in (preferably methyl) diester form and a hydroxylated
15 terephthalic or hydroxylated isophthalic acid (HA) in the form of diacid or anhydride, optionally mixed with isophthalic acid (A2) in the form of diacid or anhydride, in an (A1)/(A1)+(A2), (A1)/(A1)+(HA) or (A1)/(A1)+(HA)+(A2) molar ratio of the order of 100/100
20 to 50/100, preferably of the order of 90/100 to 70/100

- sulphoisophthalic acid in (preferably methyl) diester form

- monoethylene glycol and/or glycerol.

15. Detergent compositions for washing textile
25 articles, based especially on polyester fibres, characterized in that they contain:

- of the order of 0.01 to 10 % by weight, preferably of the order of 0.1 to 5 % by weight, very



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particularly of the order of 0.2 to 3 % by weight of a water-dispersible or water-soluble sulphonated polyester antisoiling agent the use of which forms the subject of any one of claims 9 to 14

- 5 - and of the order of 3 to 40 % by weight, preferably of the order of 5 to 35 % by weight, of at least one anionic surface-active agent chosen from the sulphates of C_5-C_{24} saturated aliphatic alcohols optionally condensed with approximately 0.5 to 30 moles
- 10 of ethylene oxide, not more than 5 % by weight of the said detergent composition being capable of consisting of another type of anionic surface-active agent with less advantageous ecotoxicological properties, such as C_1-C_{18}
- 15 alkylbenzenesulphonates.