COMMONWEALTH of AUSTRALIA
Patents Act 1952
APPLICATION FOR A STANDARD PATENT

I/We
Rhone-Poulenc Chimie
of
25 quai Paul Doumer, 92408 Courbevoie, France

hereby apply for the grant of a Standard Patent for an invention entitled:

Modified polymers based on graft polyester and their preparation

which is described in the accompanying complete specification.

Details of basic application(s):-

<table>
<thead>
<tr>
<th>Number</th>
<th>Convention Country</th>
<th>Date</th>
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<tbody>
<tr>
<td>8903268</td>
<td>France</td>
<td>8 March 1989</td>
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</tbody>
</table>

The address for service is care of DAVIES & COLLISON, Patent Attorneys, of 1 Little Collins Street, Melbourne, in the State of Victoria, Commonwealth of Australia.

DATED this SIXTH day of MARCH 1990

To: THE COMMISSIONER OF PATENTS

a member of the firm of DAVIES & COLLISON for and on behalf of the applicant(s)

Davies & Collison, Melbourne
COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952
DECLARATION IN SUPPORT OF CONVENTION OR
NON-CONVENTION APPLICATION FOR A PATENT

In support of the Application made for a patent for an invention
titled: "Modified polymers based on graft polyester and their preparation".

1 Roger RIOUFRAYS
of: Rhone-Poulenc Chimie, a French Body corporate
of: 25, quai Paul Doumer, 92408 COURBEVOIE, France.

I do solemnly and sincerely declare as follows:-

(a) I am authorized by
RHONE-POULENC CHIMIE
the applicant, for the patent to make this declaration on its behalf.

(b) EDITH CANIVENC; JEAN-FRANCOIS PIARD and
ETIENNE FLEURY, all citizens of France of:
133, Avenue des Freres Lumiere, 69008 LYON, France;
16, rue des Orteaux, 75020 PARIS, France and
135 bis, Rue de Montagny, 69008 LYON, France respectively.

The applicant would, if a patent were granted
upon an application made by the Inventors, be
entitled to have the patent assigned to it”.

3. The basic application, as defined by Section 141 of the Act, was made
in: FRANCE NO...89/03.268... on the 8th March, 1989...
by: RHONE-POULENC CHIMIE...
in: FRANCE...
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4 The basic application referred to in paragraph 3 of this Declaration was
the first application made in a Convention country in respect of the invention the subject of
the application.

Declared at Saint-Fons this 1er day of February 1990

Roger RIOUFRAYS
Un Fon6 de Pouvoir
1. A modified polymer based on a graft polyester comprising:
   - a backbone derived from a water-dispersible sulphonated polyester
   - and grafts consisting of copolymer units derived from at least one vinyl monomer and at least one ethylenically unsaturated organopolysiloxane soluble in the vinyl monomer.

7. Process for the preparation of a modified polymer, which comprises:
   - premulsifying, in water, a solution of an organopolysiloxane in one or more vinyl monomers, and
   - adding the emulsion obtained to an aqueous solution of a water-dispersible sulphonated polyester, and polymerizing the monomers in the presence of a water-soluble or water-dispersible initiator.
17. A coating made of a modified polymer as claimed in any of claims 1 to 6 or 16.
NAME & ADDRESS
OF APPLICANT:

Rhone-Poulenc Chimie
25 quai Paul Doumer
92408 Courbevoie
France

NAME(S) OF INVENTOR(S):

Edith CANIVENC
Jean-Francois FIARD
Etienne FLEURY

ADDRESS FOR SERVICE:

DAVIES & COLLISON
Patent Attorneys
1 Little Collins Street, Melbourne, 3000.

COMPLETE SPECIFICATION FOR THE INVENTION ENTITLED:

Modified polymers based on graft polyester and their preparation

The following statement is a full description of this invention, including the best method of performing it known to me/us:--
The present invention relates to modified polymers based on water-dispersible sulphonated polyesters and to their preparation and use.

The modified polymers of the invention are based on a graft polyester comprising:

- a backbone derived from a water-dispersible sulphonated polyester

- and grafts consisting of copolymer units derived from at least one vinyl monomer and at least one ethylenically unsaturated organopolysiloxane soluble in the vinyl monomer.

The water-dispersible sulphonated polyesters which can make up the backbone are known. They can be prepared by a co-condensation reaction of an organic diacid (such as a saturated or unsaturated aliphatic diacid, an aromatic diacid, a diacid containing several aromatic rings or an arylaliphatic diacid), one of its diesters or its anhydride and a sulphonated organic diacid or one of its diesters with a diol, in the presence of a catalyst customary for polyesterification, such as tetraisopropyl orthotitanate.

The following may be mentioned as starting monomers currently used for the preparation of water-dispersible sulphonated polyesters:
as organic diacids: saturated or unsaturated aliphatic diacids, aromatic diacids, such as succinic, adipic, suberic and sebacic acids, maleic, fumaric and itaconic acids, orthophthalic, isophthalic and terephthalic acids, the anhydrides of these acids and their diesters, such as the methyl, ethyl, propyl and butyl diesters. The preferred compounds are adipic acid and orthophthalic, isophthalic and terephthalic acids;

as sulphonated diacids: sodium diacid-sulphonates or their esters, such as the dialkylisophthalates and alkylsulphisuccinates, such as sodium 5-dimethylisophthalate-sulphonate or sodium dimethylsulphisuccinate;

as diols: aliphatic glycols, such as ethylene glycol, diethylene glycol and dipropylene glycol and the higher homologues, butane-1,4-diol, hexane-1,6-diol, neopentyl glycol and cycloalkane glycols, such as cyclohexanediol and dicyclopentanediolpropane. The diols chosen preferentially are ethylene glycol and diethylene glycol.

The preferred water-dispersible sulphonated polyesters are those which have a number-average molecular mass of between 10,000 and 35,000, an acid number of less than 5 mg of KOH/g and a proportion of sulphur of between 0.8 and 2 % by weight, preferably between 1.2 and 1.8 %.
Amongst the vinyl monomers from which the copolymer units making up the grafts can be derived, the following may be mentioned:

- the monoethylenically unsaturated esters of carboxylic acids (vinyl acetate, propionate, butyrate, stearate, benzoate ...)

- the saturated esters and amides of monoethylenically unsaturated carboxylic acids ($C_1$-$C_{20}$-alkyl acrylates or methacrylates, such as methyl, heptyl, propyl, heptadecanyl acrylates and methacrylates, acrylamide, methacrylamide ...)

- the monoethylenically unsaturated nitriles (acrylonitrile, methacrylonitrile ...)

- the monoethylenically unsaturated carboxylic acids (acrylic acid, methacrylic acid, itaconic acid, maleic acid ...)

- the hydroxyalkyl or aminoalkyl esters of monoethylenically unsaturated carboxylic acids (hydroxyethyl acrylate, hydroxypropyl acrylate ..., 2-aminoethyl methacrylate ...)

- the vinyl-aromatic monomers (styrene, vinyltoluene ...)

Small amounts (0 to 5 %, preferably 0 to 3 %, relative to the vinyl monomer or monomers) of crosslinking monomers (divinylbenzene, diallyl phthalate, ethylene glycol diacrylate, methylene-bis-methacrylamide, N-...
methylolacrylamide ... can also be present.

The ethylenically unsaturated organopolysiloxanes from which the copolymer units making up the grafts are derived can be represented by the following average formula:

\[ R''R'RSiO(SiR''''O)_m(SiR''''O)_nSiRR'R' \]

in which formula:
- the symbols R are identical or different and represent a C_1-C_4-alkyl radical, phenyl or 3,3,3-trifluoropropyl
- the symbols R' are identical or different and represent R or a vinyl radical
- the symbols R'' are identical or different and represent R or a radical OH
- the symbols R''' are identical or different and represent R, a vinyl radical or a -r-X unit in which r represents a divalent organic radical and X represents an ethylenically unsaturated group
- the symbols R'''' are identical or different and represent R''' or a -r'-X' unit in which r' represents a divalent organic radical and X' represents a functional group which is not ethylenically unsaturated
- at least 60 % of the radicals represented by R, R'
  and R'' are methyl radicals, and
- the symbols m and n can separately be zero, R'
  and/or R''''' representing a vinyl radical if m is zero, and
have a value sufficient to ensure a viscosity of the polymer of the order of 20 mPas to 10,000,000 mPas at 25°C, preferably of the order of 50 to 7,000,000 mPas.

The following may be mentioned as examples of diorganosiloxy units in which R''' and R'''' represent R or a vinyl radical:

\[ (\text{CH}_3)_2\text{SiO}; \text{CH}_3(\text{CH}_2=\text{CH})\text{SiO}; \text{CH}_3(\text{C}_2\text{H}_5)\text{SiO}; \text{CH}_3(\text{C}_6\text{H}_5)\text{SiO}; \]
\[ (\text{C}_6\text{H}_5)_2\text{SiO}; \text{CF}_3\text{CH}_2\text{CH}_2(\text{CH}_3)\text{SiO}. \]

Amongst the blocking triorganosiloxy units, those of the following formula may be mentioned:

\[ (\text{CH}_3)_3\text{SiO}_{0.5}; (\text{CH}_3)_2\text{CH}=\text{CHSiO}_{0.5}; (\text{CH}_3)_2\text{C}_6\text{H}_5\text{SiO}_{0.5}; \]
\[ \text{CH}_3(\text{C}_6\text{H}_5)_2\text{SiO}_{0.5}; \text{CH}_3(\text{CH}_2=\text{CH})\text{C}_6\text{H}_5\text{SiO}_{0.5}; \]
\[ \text{CH}_2=\text{CH}(\text{C}_6\text{H}_5)\text{SiO}_{0.5}; (\text{C}_6\text{H}_5)_3\text{SiO}_{0.5}. \]

Amongst the divalent organic radicals r and r', which can form part of the structure of the symbols R'''' and R''''', the following may be mentioned: straight-chain or branched \( \text{C}_1-\text{C}_8 \)-alkylene radicals, optionally extended by 1 to 5 ethylene-amine divalent groups, by 1 to 50 \( \text{C}_1-\text{C}_3 \)-alkylene oxide groups or by a group \(-\text{O}-\text{CH}_2-\text{CH}-\text{CH}_2-\); the polyoxyalkylene radicals containing from 1 to 50 \( \text{C}_1-\text{C}_3 \)-oxyalkylene chain members.

The following may be mentioned as examples of divalent radicals:

\[ -\text{CH}_2-; (\text{CH}_2)_2; (\text{CH}_2)_3; -\text{CH}_2-\text{CH}-\text{CH}_2-; (\text{CH}_2)_{10}; \]
\[ \text{CH}_3 \]
Amongst the ethylenically unsaturated groups X, the acrylyloxy and methacrylyloxy radicals may be mentioned in particular.

Amongst the functional groups X', the epoxy, hydroxyl, carboxyl, aldehyde, ester, acetoester, amino ...

Amongst the preferred ethylenically unsaturated organopolysiloxanes, those containing acrylate or methacrylate functions may be mentioned, such as those described in the European Patent Application published under No. 281,718 and the US Patents Nos. 4,293,678; 4,139,548; 4,558,082; 4,663,185; 4,640,967.

The respective amounts of backbone and grafts going into the composition of the modified polymers which are the subject of the invention correspond to:

- 2 to 60 % by weight, preferably 10 to 50 % by weight, relative to the modified polymer, of water-dispersible sulphonated polyester
- 0.05 to 30 % by weight, preferably 0.5 to 10 % by weight, relative to the modified polymer, of ethylenically unsaturated organopolysiloxane
and, making up to 100 %, units derived from vinyl monomer(s).

The relative amounts of the various units of the backbone and the grafts are a function of the desired properties of the said modified polymer: glass transition temperature, hardness, hydrophilic character, elongation, resistance to break, anti-adherence ...

If products dispersible in water at an alkaline pH are desired, it will be preferable to have units derived from a vinyl monomer composition containing more than 5 % of its weight, and generally of the order of 7 to 11 % of its weight, of ethylenically unsaturated carboxylic acid and an amount of organopolysiloxane units of less than 30 % of the total weight of the modified polymer.

The modified polymers which are the subject of the invention can be prepared by:

- preemulsion, in water, of a solution of organopolysiloxane in the vinyl monomer or monomers

- followed by addition of the emulsion obtained to an aqueous solution of water-dispersible sulphonated polyester and polymerization in the presence of a water-soluble or water-dispersible initiator.

If desired, the particles of the modified polymer obtained are separated from the aqueous medium.

The amounts of reactants used correspond to:
- 2 to 60 % by weight, preferably 10 to 50 % by weight, relative to the total weight of monomers and polymers used, of water-dispersible sulphonated polyester

- 0.05 to 30 % by weight, preferably 0.5 to 10 % by weight, relative to the total weight of monomers and polymers used, of ethylenically unsaturated organopolysiloxane

- making up to 100 % with vinyl monomer or monomers

- 0.01 to 4 %, preferably 0.05 to 2 % by weight, relative to the total weight of monomers and polymers used, of water-soluble or water-dispersible initiator.

The step for preemulsion, in water, of the solution of organopolysiloxane in the vinyl monomer or monomers can be carried out using a weight ratio of vinyl monomer or monomers + organopolysiloxane/water of the order of 1/5 to 5/1, generally of the order of 1/3 to 3/1.

The emulsifying agents which can be used are conventional anionic agents represented, in particular, by the salts of fatty acids, the alkylsulphates, the alkylsulphonates, the alkylarylsulphonates, the sulphosuccinates, the alkylphosphates of alkali metals, the salts of abietic acid, which may be hydrogenated, non-ionic agents, such as the polyethoxylated fatty alcohols, the polyethoxylated alkylphenols, the sulphated polyethoxylated alkylphenols, the polyethoxylated fatty acids ...
They can be used in an amount of 0.1 to 3 % by weight, relative to the total weight of vinyl monomer or monomers, organopolysiloxane and sulphonated polyester (that is to say of vinyl monomer or monomers and polymers).

One variant of the preemulsion step consists in carrying out this step in the presence of an initiator soluble in organic compounds. Examples which may be mentioned are the organic peroxides, such as lauroyl peroxide, benzoyl peroxide, tert.-butyl peroxide ...; the azonitriles, such as azo-bis-isobutyronitrile ...

Another variant for carrying out the preemulsion step consists in using a fraction of the water-dispersible sulphonated polyester in this step, for example up to 50 % by weight of the total weight of water-dispersible sulphonated polyester.

The preemulsion step is beneficially carried out by homogenization.

The polymerization step after addition of the emulsion to an aqueous solution of water-dispersible sulphonated polyester is carried out in the presence of a water-soluble or water-dispersible initiator, such as, for example, hydroperoxides, such as hydrogen peroxide, cumene hydroperoxide, tert.-butyl hydroperoxide or diisopropylbenzene hydroperoxide, and persulphates, such as sodium persulphate, potassium persulphate or ammonium persulphate.
If appropriate, these initiators are combined with a reducing agent, such as sodium bisulphite or sodium formaldehyde sulfoxylate, polyethyleneamines, sugars: dextrose or sucrose, or metal salts. The amounts of reducing agent used vary from 0 to 3 % by weight relative to the weight of the monomer(s) + polymers composition.

If appropriate, chain-limiting agents can be present in proportions ranging from 0 to 3 % by weight relative to the monomer + polymers composition. They are generally chosen from the mercaptans, such as N-dodecyl mercaptan or tert.-dodecyl mercaptan; cyclohexene; halogenated hydrocarbons, such as chloroform, bromoform, carbon tetrachloride or carbon tetrabromide; and dimers of α-methylstyrene.

If necessary, a supplementary amount of emulsifying agents can be used.

The polymerization operation is carried out at a temperature which is a function of the decomposition temperature of the initiator; this operation generally takes place at a temperature of the order of 60 to 80°C and preferably of the order of 75°C.

If desired, the latex obtained, which generally contains of the order of 10 to 40 % by weight of modified polymer, can be pulverized to be stored and transported more easily.
The modified polymers based on graft polyester have both adherence and anti-adherence properties. They can be used as coating agents (anti-encrustation, water-resistant paint, oiling agents, lubricants ...)

The following examples illustrate the invention.

EXAMPLE 1

Preemulsion

The following are mixed in a 1 l beaker:

- 112 g of methyl methacrylate
- 44 g of butyl acrylate
- and 4 g of methacrylic acid.

The following are added, with stirring:

- 40 g of an unsaturated organopolysiloxane oil of average formula

\[
\begin{align*}
(\text{CH}_3)_3 \text{SiO} & \{\text{Si(\text{CH}_3)_2O}\}_27,2 \{\text{Si(\text{CH}_3O)}_{1/2} \}_3,2 \text{Si(\text{CH}_3)}_3 \\
\text{CH}_2 & \\
\text{CH}_2 & \text{OH} \\
\text{CH}_2 - \text{O} - \text{CH} & \text{= CH}_2 \\
\text{O} & 
\end{align*}
\]

- 0.2 g of lauroyl peroxide.

The mixture is stirred until all of the components have dissolved.

80 g of water, 2 g of a 40.7 % by weight aqueous solution of partially sulphated, ethoxylated nonylphenol
containing 25 units of ethylene oxide, 3 g of a 20 % by weight aqueous solution of sodium dodecylbenzenesulphonate and 60 mg of ethylenediaminetetraacetic acid (EDTA) are mixed in a beaker.

The acrylic monomers/diorganopolysiloxane mixture is introduced into this solution, with stirring. The mixture obtained is emulsified using an ULTRA-TURAX type homogenizer (marketed by PROLABO) for 5 minutes at 20,000 revolutions/minute.

**Polymerization**

The following are introduced into a one litre flask:
- 360 g of water
- 1 g of 40.7 % by weight aqueous solution of partially sulphated, ethoxylated nonylphenol containing 25 units of ethylene oxide
- 2 g of 20 % by weight aqueous solution of sodium dodecylbenzenesulphonate
- 40 mg of EDTA
- 152 g of a 26.4 % aqueous solution of GEROL PS 20 (water-dispersible sulphonated polyester marketed by RHONE-POULENC), which corresponds to 40 g of dry product.

Once the mixture has been brought to 75°C, with stirring, 0.8 g of ammonium persulphate dissolved in 10 ml of water is added and the preemulsion is then introduced in the course of 3 hours.
The mixture is kept at 75°C for a further 1 hour after the end of the introduction and is then brought back to ambient temperature.

A latex containing 28% of dry extract is obtained.

**EXAMPLE 2**

**Preemulsion**

The following are mixed in a 1 l beaker:

- 120 g of vinyl acetate
- 44 g of butyl acrylate
- and 20 g of acrylic acid.

The following are added, with stirring:

- 40 g of the silicone oil from Example 1
- 0.2 g of lauroyl peroxide.

The mixture is stirred until all of the components have dissolved.

80 g of water, 2 g of 40.7% by weight aqueous solution of partially sulphated, ethoxylated nonylphenol containing 25 units of ethylene oxide, 3 g of a 20% by weight aqueous solution of sodium dodecylbenzenesulphonate and 60 mg of ethylenediaminetetraacetic acid (EDTA) are mixed in a beaker.

The acrylic monomers/diorganopolysiloxane mixture is introduced into this solution, with stirring. The mixture obtained is emulsified using an ULTRA-TURAX type homogenizer (marketed by PROLABO) for 5 minutes at 20,000
revolutions/minute.

Polymerization

The following are introduced into a one litre flask:

- 360 g of water
- 1 g of 40.7 % by weight aqueous solution of partially sulphated, ethoxylated nonylphenol containing 25 units of ethylene oxide
- 2 g of 20 % by weight aqueous solution of sodium dodecylbenzenesulphonate
- 40 mg of EDTA
- 50.5 g of a 27.7 % aqueous solution of GEROL PS 20 (water-dispersible sulphonated polyester marketed by RHONE-POULENC), which corresponds to 14 g of dry product.

Once the mixture has been brought to 75°C, with stirring, 0.8 g of ammonium persulphate dissolved in 10 ml of water is added and the preemulsion is then introduced in the course of 3 hours.

The mixture is kept at 75°C for a further 1 hour after the end of the introduction and is then brought back to ambient temperature.

A latex with a dry extract content of 27 % is obtained which is soluble in alkalis.

50 g of this latex are introduced into a beaker and 400 g of water are added; the dry extract is then 3 % by weight.
The mixture is brought to 60°C, with stirring, and a 20% by weight solution of ammonia is then added to bring the pH to a value of 8.

The dispersion then changes to a solution (or pseudo solution) of modified polymer.

EXAMPLE 3

The operation described in Example 1 is repeated using the following reactants and reactant amounts:

Preemulsion

- 100 g of methyl methacrylate
- 56 g of ethyl acrylate
- 9 g of acrylic acid
- 35 g of a silicone oil of formula

![Chemical Structure]

- 0.1 g of lauroyl peroxide.

Polymerization

- 350 g of water
- 100 g of a 25% aqueous solution of GEROL PS 30 (water-dispersible sulphonated polyester marketed by RHONE-POULENC), which corresponds to 25 g of dry product
- 0.6 g of ammonium persulphate.

A latex containing 30 % of dry extract is obtained.

**EXAMPLE 4**

The operation described in Example 1 is repeated using the following reactants and reactant amounts:

**Preemulsion**
- 150 g of methyl methacrylate
- 30 g of ethyl acrylate
- 20 g of butyl acrylate
- 20 g of methacrylic acid
- 7 g of a silicone oil of formula

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{Si} & \quad \text{CH}_3 \\
\text{(CH}_2\text{)}_3 & \quad \text{Si} \\
\text{OH} & \quad \text{Si(CH}_3\text{)}_3
\end{align*}
\]

- 0.2 g of lauroyl peroxide.

**Polymerization**
- 300 g of water
- 50 g of a 25 % aqueous solution of GEROL PHS (water-dispersible sulphonated polyester marketed by RHONE-POULENC), which corresponds to 12.5 g of dry product.
A latex containing 35% of dry extract is obtained.

**EXAMPLE 5**

The operation described in Example 2 is repeated using the following reactants and reactant amounts:

**Preemulsion**

- 130 g of vinyl acetate
- 45 g of butyl acrylate
- 5 g of acrylic acid
- 20 g of methacrylic acid
- 40 g of a silicone oil of formula

\[
\begin{align*}
&- (CH_3)_3SiO \quad SiO \quad SiO \quad SiO \\
&\quad \quad (CH_2)_3 \quad (CH_2)_3 \quad (CH_2)_3 \\
&\quad \quad \quad COCH-COCH_3 \quad COCH-COCH_3 \quad COCH-COCH_3
\end{align*}
\]

- 0.2 g of lauroyl peroxide.

**Polymerization:** unchanged

A latex containing 27% of dry extract is obtained.
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A modified polymer based on a graft polyester comprising:
   - a backbone derived from a water-dispersible sulphonated polyester
   - and grafts consisting of copolymer units derived from at least one vinyl monomer and at least one ethylenically unsaturated organopolysiloxane soluble in the vinyl monomer.

2. Modified polymer according to Claim 1, in which the respective amounts of backbone and grafts correspond to:
   - 2 to 60 % by weight, relative to the modified polymer, of water-dispersible sulphonated polyester
   - 0.05 to 30 % by weight, relative to the modified polymer, of ethylenically unsaturated organopolysiloxane
   - and, the balance to 100 %, of units derived from vinyl monomer.

3. Modified polymer according to Claim 2, in which the respective amounts of backbone and grafts correspond to
   - 10 to 50 % by weight, relative to the modified polymer, of water-dispersible sulphonated polyester
   - 0.5 to 10 % by weight, relative to the modified polymer, of ethylenically unsaturated organopolysiloxane
   - and, the balance to 100 %, of units derived from vinyl monomer.
4. Modified polymer according to any one of the preceding claims, in which the water-dispersible sulphonated polyester has a number-average molecular mass of between 10,000 and 35,000, an acid number of less than 5 mg of KOH/g and a proportion of sulphur of between 0.8 and 2 % by weight.

5. Modified polymer according to any one of the preceding claims in which the organopolysiloxane from which the grafts are derived is represented by the formula:

\[ R''R'SiO (SiR'''O)_m (SiR''''O)_n SiR''R'' \]

in which

- the symbols R are identical or different and represent a C_1-C_4-alkyl radical, phenyl or 3,3,3-trifluoropropyl
- the symbols R' are identical or different and represent R or a vinyl radical
- the symbols R'' are identical or different and represent R or a radical OH
- the symbols R''' are identical or different and represent R, a vinyl radical or a \(-r\)-X unit in which \(r\) represents a divalent organic radical and \(X\) represents an ethylenically unsaturated group
- the symbols R'''' are identical or different and represent R''' or a \(-r'\)-X' unit in which \(r'\) represents a divalent organic radical and \(X'\) represents a functional group which is not ethylenically unsaturated
at least 60 % of the radicals represented by R, R'
and R'' are methyl radicals, and
the symbols m and n can separately be zero, R'
and/or R''' representing a vinyl radical if m is zero, and
have a value sufficient to ensure a viscosity of the
polymer of the order of 20 mPas to 10,000,000 mPas at 25°C.

6. Modified polymer according to any one of the
preceding claims in which the vinyl monomer from which the
grafts are derived is one or more of monoethylenically
unsaturated esters of carboxylic acids, saturated esters
and amides of monoethylenically unsaturated carboxylic
acids, monoethylenically unsaturated nitriles, hydroxyalkyl
and aminoalkyl esters of monoethylenically unsaturated
carboxylic acids, and vinyl-aromatic monomers.

7. Process for the preparation of a modified
d polymer, which comprises:
- preemulsifying, in water, a solution of an
organopolysiloxane in one or more vinyl monomers, and
- adding the emulsion obtained to an aqueous solution
of a water-dispersible sulphonated polyester, and
polymerizating the monomers in the presence of a water-
soluble or water-dispersible initiator.

8. Process according to Claim 7, in which the
amounts of reactants used correspond to:
- 2 to 60 % by weight, relative to the total weight of
vinyl monomers and polymers used, of water-dispersible
sulphonated polyester

- 0.05 to 30 % by weight, relative to the total weight of vinyl monomers and polymers used, of ethylenically unsaturated organopolysiloxane

- the balance to 100 % of vinyl monomer, and

- 0.01 to 4 % by weight, relative to the total weight of vinyl monomers and polymers used, of water-soluble or water-dispersible initiator.

9. Process according to Claim 8, in which the amounts of reactants used correspond to:

- 10 to 50 % by weight, relative to the total weight of vinyl monomers and polymers used, of water-dispersible sulphonated polyester,

- 0.5 to 10 % by weight, relative to the total weight of vinyl monomers and polymers used, of ethylenically unsaturated organopolysiloxane

- the balance to 100 % of vinyl monomer, and

- 0.05 to 2 % by weight, relative to the total weight of vinyl monomers and polymers used, of water-soluble or water-dispersible initiator.

10. Process according to any one of Claims 7 to 9, in which the preemulsion step is carried out using an amount of reactants corresponding to a weight ratio of vinyl monomer + organopolysiloxane/water of the order of 1/5 to 5/1.

11. Process according to any one of Claims 7 to 10,
in which the preemulsion step is carried out in the presence of 0.1 to 3 % by weight, relative to the total weight of vinyl monomer or monomers + polymers, of an initiator soluble in organic compounds.

12. Process according to any one of Claims 7 to 11, in which the organopolysiloxane has the formula

\[ R''R'R'SiO(SiR''''O)_m(SiR''''O)_nSiRR'R'' \]

in which formula

- the symbols \( R \) are identical or different and represent a \( C_1-C_4 \)-alkyl radical, phenyl or 3,3,3-trifluoropropyl
- the symbols \( R' \) are identical or different and represent \( R \) or a vinyl radical
- the symbols \( R'' \) are identical or different and represent \( R \) or a radical OH
- the symbols \( R''' \) are identical or different and represent \( k \), a vinyl radical or a \(-r-X\) unit in which \( r \) represents a divalent organic radical and \( X \) represents an ethylenically unsaturated group
- the symbols \( R'''' \) are identical or different and represent \( R''' \) or a \(-r'-X'\) unit in which \( r' \) represents a divalent organic radical and \( X' \) represents a functional group which is not ethylenically unsaturated
- at least 60 % of the radicals represented by \( R \), \( R' \) and \( R'' \) are methyl radicals, and
- the symbols \( m \) and \( n \) can separately be zero, \( R' \)
and/or \( R''' \) representing a vinyl radical if \( m \) is zero, and have a value sufficient to ensure a viscosity of the polymer of the order of 20 mPas to 10,000,000 mPas at 25°C.

13. Process according to any one of Claims 7 to 12, in which the vinyl monomer is one or more of monoethylenically unsaturated esters of carboxylic acids, saturated esters and amides of monoethylenically unsaturated carboxylic acids, monoethylenically unsaturated nitriles, hydroxyalkyl and aminoalkyl esters of monoethylenically unsaturated carboxylic acids, and vinyl-aromatic monomers.

14. Process according to any one of Claims 7 to 13, in which the water-dispersible sulphonated polyester has a number-average molecular mass of between 10,000 and 35,000, an acid number of less than 5 mg of KOH/g and a proportion of sulphur of between 0.8 and 2% by weight.

15. Process according to claim 7 substantially as described in any one of the foregoing Examples.

16. A modified polymer when produced by a process as claimed in any of claims 7 to 15.

17. A coating made of a modified polymer as claimed in any of claims 1 to 6 or 16.
18. The steps, features, compositions and compounds disclosed herein or referred to or indicated in the specification and/or claims of this application, individually or collectively, and any and all combinations of any two or more of said steps or features.

DATED this SIXTH day of MARCH 1990

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