

**POLYURETHANE SYNTHESIS FROM FUNCTIONAL
GROUP TERMINATED POLYMERS
CONTAINING SULFONATE GROUPS**

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The present invention relates to water-
dispersible polyurethane polymers, and more
particularly to such products synthesized from water-
dispersible polyesters.

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Polyurethanes find use in a variety of
applications, including coatings, paints, adhesives,
and the manufacture of fibers and solid articles.
Polyurethanes are typically soluble in organic
solvents, and exhibit little if any solubility in
aqueous solvents or in systems in which water and a
second water-soluble solvent are employed. Organic
solvent-based resin solutions have thus typically been
the vehicle of choice for use in forming coatings and
the like of polyurethanes. However, many organic
solvents commonly used in conjunction with such resins
present environmental problems associated with their
toxicity. There has been a growing concern based on
the effects of such organic solvents on the
environment, as well as on the long-term health of
individuals who come into contact with such solvents.
There has, therefore, been a growing interest in the
use of aqueous resin compositions as a means of
eliminating toxicity problems associated with organic
solvents, and as a means of complying with
governmental edicts with respect to the use of such
solvents.

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Examples of aqueous polyurethane dispersions
are known in the art. The dispersion of the

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polyurethane into the aqueous medium has customarily
1 been achieved through the use of dispersing or
emulsifying agents such as nonionic or ionic
surfactants. However, the use of surfactant-
stabilized aqueous resin dispersions is far from
5 desirable, since a proportion of free surfactant can
be carried through to the final product, which can
result in a diminution of the desired properties of
the final product.

The prior art has thus attempted to
10 incorporate directly into the polyurethane polymer
molecule moieties which afford greater water
dispersibility to the polymer. Typically, these
attempts involve reaction of a water-soluble or water-
dispersible agent such as N-(2-aminoethyl)-2-
15 aminoethane sulfonic acid, sodium salt, or an adduct
of sodium bisulfite and 1, 4-dihydroxy-butene(2), as a
chain extender, with the already-formed di-capped
isocyanate prepolymer, thereby to form the desired
polymer molecule. Typical of this approach are
20 disclosures in U.S. Patent No. 4,108,814, U.S. Patent
No. 4,123,423, U.S. Patent No. 4,186,118, U.S. Patent
No. 4,306,998 and U.S. Patent No. 5,528,323.

This prior art approach to the objective of
incorporating a water-dispersible moiety into the
25 polyurethane molecule has drawbacks, such as the fact
that a very high content e.g. up to 70% of a solvent
such as acetone needs to be present to reduce the
viscosity of the mixture.

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The present invention is thus directed to an
1 improved technique for forming water-dispersible
polyurethanes, particularly those formed from water-
dispersible polyesters, which technique affords
improved ease of operation, more satisfactory yields,
5 and offers a greater variety in the selection of
reactants and in the range of properties of the
products that can be obtained.

One aspect of the present invention is a
10 process for producing a water-dispersible
polyurethane, comprising chain extending a sulfonate-
substituted prepolymer which is substituted with at
least two isocyanate groups.

15 A further aspect of the invention comprises
forming the sulfonate-substituted prepolymer, which is
substituted with at least two isocyanate groups, by
reacting a sulfonate-substituted polyester, that is
substituted with at least two hydroxyl groups, with a
20 diisocyanate compound, generally at a mole ratio of at
least 2:1 such that at least 2 hydroxyl groups on the
polyester molecule react with isocyanate groups.

One specific method of forming the
25 sulfonate-substituted polyester which is used in
forming the water-dispersible polyurethane polymer in
accordance with the present invention comprises
forming an ethylenically unsaturated polyester
precursor by condensation polymerization of reactants
30 which upon said condensation polymerization form said

polyester precursor which is substituted with at least
1 two -OH groups, wherein at least one of said reactants
contains ethylenic unsaturation; and sulfonating said
polymeric precursor by reacting it with a sulfonating
agent selected from the group consisting of
5 bisulfites, metabisulfites, and mixtures thereof,
under conditions such that said sulfonating agent
reacts with said ethylenic unsaturation and sulfonates
said polymeric precursor. The sulfonated, di-hydroxyl
substituted, product is then reacted with diisocyanate
10 and the product thereby formed is chain extended to
make the final polyurethane product.

Another specific method of forming the
sulfonate-substituted polyester which is used in
15 forming the water-dispersible polyurethane polymer in
accordance with the present invention comprises (a)
sulfonating an ethylenically unsaturated monomeric
precursor which has no aromatic ring and which is
substituted with at least two groups selected from the
20 group consisting of -OH, and -COOH, to form a
sulfonated monomeric precursor; and (b) reacting said
sulfonated monomeric precursor with a difunctional
second monomer capable of undergoing condensation
polymerization with said sulfonated monomeric
25 precursor, under conditions whereunder said precursor
and said second monomer undergo condensation
polymerization to form a polyester.

Preferably, said sulfonation is carried out
with a sulfonating agent selected from the group
30 consisting of bisulfites, metabisulfites, and mixtures

thereof, under conditions such that said sulfonating
1 agent sulfonates said monomeric precursor by reaction
at said ethylenic unsaturation.

Optionally, the monomeric precursor is
simultaneously sulfonated and end-capped with a
5 difunctional precursor to form a sulfonated,
difunctional "dimer" which is capable of undergoing
condensation polymerization in step (b).

The present invention is useful in making
water-dispersible polyurethanes. The products of the
10 process of this invention can be used per se to form
coatings, films and the like. The products of the
process of this invention can also be used to
fabricate solid articles, fibers, sheets, and other
useful products..

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A. PREPARING THE SULFONATE- AND HYDROXYL-SUBSTITUTED
POLYESTER

1. Sulfonating an ethylenically unsaturated polyester.

20 One preferred manner of introducing
sulfonate functionality into the reactants, a
polyester is prepared which includes ethylenic
unsaturation. The functionalities present on the
reactants to form the polyester include one or both of
25 -COOH (or anhydride) and/or -COH, and one or more -OH
groups. The reactants that enter into such
condensation reaction forming the polyester are
substituted with two, or more, of such
functionalities. More often, reactants are
30 substituted with the same functionalities (e.g.,

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diacids and diols) but they can be substituted with
1 two or more different functionalities (e.g.,
hydroxyacids).

Preferred examples of condensation
polymerization reactions to form polyesters include
5 the reaction of, for instance, diols with dicarboxylic
acids or anhydrides thereof. Condensation
polymerization reactions also include such reactions
of glycol or other polyols with a diacid or anhydride
to form a polyester which has 2 or more than 2 free
10 hydroxyl groups per molecule.

One essential aspect of the process of this
embodiment of the present invention is that the
polyester that is obtained contains ethylenic
unsaturation, that is, one or more carbon-carbon
15 double bonds, either in the main chain of the polymer,
or pendant from the main chain of the polymer
(connected directly to the main chain by a covalent
bond, or incorporated in or pendant from a longer
chain which is itself pendant from the main chain of
20 the polymer), or both. This ethylenic unsaturation is
provided by carrying out the condensation
polymerization with one or more reactants which
participate in the condensation polymerization
reaction and which also contain ethylenic
25 unsaturation. Under conventional condensation
polymerization conditions the ethylenic unsaturation
survives the condensation polymerization. Of the
different types of reactants present (e.g., diacid,
diol, anhydride, and so forth), the ethylenically
30 unsaturated reactant can comprise all or a portion of

one of the reactant types, or all or a portion of more
1 than one of the reactant types.

Thus, for instance, the desired ethylenic
unsaturation can be provided by incorporating into the
reactant mixture an ethylenically unsaturated diacid,
5 an ethylenically unsaturated anhydride (such as maleic
anhydride), an ethylenically unsaturated diol, or
mixtures of any two or more of such compounds. The
properties desired of the final product produced by
the process of the present invention are used to guide
10 whether all, or a portion, of the diacid component
will comprise an ethylenically unsaturated
dicarboxylic acid and/or anhydride, and whether all,
or a portion, of the diol component will comprise an
ethylenically unsaturated diol compound.

15 It will be understood that the reactants
present in the reaction mixture, which undergoes
condensation polymerization in this aspect of the
process of the present invention, can include one or
more reactants customarily employed in the synthesis
20 of such condensation polymers.

One reactant preferably employed in the
desired condensation polymerization reaction is a
diacid component by which is meant one or more
dicarboxylic acids, one or more anhydrides of
25 dicarboxylic acids, or mixtures thereof.

The dicarboxylic acids that can be used in
the present invention include aliphatic dicarboxylic
acids, alicyclic dicarboxylic acids, aromatic
dicarboxylic acids, ethylenically unsaturated alkenyl
30 dicarboxylic acids, or mixtures of two or more of any

of these acids. Preferred are alkyl dicarboxylic
1 diacids which generally will contain 4 to 36 carbon
atoms, and aromatic dicarboxylic diacids which
generally contain 9 to 20 carbon atoms. Examples of
useful dicarboxylic acids include oxalic, malonic,
5 dimethylmalonic, succinic, glutaric, adipic,
trimethyladipic, pimelic, 2,2-dimethylglutaric,
azelaic, sebacic, suberic, 1,3-
cyclopentanedicarboxylic, 1,2-cyclohexanedicarboxylic,
1,3-cyclohexanedicarboxylic, 1,4-
10 cyclohexanedicarboxylic, phthalic, terephthalic,
isophthalic, tetrahydrophthalic, hexahydrophthalic,
2,5-norbornanedicarboxylic, 1,4-naphthalic, diphenic,
4,4'-oxydibenzoic, diglycolic, thiodipropionic, 4,4'-
sulfonyldibenzoic, and 2,5-naphthalenedicarboxylic
15 acids. Anhydrides of any of the foregoing are also
contemplated.

Preferred difunctional dicarboxylic acids
include isophthalic acid, terephthalic acid, phthalic
acid, adipic acid, tetrachlorophthalic acid, pivalic
20 acid, dodecanedioic acid, sebacic acid, azelaic acid,
1,4-cyclohexanedicarboxylic acid, 1,3-
cyclohexanedicarboxylic acid, maleic acid, fumaric
acid, succinic acid, 2,6-naphthalenedicarboxylic acid,
glutaric acid, and any of the anhydrides thereof.

25 As indicated, the diacid component can
comprise in whole or in part one or more ethylenically
unsaturated polycarboxylic acids, especially
dicarboxylic acids or their anhydrides, including but
not limited to fumaric acid, maleic acid, mesaconic
30 acid, citraconic acid, muconic acid (e.g. trans-trans

muconic acid) and itaconic acid, and any anhydrides thereof, such as maleic anhydride. In general, the preferred ethylenically unsaturated dicarboxylic acids and anhydrides will contain 4 to 8 carbon atoms but may contain anywhere from 4 to 36 carbon atoms.

Diacids wherein the ethylenic unsaturation is pendant from the principle chain of the diacid are also contemplated within the scope of the present invention. Examples include any of the foregoing dicarboxylic acids and anhydrides having a pendant chain containing 2 to 8 carbon atoms at least two of which are connected by a carbon-carbon double bond, such as vinyl, propenyl, butenyl, and the like. One example is 2-vinyl-butane-1, 4-dioic acid.

Diol compounds that can be used in the present invention include glycols, of which ethylene glycol is the preferred diol.

In cases where glycols in addition to, or instead of, ethylene glycol are utilized, it is preferable for them to contain from 3 to 10 carbon atoms. In cases where glycol ethers are utilized in conjunction with ethylene glycol in the diol component, it is preferable for them to contain from 4 to 10 carbon atoms. Some representative examples of glycols that can be used in conjunction with or instead of ethylene glycol include 1,3-propylene glycol, 1,2-propylene glycol, 2,2-diethyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, 2-ethyl-2-isobutyl-1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2,4-trimethyl-1,6-

hexanediol, 2,4-dimethyl-2-ethylhexane-1,3-diol, 1,2-
1 cyclohexanediol, 1,3-cyclohexanedimethanol, 1,4-
cyclohexanedimethanol, p-xylenediol, and 2,2,4,4-
tetramethyl-1,3-cyclobutanediol.

Polyols are also contemplated. Preferred
5 polyols contain 3 or more hydroxyl groups and
generally up to 8 carbon atoms. Examples include
trimethylol propane, hexane-1, 2, 6-triol, butane-1,
2, 4-triol, trimethylolethane, pentaerythritol,
quinitol, mannitol and sorbitol.

10 Preferred ethylenically unsaturated diol
compounds contain 4 to 10 carbon atoms. Examples of
such compounds include allyl diglycol, as well as any
ethylenically unsaturated analogs of the exemplary
glycols set forth hereinabove.

15 Included within the scope of ethylenically
unsaturated diols useful in the process of the present
invention are those wherein the ethylenic unsaturation
is present in, or in a substituent pendant from, the
chain connecting the two diol groups. Preferred
20 examples include the mono-acrylates and mono-
methacrylates of triols such as glycerol, wherein two
hydroxyl groups remain available to cooperate in the
formation of the polyester molecule. Other examples
of satisfactory ethylenically unsaturated diols
25 include 1,4-butenediol, 1,4-butyne-1,3-diol, glycerine
allyl ether and glyceryl monostearate.

If branching is desirable, then it will be
advantageous to use a branching agent in the
condensation polymerization reaction. Such branching
30 agents may contain three or more functional groups,

and they preferably contain three or four functional
1 groups. The reactive groups may be carboxyl or
aliphatic hydroxyl. The branching agent may contain
both types of groups. Examples of acidic branching
agents include trimesic acid, trimellitic acid,
5 pyromellitic acid, butanetetracarboxylic acid,
naphthalene tricarboxylic acids and cyclohexane-1,3,5-
tricarboxylic acid. Examples of hydroxy acid
branching agents are 2,2-dihydroxymethyl propionic
acid, 10,11-dihydroxy-undecanoic acid, and 5-(2-
10 hydroxyethoxy)isophthalic acid. Generally from 0 to 3
percent of a polyol containing from 3 to 12 carbon
atoms will be used as the branching agent (based upon
the total diol component).

As indicated, condensation polymers useful
15 in this invention also include bifunctional compounds
such as hydroxyacids, which would be polymerized head-
to-tail in known manner. Such reactants could include
some ethylenically unsaturated compounds. Examples of
such reactants include 6-hydroxy hexenedioic acid, and
20 the like.

The acid component (which, as defined above,
comprises one or more acids and/or anhydrides) and the
one or more reactants destined to react with the acid
or anhydride component are selected so that the
25 reactants that enter into the condensation
polymerization include a sufficient amount of
ethylenic unsaturation so that the sulfonation which
occurs at the ethylenically unsaturated sites provides
a satisfactory degree of water dispersibility in the
30 eventual polyurethane.

Thus, the amount of reactant bearing
1 ethylenic unsaturation can comprise 1 mol.% to 50
mol.% of the reaction mixture. Generally, the
unsaturated reactant(s) comprise about 1 mol.% to
about 10 mol.% of the reaction mixture. The reactants
5 are otherwise selected to be approximately equimolar
in relationship to each other with the proviso that
the component which carries the desired terminal
hydroxyl group or groups of the polymer should be
provided in stoichiometric excess. Thus, for
10 instance, when reacting diols and diacids, to ensure
that the polymer should be endcapped with hydroxyl
terminal groups, an excess of the diol component
should be supplied. It will be recognized that to
ensure that the polymer is capped with the desired
15 terminal groups, it may be necessary to provide in the
reaction mixture more than simply a slight
stoichiometric excess of the indicated component; the
degree of excess is tempered, however, by the effect
of that excess on the distribution of polymeric chain
20 lengths formed by the condensation polymerization.

The reaction mixture is then subjected to
condensation polymerization conditions effective to
cause the reactants to react with each other to form
the desired polyester. In general, effective
25 condensation polymerization conditions are readily
familiar to (and ascertainable by) the practitioner.
It is preferred not to carry out the reaction in a
solvent. However, if a solvent is desired, it should
be high boiling (i.e. a boiling point above about
30 140°C.) Examples of suitable solvents include DMF

(dimethylformamide), DMA (N,N-dimethylacetamide),
1 xylene and DMSO.

Preferably, the reactant mixture for
carrying out the condensation polymerization includes
a small but effective amount such as up to about 0.02
5 wt.% of a catalyst for the polymerization. Useful
catalytic compounds include protonic acids, tin
compounds, titanium compounds and antimony compounds.

Typical condensation polymerization
conditions are provided by exposing the reactants to
10 temperatures on the order of about 150°C to about
250°C. During the progress of the reaction, it is
preferred to draw off water of condensation. To
effectively carry out the desired condensation
polymerization it is preferred to use nitrogen to
15 purge the reaction mixture in order to carry out the
water.

The chain lengths and molecular weights of
the polymers that are useful and produced in the
process of the present invention can fall within a
20 rather wide range; typically, polyesters most useful
in preparing polyurethanes as described herein will
have a molecular weight in the range of about 500 to
about 6,000. Thus, amounts and identities of the
reactants can readily be tailored to achieve any
25 desired molecular weight and molecular weight
distribution.

At the end of the condensation
polymerization, the product can be recovered and
separated from the reaction mixture, or can be

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subjected to the sulfonation reaction in situ without
1 first being recovered.

When the sulfonate functionality is added
into the overall scheme at this point, sulfonation is
carried out by reacting the ethylenically unsaturated
5 polyester under appropriate sulfonating conditions
with a sulfonating agent which comprises one or more
bisulfites and/or one or more metabisulfites.
Preferred sulfonating agents are the ammonium and
alkali metal sulfites and alkali metal metabisulfites.
10 The more preferred sulfonating agents are sodium
bisulfite and sodium metabisulfite. Other preferred
sulfonating agents include lithium bisulfite, lithium
metabisulfite, potassium bisulfite, potassium
metabisulfite, ammonium bisulfite and ammonium
15 metabisulfite.

Sulfonation should be carried out using a
stoichiometric excess of the sulfonating agent,
calculated on the basis of the degree of ethylenic
unsaturation present in the condensation polymer
20 resulting from the foregoing condensation
polymerization step. The sulfonation is preferably
carried out in a suitable solvent such as water.
Satisfactory sulfonation conditions include
maintaining a temperature of about 10°C to about 120°C
25 for a time on the order of 2-15 hours. The
sulfonation also can be catalyzed by fine air bubbles
purged through the reaction medium.

30 2. Forming the polyester from sulfonate-substituted monomers

Another preferred technique for forming the
1 sulfonate-substituted and hydroxyl-substituted
polyester is to carry out the condensation
polymerization reaction which forms the polyester from
monomers which are already sulfonate-substituted.

5 One essential condition of this aspect of
the present invention is that at least a portion, or
all, of at least one of the difunctional monomeric
reactants contains ethylenic unsaturation, that is, a
carbon-carbon double bond, either in its main chain or
10 pendant from its main chain.

In the first step of this aspect of the
present invention, the ethylenically unsaturated
monomeric precursor (e.g. diacid, anhydride, or diol)
is sulfonated. Sulfonation is carried out by reacting
15 the compound under appropriate sulfonating conditions
with a sulfonating agent which comprises one or more
bisulfites and/or one or more metabisulfites.
Preferred sulfonating agents are the ammonium and
alkali metal sulfites and alkali metal metabisulfites.
20 Thus, the more preferred sulfonating agents are sodium
bisulfite and sodium metabisulfite. Other preferred
sulfonating agents include lithium bisulfite, lithium
metabisulfite, potassium bisulfite, potassium
metabisulfite, ammonium bisulfite and ammonium
25 metabisulfite.

Sulfonation of the monomeric precursor
should be carried out using a stoichiometric excess of
the sulfonating agent. The sulfonation is preferably
carried out in a suitable solvent such as water.
30 Satisfactory sulfonation conditions include

maintaining a temperature of about 10°C to about 120°C
1 for a time on the order of 2-15 hours. The
sulfonation also can be catalyzed by fine air bubbles
purged through the reaction medium, or by any
peroxides such as hydrogen peroxide, benzoyl peroxide,
5 or t-butyl hydrogen peroxide.

Optionally, one may include in the reaction
mixture of ethylenically unsaturated difunctional
monomeric precursor and sulfonating agent, a second
difunctional precursor reactant which enters into a
10 condensation reaction with the ethylenically
unsaturated monomeric precursor and endcaps it. If
such another reactant is present, the reaction product
is a sulfonated difunctional dimer which contains an
amide, ether or ester linkage, depending on the
15 chemical identity of the reactants and thus the nature
of the endcapping reaction. Compounds suitable for
use as the second difunctional precursor include
compounds substituted with at least two groups
selected from the group consisting of -OH and
20 -COOH at least one of which can enter into a
condensation reaction with the monomeric precursor.
Examples include diacids and diols containing 2 to 8
carbon atoms, such as 1,6-hexanediol and 1,6-
diaminohexane.

25 The desired ethylenic unsaturation is
present as an ethylenically unsaturated diacid, an
ethylenically unsaturated anhydride (such as maleic
anhydride), or an ethylenically unsaturated diol, or
mixtures of any two or more of such compounds. Also,

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ethylenically unsaturated compounds which contain
1 nonidentical functional groups can be used.

The ethylenically unsaturated diacid
component can comprise in whole or in part one or more
ethylenically unsaturated polycarboxylic acids,
5 especially dicarboxylic acids or their anhydrides,
including but not limited to fumaric acid, maleic
acid, mesaconic acid, citraconic acid, muconic acid
(e.g. trans-trans muconic acid) and itaconic acid, and
any anhydrides thereof, such as maleic anhydride. In
10 general, the preferred ethylenically unsaturated
dicarboxylic acids and anhydrides will contain 4 to 8
carbon atoms but may contain anywhere from 4 to 36
carbon atoms.

Diacids wherein the ethylenic unsaturation
15 is pendant from the principal chain of the diacid are
also contemplated within the scope of the present
invention. Examples include any of the dicarboxylic
acids disclosed herein, and their anhydrides, having a
pendant chain containing 2 to 8 carbon atoms at least
20 two of which are connected by a carbon-carbon double
bond, such as vinyl, propenyl, butenyl, and the like.
One example is 2-vinyl-butane-1, 4-dioic acid.

Preferred ethylenically unsaturated diol
compounds contain 4 to 10 carbon atoms. Examples of
25 such compounds include allyl diglycol, as well as any
ethylenically unsaturated analogs of the exemplary
glycols set forth herein.

Included within the scope of ethylenically
unsaturated diols useful in the process of the present
30 invention are those wherein the ethylenic unsaturation

is present in, or in a substituent pendant from, the
1 chain connecting the two diol groups. Preferred
examples include the mono-acrylates and mono-
methacrylates of triols such as glycerol, wherein two
hydroxyl groups remain available to cooperate in the
5 formation of the polyester molecule. Other examples
of satisfactory ethylenically unsaturated diols
include 1,4-butenediol, 1,4-butyne-2,3-diol, glycerine
allyl ether and glyceryl monostearate.

Whether or not the indicated optional
10 reactant was also present, the product of this first
step of the process of the present invention is a
sulfonated product, at least di-substituted with
groups selected from the group consisting of -OH and
-COOH. This product is termed a monomeric precursor
15 in that it has either no, or at most one,
-C(O)O-linkage. This product must be capable of
undergoing condensation polymerization with a suitable
difunctional second monomer in the second step of this
embodiment of the present invention.

20 The second step of this embodiment of the
present invention can be carried out with any of a
considerable number of reactants. The choice depends
on the nature of the functional groups present, and in
part on the properties desired of the eventual
25 product.

One reactant preferably employed in the
desired condensation polymerization reaction is a
diacid component, by which is meant one or more
dicarboxylic acids, one or more anhydrides of
30 dicarboxylic acids, or mixtures thereof.

The dicarboxylic acids that can be used in
1 the present invention include aliphatic dicarboxylic
acids, alicyclic dicarboxylic acids, aromatic
dicarboxylic acids, ethylenically unsaturated alkenyl
dicarboxylic acids, or mixtures of two or more of
5 these acids. Preferred are alkyl dicarboxylic diacids
which generally will contain 4 to 36 carbon atoms, and
aromatic dicarboxylic diacids which generally contain
9 to 20 carbon atoms. Examples of useful dicarboxylic
acids include oxalic, malonic, dimethylmalonic,
10 succinic, glutaric, adipic, trimethyladipic, pimelic,
2,2-dimethylglutaric, azelaic, sebacic, suberic, 1,3-
cyclopentanedicarboxylic, 1,2-cyclohexanedicarboxylic,
1,3-cyclohexanedicarboxylic, 1,4-
cyclohexanedicarboxylic, phthalic, terephthalic,
15 isophthalic, tetrahydrophthalic, hexahydrophthalic,
2,5-norbornanedicarboxylic, 1,4-naphthalic, diphenic,
4,4'-oxydibenzoic, diglycolic, thiodipropionic, 4,4'-
sulfonyldibenzoic, and 2,5-naphthalenedicarboxylic
acids. Anhydrides of any of the foregoing are also
20 contemplated.

Preferred difunctional dicarboxylic acids
include isophthalic acid, terephthalic acid, phthalic
acid, adipic acid, tetrachlorophthalic acid, pivalic
acid, dodecanedioic acid, sebacic acid, azelaic acid,
25 1,4-cyclohexanedicarboxylic acid, 1,3-
cyclohexanedicarboxylic acid, maleic acid, fumaric
acid, succinic acid, 2,6-naphthalenedicarboxylic acid,
glutaric acid, and any of the anhydrides thereof.

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Diol compounds that can be used in the present invention include glycols, of which ethylene glycol is the preferred diol.

In cases where glycols in addition to, or instead of, ethylene glycol are utilized, it is preferable for them to contain from 3 to 10 carbon atoms. In cases where glycol ethers are utilized in conjunction with ethylene glycol in the diol component, it is preferable for them to contain from 4 to 10 carbon atoms. Some representative examples of glycols that can be used in conjunction with or instead of ethylene glycol include 1,3-propylene glycol, 1,2-propylene glycol, 2,2-diethyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, 2-ethyl-2-isobutyl-1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2,4-trimethyl-1,6-hexanediol, 2,4-dimethyl-2-ethylhexane-1,3-diol, 1,2-cyclohexanediol, 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol, p-xylenediol, and 2,2,4,4-tetramethyl-1,3-cyclobutanediol.

As the diol component, polyether glycols can also be used, such as polypropylene glycol having a molecular weight of 200 to 6,000 (examples of which include ("Rezol ED-1000" and "Rezol ED-2000", sold by Witco Corporation); polyethylene glycol having a molecular weight of 200 to 6,000 (examples of which include ("Rezol PEG-400" and "Rezol PEG-1000", sold by Witco Corporation); and block and random copolymers of propylene glycol and ethylene glycol, having a molecular weight of 200 to 6,000 (examples of which

include "Rezol EPD-112", "Rezol EPD-225", "Rezol EPD-
1 56", and "Rezol EPD-28" sold by Witco Corporation).

If branching is desirable, then it will be advantageous to use a branching agent in the condensation polymerization reaction. Such branching
5 agents may contain three or more functional groups, and they preferably contain three or four functional groups. The reactive groups may be carboxyl or aliphatic hydroxyl. The branching agent may contain both types of groups. Examples of acidic branching
10 agents include trimesic acid, trimellitic acid, pyromellitic acid, butanetetracarboxylic acid, naphthalene tricarboxylic acids and cyclohexane-1,3,5-tricarboxylic acid. Examples of hydroxyl branching agents (polyols) include glycerin, trimethylpropane,
15 pentaerythritol, dipentaerythritol, 1,2,6-hexanetriol and 1,3,5-trimethylolbenzene. Examples of hydroxy acid branching agents are 2,2-dihydroxymethyl propionic acid, 10,11-dihydroxy-undecanoic acid, and 5-(2-hydroxyethoxy)isophthalic acid. Generally from 0
20 to 3 percent of a polyol containing from 3 to 12 carbon atoms will be used as the branching agent (based upon the total diol component).

As indicated, condensation polymers useful in this invention also include bifunctional compounds
25 such as hydroxyacids, which are polymerized head-to-tail in known manner. Such reactants would have to include some ethylenically unsaturated compounds. Examples of such reactants include 6-hydroxy (or 6-amino) hexanedioic acid, and the like.

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The acid component (which, as defined above,
1 comprises one or more acids and/or anhydrides) and the
one or more reactants destined to react with the acid
or anhydride component are selected so that the
reactants that enter into the condensation
5 polymerization include a sufficient amount of
sulfonation so that the sulfonated reaction product of
the present invention provides a satisfactory degree
of water dispersibility in the polymer.

Thus, the amount of sulfonated reactant can
10 comprise 1 mol.% to 50 mol.% of the reaction mixture
in the second step of the process. Generally, the
sulfonated reactant(s) comprise about 1 mol.% to about
10 mol.% of the reaction mixture. The reactants are
otherwise selected to be approximately equimolar in
15 relationship to each other with the proviso that the
component which carries the substituent group
identical to the desired terminal group or groups of
the polymer should be provided in stoichiometric
excess.

20 Thus, since it is desired that the polyester
should be endcapped with hydroxyl terminal groups,
then an excess of the diol component should be
supplied. It will be recognized that to ensure that
the polymer is capped with the desired terminal
25 hydroxyl groups, it may be necessary to provide in the
reaction mixture more than simply a slight
stoichiometric excess of the indicated component; the
degree of excess is tempered, however, by the effect
of that excess on the distribution of polymeric chain
30 lengths formed by the condensation polymerization.

The reaction mixture is then subjected to
1 condensation polymerization conditions effective to
cause the reactants to react with each other to form
the desired condensation polymers. In general,
effective condensation polymerization conditions are
5 readily familiar to (and ascertainable by) the
practitioner. It is preferred not to carry out the
reaction in a solution. However, if a solvent is
desired, it should be high boiling (i.e. a boiling
point above about 140°C.) Examples of suitable
10 solvents include DMF (dimethylformamide), DMA (N,N-
dimethylacetamide), xylene and DMSO.

Preferably, the reactant mixture for
carrying out the condensation polymerization includes
a small but effective amount such as up to about 0.02
15 wt.% of a catalyst for the polymerization. Useful
catalytic compounds include protonic acids, tin
compounds, titanium compounds and antimony compounds.

Typical condensation polymerization
conditions are provided by exposing the reactants to
20 temperatures on the order of about 150°C to about
250°C. During the progress of the reaction, it is
preferred to draw off water of condensation. To
effectively carry out the desired condensation
polymerization it is preferred to use nitrogen to
25 purge the reaction mixture in order to carry out the
water.

The chain length or molecular weight of the
polymers that are useful and produced in the process
of the present invention can fall within a rather wide
30 range; typically, useful polymers will have a

molecular weight in the range of about 200 to about
1 50,000. Thus, amounts and identities of the reactants
can readily be tailored to achieve any desired
molecular weight and distribution.

At the end of the condensation
5 polymerization, the product can be recovered and
separated from the reaction mixture.

This aspect of the present invention affords
several significant advantages compared to other
processes for producing water-dispersible sulfonated
10 polymers. In particular, each of the foregoing steps
can be carried out under relatively mild conditions
and are not particularly constrained by the choice of
reactants. In particular, a much greater freedom in
choice of reactants is provided, as the reactants in
15 the condensation polymerization step can be
polymerized under relatively straightforward
condensation polymerization conditions and the
sulfonation step can be carried out under fairly
conventional sulfonation conditions. This freedom in
20 the choice of reactants is an advantage in that it
affords greater range in the tailoring of the
properties of the final, water-dispersible sulfonated,
hydroxyl-terminated polyester that is produced.

25 B. FORMATION OF SULFONATE-SUBSTITUTED PREPOLYMERS

The sulfonate-substituted polyesters made by
the foregoing description are useful in synthesizing
polyurethane polymers. Preferably, the sulfonate-
substitute polyesters used in polyurethane synthesis
30 are polyesters which are made (as described above)

using a coreactant containing two or more hydroxyl
1 groups so that the sulfonate-substituted polyester
contains unreacted hydroxyl groups.

There should be an average of at least 2
hydroxyl groups per mole of sulfonate-substituted
5 polyester. More preferably, the hydroxyl substitution
corresponds to at least 2 hydroxyls per molecule of
polymer; or a hydroxyl number of at least about 15,
preferably in the range of about 25 to about 225. The
hydroxyl number is defined as the number of milligrams
10 of potassium hydroxide equivalent to the hydroxyl
content of the sample. To determine a hydroxyl
number, the material is reacted with acetic anhydride
in pyridine and the excess anhydride is hydrolyzed and
titrated. The hydroxyl number is calculated from the
15 amount of reagent consumed. One equivalent of
hydroxyl uses one equivalent of anhydride.

The sulfonate-substituted polyester used in
polyurethane synthesis preferably has a molecular
weight of about 500 to about 6,000 to function
20 satisfactorily as a segment (in polymer technology,
the "soft segment") of the eventual polyurethane.
Those practitioners familiar with this chemical field
can readily select reactants and reaction conditions
which are effective to prepare polymers having a
25 molecular weight desired for further use in the
synthesis of polyurethanes.

Then, the sulfonate-substituted polyester is
reacted with one or more polyisocyanates, preferably
one or more diisocyanates, and with one or more chain
30 extenders, to produce the desired polyurethane.

Any organic polyisocyanates may be used in
1 the process according to the invention. It is
preferred to use polyisocyanates of the formula
 $Q(NCO)_2$, wherein Q represents an aliphatic hydrocarbon
group containing from 4 to 12 carbon atoms, a
5 cycloaliphatic hydrocarbon group containing from 6 to
15 carbon atoms, an aromatic hydrocarbon group
containing from 6 to 15 carbon atoms or an araliphatic
hydrocarbon group containing from 7 to 15 carbon
atoms. The most preferred diisocyanate is isophorone
10 diisocyanate. The following are examples of other
preferred diisocyanates: tetramethylene-diisocyanate,
hexamethylene diisocyanate, dodecamethylene-
diisocyanate, 1,4-diisocyanato-cyclohexane, 1-
isocyanato-3, 3, 5-trimethyl-5-isocyanatomethyl
15 cyclohexane, 4,4'-diisocyanatodicyclohexylethane,
4,4'-diisocyanato-dicyclohexyl-propane-(2,2); 1,4-
diisocyanato-benzene, 2,4-diisocyanatotoluene, 2,6-
diisocyanatotoluene, 4,4'-diisocyanatodiphenylmethane,
4,4'-diisocyanatodiphenyl-propane-(2,2), p-xylylene-
20 diisocyanate, a,a,a',a'-tetramethyl-m-or p-xylylene-
diisocyanate and mixtures of these compounds.
Mixtures of any of the foregoing can also be used.
The mole ratio of diisocyanate to polyester is
generally stoichiometric, e.g. (1.9-2.1):1.

25 The reaction of the hydroxyl-substituted
("polyol") polyester with the diisocyanate can
optionally be carried out in the presence of a
comonomer such as a lower diol containing 2 to 10
carbon atoms. Typical amounts of such a comonomer are

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up to about 10 wt.% of the amount of all reactants
1 present.

Reaction of the diisocyanate and the polyol
polymer can be carried out at moderately elevated
temperatures, e.g. 50°C.-100°C. The reaction is
5 generally carried out in an inert solvent or without a
solvent. One preferred solvent is N-methyl
pyrrolidone. Other suitable solvents include acetone,
methyl ethyl ketone, toluene, dimethyl formamide,
ethyl acetate, tetrahydro furan, and dioxane.

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C. CHAIN EXTENDING THE PREPOLYMER

The polymeric isocyanate-dicapped product of
the reaction with the diisocyanate is next reacted
with a suitable chain extender, preferably dispersed
15 in water. Satisfactory chain extenders include
diamines such as hydrazine, and alkyl and aromatic
polyols, especially diols, and alkyl and aromatic
diamines and triamines, wherein the alkyl compounds
contain a total of 2 to 12 carbon atoms or the
20 aromatic moiety contains 6 to 10 carbon atoms. Other
examples of chain extenders include ethylene diamine,
diethylene triamine, 1,2-diaminopropane, 1,3-
diaminopropane, 1,4-diaminobutane, and 3,3,5-
trimethyl-5-aminomethyl cyclohexylamine; and ethylene
25 glycol, 1,2-dihydroxypropane, 1,6-dihydroxyhexane, and
the polyols described herein as useful reactants to
make the polyester.

The product of reaction with the chain
extender is a dispersion of polymeric polyurethane
30 particles. This dispersion can be dissolved or

suspended in a suitable vehicle for application as a
1 coating or film, or for compounding into any of the
large variety of industrial and domestic products
which can be fabricated from polyurethanes.

The invention will be described further in
5 the following examples. These examples are intended
for illustrative purposes, and are not intended to
limit the scope of applicants' invention.

Examples 1 and 2 illustrate preparation of
sulfonate-substituted polyester by preparation of an
10 ethylenically unsaturated polyester which is then
sulfonated.

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EXAMPLE 1

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Sulfonation of Ethylenically Unsaturated
Polyester Terminated with Hydroxyl Groups

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Raw Materials:

	1,4-Butanediol	857	grams
	1,6-Hexanediol	1,124	grams
	Adipic Acid	2,074	grams
	Maleic Anhydride	155	grams
10	Total Load	4,210	grams
	Organotin Catalyst	0.30	grams
	Water to distill	540	grams
	Theoretical Yield	3,670	grams
	Sodium Bisulfite	162	grams
15	Water	379	grams

Procedure:

A four neck glass flask, equipped with a
nitrogen inlet, a stirrer, a column, and a
20 thermometer, was charged with catalyst, 1,4-
butanediol, 1,6-hexanediol, and maleic anhydride, and
the contents were heated to approximately 80°C.
Adipic acid was added at an appropriate rate for the
reaction to proceed under control. The temperature
25 was increased to 225°C, while the column was kept hot
using steam. The nitrogen and agitation were
increased, as the reaction proceeded, to facilitate
the water removal, but not rapid enough to expel the
glycol.

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The hydroxyl value and acid number were
1 checked as needed and the loss of glycol during the
reaction was adjusted to reach the theoretical
hydroxyl value. Reaction was considered complete when
the hydroxyl number and the acid number reached the
5 expected values.

The reactor contents were then cooled to
85°C. The column was replaced with a water condenser
and nitrogen was shut off. A clear water solution of
sodium bisulfite was added under constant agitation,
10 and the temperature was maintained at 75 to 80°C for 8
hours. Vacuum was then applied in order to strip the
water, and reaction was considered complete when the
percent moisture value reached the desired result.
The final product had a hydroxyl number of 93.6, an
15 acid number of 0.65, a moisture content of 0.06%, a
viscosity at 40° of 16,300 cps, an active anionic
group of 0.344 meq/g, and a sulfonation conversion of
88.3%. The polymer, a sulfonated polyester, was
dispersed in water very easily, and the dispersed
20 polyester demonstrated good stability.

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EXAMPLE 2

Sulfonation of Ethylenically Unsaturated Polyester Terminated with Dihydroxyl Groups

Raw Materials:

Ethylene Glycol	1,187 grams
Adipic Acid	2,163 grams
Maleic Anhydride	156 grams
Total Load	3,506 grams
Organotin Catalyst	0.30 grams
Water to Distill	562 grams
Theoretical Yield	2,936 grams
Sodium Bisulfite	165 grams
Water	660 grams

Procedure:

A four neck glass flask, equipped with a nitrogen inlet, a stirrer, a column, and a thermometer, was charged with catalyst, ethylene glycol, and maleic anhydride and heated to approximately 80°C. Adipic acid was added at an appropriate rate for the reaction to proceed under control. The temperature was increased to 225°C, while the column was kept hot using steam. The nitrogen and agitation were increased, as the reaction proceeded, to facilitate the water removal, but not rapid enough to expel the glycol.

The hydroxyl value and acid number were checked as needed, and the loss of glycol during the reaction was adjusted to reach the theoretical hydroxy

value. Reaction was considered complete when the
1 hydroxyl number and the acid number reached the
expected values.

The reactor contents were then cooled to
85°C. The column was replaced with a water condenser,
5 and nitrogen was shut off. A clear water solution of
sodium bisulfite was added under constant agitation,
and the temperature was maintained at 75 to 80°C for 8
hours. Vacuum was then applied in order to strip the
water, and reaction was considered complete when the
10 percent moisture value reached the desired result.
The final product had a hydroxyl number of 96.6, an
acid number of 1.00, and a moisture content of 0.08%.
The polymer, a sulfonated polyester, was dispersed in
water very easily, and the dispersed polyester
15 demonstrated good stability.

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Examples 3-6 illustrate the formation of
1 water-dispersible polyurethanes employing as one
reactant sulfonate-substituted polyester which had
been prepared by sulfonation of an ethylenically
unsaturated polyester in a manner analogous to that
5 shown in Examples 1 and 2.

EXAMPLE 3

A water dispersible polyurethane was
10 prepared from sodium sulfonate-grafted
poly(butylene/hexamethylene adipate) glycol with a
molecular weight of 1,200 and a hydroxyl number of 95.

RAW MATERIAL

15 1. NCO-Terminated Prepolymer

IPDI (Isophorone diisocyanate)	198.6 grams
Sulfonate-grafted polyester, OH no.= 95	589.2 grams
N-methylpyrrolidone ("NMP")	200.0 grams

2. Dispersion

20 NCO-terminated prepolymer	900.0 grams
Water	1,510.0 grams
Hydrazine (54.4%)	15.9 grams

PROCEDURE:

The polyester and the NMP were added to a
25 reaction kettle and dehydrated by a vacuum pump at
100°C with stirring for 30 minutes. The mixture was
then cooled to 80°C. and the diisocyanate was added.
Stirring was continued at 80°C. until the theoretical
isocyanate content was reached (about 5 hours). The
30 resulting prepolymer at a temperature of 80°C was

dispersed in the solution of hydrazine in water at a
1 temperature of 25°C. Stirring was continued for 4
hours. The reaction mixture was cooled to room
temperature and filled into containers through a 200
micron sieve.

5 The product was a fine dispersion which had
a particle size of 60 nm and a solids content of 30%.
The pH of the dispersion was 7.5. A dry film was
formed from this dispersion which had a tensile
strength of 2,200 psi, a 100% modulus of 185 psi, a
10 200% modulus of 225 psi, a 300% modulus of 270 psi,
and an elongation of 650%.

EXAMPLE 4

15 A water dispersible polyurethane was prepared from
sodium sulfonate-grafted poly(butylene adipate) glycol
with a molecular weight of 1,200 and a hydroxyl number
of 95.

20 RAW MATERIAL

1. NCO-Terminated Prepolymer

IPDI (Isophorone diisocyanate)	225.5 grams
Sulfonate-grafted polyester	574.1 grams
OH no.= 95	
1,4-Butanediol	12.2 grams
25 NMP	90.0 grams

2. Dispersion

NCO-terminated prepolymer	810.0 grams
Water	1,630.0 grams
Hydrazine (35%)	28.6 grams

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PROCEDURE:

1 The polyester, 1,4-butanediol, and NMP were
added to a reaction kettle and dehydrated by a vacuum
pump at 100°C with stirring for 30 minutes. The
mixture was then cooled to 80°C. and the diisocyanate
5 was added. Stirring was continued at 80°C. until the
theoretical isocyanate content was reached (about 5
hours). The prepolymer at a temperature of 80°C. was
dispersed in the aqueous hydrazine solution at a
temperature of 25°C. Stirring was continued for 4
10 hours. The reaction mixture was cooled to room
temperature and filled into containers through a 200 -
micron sieve.

The product was a fine dispersion which had
a particle size of 35 nm and a solids content of 30%.
15 The pH of the dispersion was 7.2. A dry film formed
from this dispersion had a tensile of 30%. The pH of
the dispersion was 7.2. A dry film formed from this
dispersion had a tensile strength of 1,250 psi, a 100%
modulus of 183 psi, a 200% modulus of 206 psi, a 300%
20 modulus of 226 psi, and an elongation of 800%.

EXAMPLE 5

A water dispersible polyurethane was
prepared from sodium sulfonate-grafted poly(ethylene
25 adipate) glycol with a molecular weight of 1,200 and a
hydroxyl number of 95.

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RAW MATERIAL

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1. NCO-Terminated Prepolymer

IPDI (Isophorone diisocyanate)	223.3 grams
Sulfonate-grafted polyester,	574.6 grams
OH no.= 95	
1,4-Butanediol	12.2 grams
NMP	90.0 grams

5

2. Dispersion

NCO-terminated prepolymer	810.0 grams
Water	1,628.0 grams
Hydrazine (35%)	26.6 grams

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PROCEDURE:

1 The polyester, 1,4-butanediol, and NMP were
added to a reaction kettle and dehydrated by a vacuum
pump at 100°C with stirring for 30 minutes. The
mixture was then cooled to 80°C. and the diisocyanate
5 was added. Stirring was continued at 80°C. until the
theoretical isocyanate content was reached (about 5
hours). The prepolymer at a temperature of 80°C was
dispersed in the aqueous hydrazine solution at a
temperature of 25°C. Stirring was continued for 4
10 hours. The reaction mixture was cooled to room
temperature and filled into containers through a 200 -
micron sieve.

 The product was a fine dispersion which had
a particle size of 37 nm and a solids content of 30%.
15 The pH of the dispersion was 7.7. A dry film formed
from this dispersion had a tensile strength of 3,309
psi, a 100% modulus of 223 psi, a 200% modulus of 278
psi, a 300% modulus of 358 psi, and an elongation of
730%.

20 EXAMPLE 6

 A water dispersible polyurethane was
prepared from sodium sulfonate-grafted
poly(butylene/hexamethylene adipate) glycol with a
25 molecular weight of 1,100 and a hydroxyl number of
100.

RAW MATERIAL

1. NCO-Terminated Prepolymer
30

1	IPDI (Isophorone diisocyanate)	243.7 grams
	Sulfonate-grafted polyester,	592.3 grams
	OH no.= 95	
	1,4-Butanediol	8.4 grams
	NMP	55.5 grams
2. Dispersion		
5	NCO-terminated prepolymer	810.0 grams
	Water	1,738.0 grams
	Hydrazine (35%)	34.6 grams

PROCEDURE:

10 The polyester, 1,4-butanediol, and NMP were added to a reaction kettle and dehydrated by a vacuum pump at 100°C with stirring for 30 minutes. The mixture was then cooled to 80°C. and the diisocyanate was added. Stirring was continued at 80°C. until the theoretical isocyanate content was reached (about 5
15 hours). The prepolymer at a temperature of 80°C was dispersed in the aqueous hydrazine solution at a temperature of 25°C. Stirring was continued for 4 hours. The reaction mixture was cooled to room temperature and filled into containers through a 200 -
20 micron sieve.

The product was a fine dispersion which had a particle size of 60 nm and a solids content of 30%. The pH of the dispersion was 7.4. A dry film formed from this dispersion had a tensile strength of 8,978
25 psi, a 100% modulus of 1,410 psi, a 300% modulus of 5,744 psi, and an elongation of 400%.

30 Examples 7 through 10 illustrate the preparation of sulfonate-substituted polyester via polymerization of sulfonated monomer, and its use in the preparation of polyurethane.

EXAMPLE 7

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A. Preparation of adduct (50%) [2-(sodiosulfo)-1,4- butanedioic acid]

5 RAW MATERIAL

Maleic Anhydride	111.4	grams
Water	270.5	grams
Sodium Bisulfite	118.2	grams

10 PROCEDURE

A four neck glass flask, equipped with a nitrogen inlet, a stirrer, a water condenser, and a thermometer, was charged with maleic anhydride. A clear water solution of sodium bisulfite was added under constant agitation and the temperature was maintained at 75-80°C for four hours. The conversion of sulfonation was 100%, and the solid content was 50%.

20 B. Preparation of sodium sulfonate-containing polyester.

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RAW MATERIAL

1	1,6-Hexanediol	997 grams
	Neopentyl Glycol (90%)	853 grams
	Product of step A. (as 50 wt.% aqueous solution)	1,017 grams
	Adipic Acid	1,821 grams
5	Total Load	4,688 grams
	Organotin Catalyst	0.30 grams
	Water to distill	1,156 grams
	Theoretical Yield	3,532 grams

10 PROCEDURE

A four neck glass flask, equipped with a nitrogen inlet, a stirrer, a column, and a thermometer, was charged with catalyst, 1,6-hexanediol, neopentyl glycol, a 50 wt.% solution of the product of step A, and adipic acid. The temperature was increased to 150°C +/-5°, while the column was kept hot using steam. The nitrogen and agitation were increased, as the reaction proceeded, to facilitate the water removal, but not rapid enough to blow out the glycol.

Hydroxyl value and acid number were checked as needed and the loss of glycol during the reaction was adjusted to reach the theoretical hydroxyl value. Reaction was considered complete when the hydroxyl number and the acid number reached the expected values. The final sodium sulfonate-containing polyester had a hydroxyl number of 108, and an acid number of 3.0. The polymer, a sulfonate polyester, dispersed in water very easily, and demonstrated good stability.

EXAMPLE 8

1

A water dispersible polyurethane was prepared from sodium sulfonate-grafted poly(hexamethylene/neopentyl adipate) glycol, obtained
5 via polymerization of sulfonated monomer, with a molecular weight of 1,040 and a hydroxyl number of 108 prepared according to Example 7.

RAW MATERIAL

10

1. NCO-Terminated Prepolymer

15

IPDI(Isophorone diisocyanate)	77.69 grams
Sulfonated-grafted Polyester, OH no.=108	243.3 grams
N-methylpyrrolidone ("NMP")	80.0 grams

2. Dispersion

NCO-terminated prepolymer	400	grams
Water	669	grams

20

PROCEDURE:

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The polyester and the NMP were added to a reaction kettle and dehydrated by a vacuum pump at 100°C with stirring for 30 minutes. The mixture was
25 then cooled to 80°C until the theoretical isocyanate content was reached. The resulting prepolymer at a temperature of 80°C was dispersed in water at a temperature of 25°C. Stirring was continued for 4
30 hours. The reaction mixture was cooled to room

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temperature and filled into containers through a 200
1 micron sieve.

The product was a fine dispersion and had a
solid content of about 30%. The dispersion was very
stable: under heat aging at 52°C in an oven for 1
5 month, no phase separation or gellation were found.

EXAMPLE 9

A. Preparation of Adduct [half ester from
10 one mole of maleic anhydride and one mole of 1,4-
butanediol].

RAW MATERIAL

15	1,4-Butanediol	670 grams
	Maleic Anhydride	730 grams
	Total Load	1,400 grams
	Theoretical Yield	1,400 grams
	Sodium Bisulfite	758 grams
20	Water	2,158 grams

PROCEDURE

A four neck glass flask, equipped with a
nitrogen inlet, a stirrer, a water condenser, and a
25 thermometer, was charged with 1,4-butanediol, and
maleic anhydride (the molar ratio of 1,4-butanediol to
maleic anhydride was 1/1), and heated to approximately
80°C. After two hours, a clear water solution of
sodium bisulfite was added under constant agitation
30 and the temperature was maintained at 75-80°C for

eight hours. The conversion of sulfonation was 100%,
1 the solid content was 50%, and the pH of the aqueous
solution was 3.0.

B. Preparation of sodium sulfonate-
containing
5 polyester.

RAW MATERIAL

1,4-Butanediol	1,662 grams
10 Product of step A. of Ex. 6	
(as 50 wt.% aqueous solution)	631 grams
Adipic Acid	2,294 grams
Total Load	4,587 grams
Organotin Catalyst	0.30 grams
15 Water to distill	900 grams
Theoretical Yield	3,600 grams

PROCEDURE

A four neck glass flask, equipped with a
20 nitrogen inlet, a stirrer, a column, and a
thermometer, was charge with catalyst, 1,4-butanediol,
a 50 st.% aqueous solution of the product was
increased to 150°C +/-5°, while the column was kept
hot using steam. The nitrogen and agitation were
25 increased, as the reaction proceeded, to facilitate
the water removal, but not rapid enough to blow out
the glycol.

Hydroxyl value and acid number were checked
as needed and the loss of glycol during the reaction
30 was adjusted to reach the theoretical hydroxyl value.

Reaction was considered complete when the hydroxyl
1 number and the acid number reached the expected
values. The final sodium sulfonate-containing
polyester had a hydroxyl number of 63.4, an acid
number of 2.2. The polymer, a sulfonate polyester,
5 dispersed in water very easily, and the dispersed
polyester demonstrated good stability.

EXAMPLE 10

10 A water dispersible polyurethane was
prepared from sodium sulfonate-grafted poly(butylene
adipate) glycol, obtained via polymerization of
sulfonated monomer, with a molecular weight of 1,750
and a hydroxyl number of 64.

15

RAW MATERIAL

1. NCO-Terminated Prepolymer

20	IPDI(Isophorone diisocyanate)	19.68 grams
	HDI(Hexamethylene diisocyanate)	29.51 grams
	Sulfonate-grafted Polyester, OH no.=64	154.16 grams
	Dimethylolpropionic acid("DMPA")	15.64 grams
	N-methylpyrrolidone("NMP")	51.7 grams
	Triethylamine("TEA")	4.95 grams

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2. Dispersion

	NCO-terminated prepolymer	275.64 grams
	Water	495 grams

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PROCEDURE:

1 The polyester and the DMPA and the NMP were
added to a reaction kettle and dehydrated by a vacuum
pump at 100°C with stirring for 30 minutes. The
mixture was then cooled to 80°C until the theoretical
5 isocyanate content was reached. The resulting
prepolymer at a temperature of 80°C, and the HDI and
IPDI were added. After 1 hour, the TEA was added.
Stirring was continued at 80°C until the theoretical
isocyanate content was reached. The resulting
10 prepolymer, at a temperature of 80°C, was dispersed in
water at a temperature of 25°C. Stirring was
continued for 4 hours. The reaction mixture was
cooled to room temperature and filled into containers
through a 200 micron sieve.

15 The product was a fine dispersion which had
a particle size of 195nm and a solid content of about
30%. The dispersion was very stable under heat aging;
in a 52°C oven for 1 month, no phase separation or
gellation were found.

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WHAT IS CLAIMED IS:

1. A process for producing a water-dispersible polyurethane comprising:

(a) providing a sulfonate-substituted polyester which is substituted with an average of at least two hydroxyl groups per molecule;

(b) reacting said sulfonate-substituted polyester with one or more polyisocyanate compounds to form a sulfonate-substituted prepolymer substituted with at least two isocyanate groups; and

(c) reacting said prepolymer with one or more chain extenders free of salt-forming groups, thereby forming a polyurethane, wherein said polyester is sufficiently sulfonate-substituted that said polyurethane is water-dispersible.

2. A process according to claim 1 wherein said sulfonate-substituted polyester is formed by :

forming an ethylenically unsaturated polyester which is substituted with at least two hydroxyl groups by condensation polymerization of reactants capable of undergoing condensation polymerization, wherein said reactants comprise one or more compounds substituted with two or more hydroxyl groups, and comprise one or more compounds containing ethylenic unsaturation which may be substituted with hydroxyl;

sulfonating said ethylenically unsaturated polyester by reacting it with a sulfonating agent under conditions such that said sulfonating agent reacts with said ethylenic unsaturation and sulfonates said polyester.





3. A process according to claim 2 wherein said polyester has a molecular weight of 500 to 6,000.

4. A process according to claim 2 wherein said ethylenically unsaturated polyester is formed by condensation polymerization of a diol with a diacid or anhydride.

5. A process according to claim 4 wherein said diol is ethylenically unsaturated.

6. A process according to claim 4 wherein diacid or anhydride is ethylenically unsaturated.

7. A process according to claim 4 wherein said diol contains 4 to 10 carbon atoms.

8. A process according to claim 4 wherein said diacid or anhydride contains 4 to 36 carbon atoms.

9. A process according to claim 4 wherein said diacid or anhydride contains 4 to 8 carbon atoms.

10. A process according to claim 4 wherein said diol is reacted with maleic anhydride.

11. A process according to claim 4 wherein said diol is selected from the group consisting of alkyl diols containing 2 to 6 carbon atoms.

12. A process according to claim 2 wherein said polyisocyanate is selected from the group consisting of compounds of the formula $Q(NCO)_2$, wherein Q is an aliphatic hydrocarbon group containing 4 to 12 carbon atoms, a cycloaliphatic group containing 6 to 15 carbon atoms, an aromatic hydrocarbon group containing 6 to 15 carbon atoms, or an araliphatic hydrocarbon group containing 7 to 15 carbon atoms.



13. A process according to claim 2 wherein said polyisocyanate is isophorone diisocyanate.

14. A process according to claim 2 wherein said one or more chain extenders are selected from the group consisting of hydrazine, alkyl and aromatic polyols, and alkyl and aromatic diamines and triamines, wherein the alkyl compounds contain a total of 2 to 12 carbon atoms and the aromatic compounds contain 6 to 10 carbon atoms.

15. A process according to claim 2 wherein the chain extender is hydrazine.

16. A process according to claim 1 wherein said sulfonate-substituted polyester is formed by providing a sulfonate-substituted monomeric precursor substituted with a difunctional comonomer capable of undergoing condensation polymerization with said monomeric precursor, under conditions whereunder said monomeric precursor and said comonomer undergo condensation polymerization to form said polyester.

17. A process according to claim 16 wherein said polyester has a molecular weight of 500 to 6,000.

18. A process according to claim 16 wherein said sulfonate-substituted monomeric precursor is a diol and said comonomer is a diacid or anhydride.

19. A process according to claim 16 wherein said sulfonate-substituted monomeric precursor is a diacid or anhydride and said comonomer is a diol.

20. A process according to claim 18 or 19 wherein said diol contains 4 to 10 carbon atoms.



21. A process according to claim 18 or 19 wherein said diacid or anhydride contains 4 to 36 carbon atoms.

22. A process according to claim 18 or 19 wherein said diacid or anhydride contains 4 to 8 carbon atoms.

23. A process according to claim 18 wherein said sulfonate-substituted diol is polymerized with maleic anhydride.

24. A process according to claim 19 wherein said diol is polymerized with sulfonate-substituted maleic anhydride.

25. A process according to claim 18 or 19 wherein said diol is selected from the group consisting of alkyl diols containing 2 to 6 carbon atoms.

26. A process according to claim 16 wherein said polyisocyanate is selected from the group consisting of compounds of the formula $Q(NCO)_2$, wherein Q is an aliphatic hydrocarbon group containing 4 to 12 carbon atoms, a cycloaliphatic group containing 6 to 15 carbon atoms, an aromatic hydrocarbon group containing 6 to 15 carbon atoms, or an araliphatic hydrocarbon group containing 7 to 15 carbon atoms.

27. A process for producing a water-dispersible polyurethane, comprising providing a water-dispersible, sulfonate-substituted polyester which is substituted with at least two hydroxyl groups, reacting said polyester with one or more polyisocyanates to form a prepolymer substituted with at least two isocyanate groups, and reacting said





prepolymer with one or more chain extenders free of salt-forming groups thereby forming a polyurethane product, wherein said polyester contains sufficient sulfonate substitution to render said polyurethane product water-dispersible.

28. A process according to claim 27 wherein said polyester has a molecular weight of 500 to 6,000.

29. A process according to claim 27 wherein said polyisocyanate is selected from the group consisting of compounds of the formula $Q(NCO)_2$, wherein Q is an aliphatic hydrocarbon group containing 4 to 12 carbon atoms, a cycloaliphatic group containing 6 to 15 carbon atoms, an aromatic hydrocarbon group containing 6 to 15 carbon atoms, or an araliphatic hydrocarbon group containing 7 to 15 carbon atoms.

30. A process according to claim 16 or 27 wherein said polyisocyanate is isophorone diisocyanate.

31. A process according to claim 16 or 27 wherein said one or more chain extenders are selected from the group consisting of hydrazine, alkyl and aromatic polyols, and alkyl and aromatic diamines and triamines, wherein the alkyl compounds contain a total of 2 to 12 carbon atoms and the aromatic compounds contain 6 to 10 carbon atoms.

32. A process according to claim 16 or 27 wherein the chain extender is hydrazine.

33. A process for producing a water-dispersible polyurethane, comprising reacting a prepolymer which is a sulfonate-substituted polyester terminated with at least 2 isocyanate groups, with one





or more chain extenders that are free of salt-forming groups.

34. A process according to claim 33 wherein said polyester has a molecular weight of 500 to 6,000.

35. A process according to claim 33 wherein said polyisocyanate is selected from the group consisting of compounds of the formula $Q(NCO)_2$, wherein Q is an aliphatic hydrocarbon group containing 4 to 12 carbon atoms, a cycloaliphatic group containing 6 to 15 carbon atoms, an aromatic hydrocarbon group containing 6 to 15 carbon atoms, or an araliphatic hydrocarbon group containing 7a to 15 carbon atoms.

36. A process according to claim 33 wherein said polyisocyanate is isophorone diisocyanate.

37. A process according to claim 33 wherein said one or more chain extenders are selected from the group consisting of hydrazine, alkyl and aromatic polyols, and alkyl and aromatic diamines and triamines, wherein the alkyl compounds contain a total of 2 to 12 carbon atoms and the aromatic compounds contain 6 to 10 carbon atoms.

38. A process according to claim 33 wherein the chain extender is hydrazine.

39. A water-dispersible polyurethane prepared by the process of any one of claims 1-38.

