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FUNCTIONAL GROUP TERMINATED POLYMERS CONTAINING
SULFONATE GROUP VIA SULFONATION OF
ETHYLENICALLY UNSATURATED POLYMERS

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The present invention relates to water-dispersible polymers, and more particularly to water-dispersible polyesters, polyamides and polyethers as well as copolymers thereof.

5 Polyester resins, as well as polyamide and polyether resins, find use in a variety of applications, including coatings, paints, adhesives, and the like. Such resins are typically soluble in
10 organic solvents, and exhibit little if any solubility in aqueous solvents or in systems in which water and a second water-soluble are employed. Organic solvent-based resin solutions have thus typically been the vehicle of choice for use in forming coatings and the
15 like of the resins. 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
20 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,
25 and as a means of complying with governmental edicts with respect to the use of such solvents.

Examples of aqueous polyester and other resin dispersions are known in the art. The dispersion of the resin into the aqueous medium has
30 customarily been achieved through the use of



1 dispersing or emulsifying agents such as nonionic or
ionic surfactants. However, the use of surfactant-
stabilized aqueous resin dispersions is far from
desirable, since a proportion of free surfactant can
5 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
incorporate moieties directly into the polymer
10 molecule which affords greater water dispersibility to
the polymer. Typically, these attempts involve
copolymerization of a water-soluble or water-
dispersible comonomer together with the other monomers
which react together to form the desired polymer
15 molecule. Typical of this approach is U.S. Patent No.
3,563,942, which discloses copolymerization of an
aromatic sulfonate moiety in the synthesis of the
desired polyester polymer.

Similar approaches are disclosed in U.S.
20 Patent No. 4,525,524, U.S. Patent No. 4,910,292, and
U.S. Patent No. 4,973,656, which disclose other
techniques for copolymerizing a sulfonate-type monomer
directly into the polymer when it is formed from its
monomeric constituents. These techniques require very
25 high reaction temperatures, whereas the process of the
present invention can be carried out at much milder,
less energy-intensive conditions.

The prior art approach to the objective of
incorporating a water-dispersible moiety into the
30 polymer molecule has other drawbacks in addition to

1 the severe reaction conditions themselves. Notable
among these is the fact that under such severe
reaction conditions, the polymer easily decomposes
and/or is converted to a yellowish or dark product.
5 This decomposition is difficult to control or
eliminate. Also, aromatic sulfonates can cause 1,4-
butanediol, which is ordinarily a preferred reactant,
to be converted to tetrahydrofuran; and can cause
diethylene glycol, another preferred reactant to be
10 converted to dioxane. These conversions occur because
of the strong acidity of the aromatic sulfonate. Both
such conversions are undesirable as they lead to
losses of yield and to unsatisfactory properties of
the product. It is also difficult to identify
15 satisfactory water-dispersible, e.g. sulfonate-based,
comonomers which can successfully copolymerize with
the other comonomers to form the desired copolymeric
product. The reaction conditions that become
necessary are constrained by the additional comonomer
20 present, such that harsher reaction conditions are
often required that are in turn more difficult to
control.

The present invention thus is directed to an
improved technique for forming water-dispersible
25 polymeric resins, particularly resins formed by
condensation polymerization such as polyesters,
polyamides and polyethers, which technique affords
improved ease of operation, more satisfactory yields,
improved properties (such as a desirable light color
30 of polyesters and polyethers produced by this

1 invention), and offers a greater variety in the
selection of reactants and in the range of properties
of the products that can be obtained.

5 The present invention is further directed to
an improved process for obtaining such water-
dispersible polymers which can be used as final
products or can be used as intermediates for the
subsequent formulation of other polymeric derivatives
such as polyurethanes.

10 One aspect of the present invention is a
process for producing a water-dispersible polymer
comprising: (a) forming an ethylenically unsaturated
polymeric precursor which is terminated at one or both
its ends with -COOH, -NH₂, or -OH, by condensation
15 polymerization of reactants which upon said
condensation polymerization form said polymeric
precursor wherein at least a portion of at least one
of said reactants contains ethylenic unsaturation; and
(b) sulfonating said polymeric precursor by reacting
20 it with a sulfonating agent such as a compound
selected from the group consisting of bisulfites,
metabisulfites, and mixtures thereof, under conditions
such that said sulfonating agent reacts with said
ethylenic unsaturation and sulfonates said polymeric
25 precursor.

The polymeric precursor can be all of one
type of polymer, or can comprise two or more
(preferably up to four) blocks each of which is a
polyester, a polyamide, or a polyether, wherein the
30 blocks are either bonded directly to each other or are

1 each bonded through a -C(O)NH-, -C(O)- or -O- linkage
to an intervening alkyl moiety containing 2 to 20
carbon atoms which is saturated or contains ethylenic
unsaturation; provided that adjacent blocks bonded
5 directly to each other are types of polymer different
from each other.

The present invention is useful in making
water-dispersible polymers, particularly water-
dispersible condensation polymers. The products of
10 the process of this invention can be used per se
to form coatings, film and the like. The products of
the process of this invention can also be used as
intermediates in the formation of other polymeric
species, for instance by reacting appropriate di-
15 isocyanate compounds or other di-substituted cross
linking agents with the carboxylic acid, amino, or
hydroxyl substituent groups present on the polymers
produced by the present invention.

The condensation polymerization reactions
20 with which the present invention may be used include
any reactions among reactants in which appropriate
functionalities on the reactants react to form a
covalent linkage, the reaction typically (but not
always) resulting in the formation of a byproduct
25 molecule, typically water, as a result of the
reaction. The functionalities present on the
reactants usually include one or both of -COOH (or
anhydride) and/or -COH, and one or both of -OH and -
NH₂. The reactants that enter into such condensation
30 reactions are usually substituted with two, or more,

1 of such functionalities. More often, reactants are
substituted with the same functionalities (e.g.,
diacids, diols, diamines), but they can be substituted
with two or more different functionalities (e.g.,
5 amino acids, hydroxyacids).

Preferred examples of condensation
polymerization reactions include reactions which form
polyesters, polyethers and polyamides. As is well
known, polyesters form by the reaction of, for
10 instance, diols with dicarboxylic acids or anhydrides
thereof. Polyamides form by the reaction of, for
instance, diamines with dicarboxylic acids or
anhydrides thereof. Polyethers within the scope of
the present invention can be formed by the
15 polymerization of, for instance, ethylene oxide or
propylene oxide under ring-opening conditions.
Condensation polymerization reactions also include
such reactions of glycol or alkoxy-terminated
polyethylene glycol with a diacid or anhydride to form
20 a polyester of the polyethylene glycol.

The polymers within the scope of the present
invention also include those composed of blocks
wherein blocks adjoining each other are different
types of condensation polymers. Examples include
25 polyester/polyamide, polyester/polyether, and
polyamide/polyether. Other examples include triblock
polymers, wherein the inner block is different from
each of the outer blocks which can be the same as each
other or different from each other. Examples include
30 polyether/polyester/polyether, and so forth.

1 Also included are molecules wherein one or
two polymeric chains meeting any of the descriptions
herein is pendant from an alkyl moiety containing 2 to
20 carbon atoms through a -C(O)NH-, -C(O)O-, or -C-O-
5 C- linkage. An example of this type of compound is
that formed by esterifying both carboxylic
functionalities of maleic acid or maleic anhydride
with polyethylene glycol or polypropylene glycol at a
molar ratio of glycol to maleic acid or anhydride of
10 at least 2:1. In such molecules the necessary
ethylenic unsaturation is in the polymeric chain or
chains, in the C₂-C₂₀ moiety, or both.

One essential aspect of the process of the
present invention is that the condensation polymer
15 that is obtained contains ethylenic unsaturation, that
is, a carbon-carbon double bond, either in the main
chain of the polymer, or in a moiety or moieties of 2
to 20 carbon atoms linking polymeric blocks, or
pendant from the main chain of the polymer (connected
20 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 the polymer),
or both. This ethylenic unsaturation is provided by
carrying out the condensation polymerization with one
25 or more reactants which participate in the
condensation polymerization reaction and which also
contain ethylenic unsaturation. Under conventional
condensation polymerization conditions the ethylenic
unsaturation survives the condensation polymerization.
30 Of the different types of reactants present (e.g.,

1 diacid, diol, diamine, hydroxylamine, and so forth),
the ethylenically unsaturated reactant can comprise
all or a portion of one of the reactant types, or all
or a portion of more than one of the reactant types.

5 Thus, for instance, the desired ethylenic
unsaturation can be provided by incorporating into the
reactant mixture an ethylenically unsaturated diacid,
an ethylenically unsaturated anhydride (such as maleic
anhydride), an ethylenically unsaturated diol, an
10 ethylenically unsaturated diamine, or mixtures of any
two or more of such compounds. Depending on the
properties desired of the final product produced by
the process of the present invention, all or part of
the diacid component can comprise ethylenically
15 unsaturated dicarboxylic acid and/or anhydride, all or
part of the diol component can comprise ethylenically
unsaturated diol compound, and all or part of the
diamine component that may be employed can comprise
ethylenically unsaturated diamines.

20 It will be understood that the reactants
present in the reaction mixture, which undergoes
condensation polymerization in the first step of the
process of the present invention, can include one or
more reactants customarily employed in the synthesis
25 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
30 dicarboxylic acids, or mixtures thereof.

1 The dicarboxylic acids that can be used in
the present invention include aliphatic dicarboxylic
acids, alicyclic dicarboxylic acids, aromatic
dicarboxylic acids, ethylenically unsaturated alkenyl
5 dicarboxylic acids, or mixtures of two or more of
these acids. Preferred are alkyl dicarboxylic diacids
which generally contain 4 to 36 carbon atoms, and
aromatic dicarboxylic diacids which generally contain
9 to 20 carbon atoms. Examples of useful dicarboxylic
10 acids include oxalic, malonic, dimethylmalonic,
succinic, glutaric, adipic, trimethyladipic, pimelic,
2,2-dimethylglutaric, azelaic, sebacic, suberic, 1,3-
cyclopentanedicarboxylic, 1,2-cyclohexanedicarboxylic,
1,3-cyclohexanedicarboxylic, 1,4-
15 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
20 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
25 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.

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1 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
5 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 general, the
preferred ethylenically unsaturated dicarboxylic acids
10 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
15 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
20 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
25 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
30 to 10 carbon atoms. Some representative examples of

1 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-
5 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-
10 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
15 include "Rezol ED-1000" and "Rezol ED-2000", sold by
Witco Corp.); 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
Corp.); and block and random copolymers of propylene
20 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-56", and "Rezol EPD-
28", sold by Witco Corp.)

Preferred ethylenically unsaturated diol
25 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.

Included within the scope of the
30 ethylenically unsaturated diols useful in the process

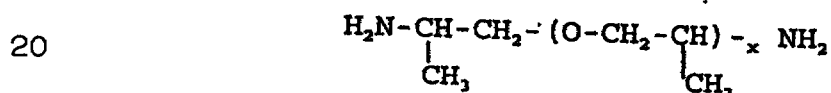
1 of the present invention are those wherein the
ethylenic unsaturation is present in, or in a
substituent pendant from, the chain connecting the two
diol groups. Preferred examples include the mono-
5 acrylates and mono-methacrylates of triols (preferably
containing 2 to 20, and more preferably 2 to 6, carbon
atoms) such as glycerol, wherein two hydroxyl groups
remain available to cooperate in the formation of the
polyester molecule. Other examples of satisfactory
10 ethylenically unsaturated diols include 1,4-
butenediol, 1,4-butyne-2,3-diol, glycerine allyl ether and
glyceryl monostearate.

If branching is desirable, then it will be
advantageous to use a branching agent in the
15 condensation polymerization reaction. Such branching
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
20 both types of groups. Examples of acidic branching
agents include trimesic acid, trimellitic acid,
pyromellitic acid, butanetetracarboxylic acid,
naphthalene tricarboxylic acids and cyclohexane-1,3,5-
tricarboxylic acid. Examples of hydroxyl branching
25 agents (polyols) include glycerin, trimethylolpropane,
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
30 5-(2-hydroxyethoxy)isophthalic acid. Generally from 0

1 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).

5 Instead of, or in addition to, the diol and
polyol components, there can be present a diamine
component. One type of suitable diamine is di-amino-
substituted alkyl, and alkylene compounds, preferably
10 containing 3 to 8 carbon atoms, examples of which
include compounds analogous to the aforementioned
saturated, and ethylenically unsaturated, glycols and
diols, wherein the hydroxyl substituents are replaced
by amino groups.

Another type of suitable diamine is diamine-
substituted polyoxyalkylene compounds, preferably
15 poly(ethoxy) or poly(propoxy) compounds encapped with
aminopropyl groups. Examples of this type of reactant
include compounds generalizable by the formula



known as Jeffamine D230, D400, D2000, and D4000
(previously sold by Texaco Chemical Co., now Huntsman
25 Chemical) corresponding to said formula wherein x is
2-3, 5-6, about 33, and about 68, respectively.

As indicated, condensation polymers useful
in this invention also include bifunctional compounds
such as hydroxyacids and amino acids, which are
30 polymerized head-to-tail in known manner. Such

1 reactants would have to include some ethylenically
unsaturated compounds. Examples of such reactants
include 6-hydroxy (or 6-amino) hexenedioic acid, and
the like.

5 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
reactants that enter into the condensation
10 polymerization include a sufficient amount of
ethylenic unsaturation so that the sulfonation which
occurs in the second step of the process of the
present invention provides a satisfactory degree of
water dispersibility in the polymer.

15 Thus, the amount of reactant bearing
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.% of the reaction mixture. The reactants are
20 otherwise selected to be approximately equimolar in
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
25 excess.

 Thus, for instance, if it is desired that
the polymer product contains carboxylic terminal
groups, then an excess of the acid component should be
provided. If it is desired that the polymer should be
30 endcapped with hydroxyl terminal groups, then an

1 excess of the diol component should be supplied. On
the other hand, if it is desired that the polymer
should be endcapped with amino terminal groups, then
an excess of the diamine component should be supplied.
5 It should be recognized that for these purposes the
terms "diacid component," "diol component, " and
"diamine component" are intended to include all
components of the reaction mixture whether or not
ethylenically unsaturated. It will also be recognized
10 that to ensure that the polymer is capped with the
desired 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,
15 by the effect of that excess on the distribution of
polymeric chain lengths formed by the condensation
polymerization.

The condensation polymer can also be one
which contains only one terminal carboxylic acid,
20 hydroxyl or amino group. For instance, a C₁-C₆ alkoxy
(e.g. methoxy)-capped polyethylene glycol is reacted
with ethylene glycol, acetic anhydride and maleic
anhydride to form a polyester which is capped with a
hydroxyl group and a methyl group, and which contains
25 ethylenic unsaturation. In addition, one can prepare
a polymer that is mono-capped with a desired
functional group by preparing a condensation polymer
which is disubstituted with functional terminal
groups, and then capping one end of the molecule. For
30 instance, a diamine-capped or di-hydroxyl-capped

- 1 polymer can be reacted with a lower (C_1-C_6) alkanolic
carboxylic acid to cap one end of the polymer with an
ester or amide. Likewise, a dicarboxylic acid-capped
polymer can be reacted with a (C_1-C_6) alcohol or (C_1-C_6)
5 alkyl amine, to cap one of the two carboxylic acid
moieties with an ester or amide.

The reaction mixture is then subjected to
condensation polymerization conditions effective to
cause the reactants to react with each other to form
10 the desired condensation polymers. In general,
effective condensation polymerization conditions are
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
15 desired, it should be high boiling (i.e. a boiling
point above about 140°C .) Examples of suitable
solvents include DMF (dimethylformamide), DMA (N,N-
dimethylacetamide), xylene and DMSO.

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

25 Typical condensation polymerization
conditions are provided by exposing the reactants to
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
30 effectively carry out the desired condensation

1 polymerization it is preferred to use nitrogen to
purge the reaction mixture in order to carry out the
water.

5 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
range; typically, useful polymers will have a
molecular weight in the range of about 200 to about
50,000. Thus, amounts and identities of the reactants
10 can readily be tailored to achieve any desired
molecular weight and distribution.

At the end of the condensation
polymerization, the product can be recovered and
separated from the reaction mixture, or can be
15 subjected to the sulfonation reaction in situ without
first being recovered.

Sulfonation is carried out by reacting the
polymer under appropriate sulfonating conditions with
a sulfonating agent which comprises one or more
20 bisulfites and/or one or more metabisulfites.
Preferred sulfonating agents are the ammonium and
alkali metal sulfites and alkali metal metabisulfites.
Thus, the more preferred sulfonating agents are sodium
bisulfite and sodium metabisulfite. Other preferred
25 sulfonating agents include lithium bisulfite, lithium
metabisulfite, potassium bisulfite, potassium
metabisulfite, ammonium bisulfite and ammonium
metabisulfite.

Sulfonation should be carried out using a
30 stoichiometric excess of the sulfonating agent,

1 calculated on the basis of the degree of ethylenic
unsaturation present in the condensation polymer
resulting from the foregoing condensation
polymerization step. The sulfonation is preferably
5 carried out in a suitable solvent such as water.
Satisfactory sulfonation conditions include
maintaining a temperature of about 10°C to about 120°C
for a time on the order of 2-15 hours. The
sulfonation also can be catalyzed by fine air bubbles
10 purged through the reaction medium. Any peroxide can
also be used as a catalyst in this step, such as
hydrogen peroxide, benzoyl peroxide, t-butyl hydrogen
peroxide, and many others known in this field.

The process of the present invention affords
15 several significant advantages compared to other
processes for producing water-dispersible sulfonated
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
20 reactants. In particular, a much greater freedom in
choice of reactants is provided, as the reactants in
the condensation polymerization step can be
polymerized under relatively straightforward
condensation polymerization conditions and the
25 sulfonation step can be carried out under fairly
conventional sulfonation conditions. This freedom in
the choice of reactants is an advantage in that it
affords greater range in the tailoring of the
properties of the final, water-dispersible product.

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1 In addition, the ability to select the
identity of the terminal groups on the polymers
affords the operator greater freedom in incorporating
the process of the present invention into processes
5 that use the water-dispersible product as an
intermediate in the synthesis of, for example,
polyurethanes by reaction of the appropriately end-
capped polymer with other reactive species such as
diisocyanates or additional quantities of dicarboxylic
10 acids, as the case may be.

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

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EXAMPLE 1

Sodium Sulfonate-Containing
Polyesters with Hydroxyl Terminated End Groups

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Raw Materials:

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

Procedure:

20 A four neck glass flask, equipped with a
nitrogen inlet, a stirrer, a column, and a
thermometer, was charged with catalyst, 1,4-
butanediol, 1,6-hexanediol, and maleic anhydride, and
the contents were heated to approximately 80°C.
25 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
30 the water removal, but not rapid enough to expel the
glycol.

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1 The 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
5 the 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
and nitrogen was shut off. A clear water solution of
10 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
percent moisture value reached the desired result.

15 The final product had a hydroxyl number of 93.6, an
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
20 dispersed in water very easily, and the dispersed
polyester demonstrated good stability.

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EXAMPLE 2

Sodium Sulfonate-Containing
Polyesters with Dihydroxyl Terminated End Groups

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Raw Materials:

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

Procedure:

20 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
25 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.

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checked as needed, and the loss of glycol during the

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1 reaction was adjusted to reach the theoretical hydroxy
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expected values.

5 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,
and the temperature was maintained at 75 to 80°C for 8
10 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 96.6, an
acid number of 1.00, and a moisture content of 0.08%.
15 The polymer, a sulfonated polyester, was dispersed in
water very easily, and the dispersed polyester
demonstrated good stability.

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EXAMPLE 3

Sodium Sulfonate-Containing
Polyamide with Diamino Terminated End Groups

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Raw Materials:

	Jeffamine D-400 *	357.2 grams
	Maleic Anhydride	30.6 grams
	Total Load	387.8 grams
	Water to Distill	5.6 grams
10	Theoretical Yield	382.2 grams
	Sodium Bisulfite	32.6 grams
	Water	76.0 grams

* ("Jeffamine D-400" has the structure
 $\text{H}_2\text{N}-\text{CH}(\text{CH}_3)\text{CH}_2-(\text{OCH}_2\text{CH}(\text{CH}_3))_{5-6}-\text{NH}_2$).

15 Procedure:

A four neck glass flask, equipped with a nitrogen inlet, a stirrer, a column, and a thermometer, was charged with Jeffamine D-400 and maleic anhydride. The temperature was increased to
20 200°C, while the column was kept hot using steam. The nitrogen and agitation were increased, as the reaction proceeded, to facilitate the water removal.

Amine value and acid number were checked as needed. Reaction was considered complete when the
25 amine 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, and nitrogen was shut off. A clear water solution of
30 sodium bisulfite was added under constant agitation,

- 1 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.
- 5 The polymer, a sulfonated polyamide, was dispersed in
water very easily, and the dispersed polyamide
demonstrated good stability.

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EXAMPLE 4

Sodium Sulfonate-Containing Polyester
with Dicarboxylic Acid Terminated End Groups

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Raw Materials:

	Diethylene Glycol	1,394 grams
	Adipic Acid	2,082 grams
	Maleic Anhydride	171 grams
10	Total Load	3,647 grams
	Water to Distill	448 grams
	Theoretical Yield	3,200 grams
	Sodium Bisulfite	181 grams
15	Water	726 grams

Procedure:

A four neck glass flask, equipped with a nitrogen inlet, a stirrer, a column, and a thermometer, was charged with diethylene 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.

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

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

5 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,
and the temperature was maintained at 75 to 80°C for 8
10 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 an acid number of 95.0, an
active anionic group of 0.464 meq/g, and a sulfonation
conversion of 86.4%. The polymer, a sulfonated
15 polyester, was dispersed in water very easily, and the
dispersed polyester demonstrated good stability.

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THIS SHEET HAS BEEN
REPLACED

WHAT IS CLAIMED IS:

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

(a) forming an ethylenically unsaturated polymeric precursor terminated at one or both ends thereof with a functional group selected from the group consisting of -OH, -NH₂ and -COOH; by condensation polymerization of reactants capable of undergoing condensation polymerization, wherein at least one of said reactants contains ethylenic unsaturation; and

(b) sulfonating said ethylenically unsaturated polymeric precursor by reacting it with a sulfonating agent under conditions such that said sulfonating agent reacts with said ethylenic unsaturation and sulfonates said precursor.

2. A process according to Claim 1 wherein said sulfonating agent is selected from the group consisting of bisulfites, metabisulfites, and mixtures thereof.

3. A process according to Claim 1 or 2 wherein said ethylenically unsaturated polymeric precursor is a polyester.

4. A process according to Claim 3 wherein said ethylenically unsaturated precursor polymer is terminated at one or both ends thereof with the same





THIS SHEET HAS BEEN
REPLACED

functional group selected from the group consisting of
-OH and -COOH.

5. A process according to Claim 1 or 2
wherein said ethylenically unsaturated polymeric
precursor is a polyamide.

6. A process according to Claim 5 wherein
said ethylenically unsaturated precursor polymer is
terminated at one or both ends thereof with a
functional group selected from the group consisting of
-OH, -NH₂ and -COOH.

7. A process according to Claim 1 or 2
wherein said ethylenically unsaturated polymeric
precursor is a polyether.

8. A process according to Claim 7 wherein
said ethylenically unsaturated precursor polymer is
terminated at one or both ends thereof with a
functional group selected from the group consisting of
-OH, -NH₂ and -COOH.

9. A process according to claim 1 or 2
wherein said ethylenically unsaturated polymeric
precursor is a polyester formed by condensation
polymerization of a diacid and a diol one or both of
which are ethylenically unsaturated.





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REPLACED

10. A process according to claim 1 or 2 wherein said ethylenically unsaturated polymeric precursor is a polyamide formed by condensation polymerization of a diacid and a diamine one or both of which are ethylenically unsaturated.

11. A process according to Claim 1 or 2 wherein said ethylenically unsaturated polymeric precursor comprises two or more blocks, each of which is a polymer selected from the group consisting of polyesters, polyamides, and polyethers, which blocks are either bonded directly to each other or are each bonded through a $-C(O)NH-$, $-C(O)O-$ or $-O-$ linkage to an intervening moiety containing 2 to 20 carbon atoms which is saturated or contains ethylenic unsaturation; provided that blocks which are bonded directly to each other are of types different from each other.

12. A process according to Claim 11 wherein said polymeric precursor comprises a polyester block and a polyamide block.

13. A process according to Claim 11 wherein said polymeric precursor comprises a polyester block and a polyether block.

14. A process according to Claim 11 wherein said polymeric precursor comprises a polyether block and a polyamide block.

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THIS SHEET HAS BEEN
REPLACED

15. A water-dispersible polymer prepared by
the process of any one of claims 1-14.

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ABSTRACT OF THE DISCLOSURE

Disclosed is a process for producing water-
dispersible polymers, particularly condensation
5 polymers such as polyesters, polyethers and
polyamides, by forming an ethylenically unsaturated
polymeric precursor by condensation polymerization of
reactants including ethylenically unsaturated
reactants and then sulfonating the ethylenic
10 unsaturation of said polymeric precursor by reacting
it with a sulfonating agent such as bisulfite,
metabisulfite, or a mixture thereof.

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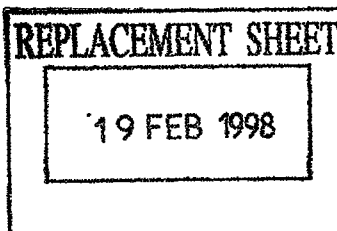
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FUNCTIONAL GROUP TERMINATED POLYMERS CONTAINING
SULFONATE GROUP VIA SULFONATION OF
ETHYLENICALLY UNSATURATED POLYMERS

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The present invention relates to water-dispersible polymers, and more particularly to water-dispersible polyesters, polyamides and polyethers as
5 well as copolymers thereof.

Polyester resins, as well as polyamide and polyether resins, find use in a variety of applications, including coatings, paints, adhesives, and the like. Such resins are typically soluble in
10 organic solvents, and exhibit little if any solubility in aqueous solvents or in systems in which water and a second water-soluble are employed. Organic solvent-based resin solutions have thus typically been the vehicle of choice for use in forming coatings and the
15 like of the resins. 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
20 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,
25 and as a means of complying with governmental edicts with respect to the use of such solvents.

Examples of aqueous polyester and other resin dispersions are known in the art. The dispersion of the resin into the aqueous medium has
30 customarily been achieved through the use of

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FUNCTIONAL GROUP TERMINATED POLYMERS CONTAINING
SULFONATE GROUP VIA SULFONATION OF ETHYLENICALLY
UNSATURATED POLYMERS

1 ABSTRACT OF THE DISCLOSURE

Disclosed is a process for producing water-
dispersible polymers, particularly condensation
5 polymers such as polyesters, polyethers and
polyamides, by forming an ethylenically unsaturated
polymeric precursor by condensation polymerization of
reactants including ethylenically unsaturated
reactants and then sulfonating the ethylenic
10 unsaturation of said polymeric precursor by reacting
it with a sulfonating agent such as bisulfite,
metabisulfite, or a mixture thereof.

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REPLACEMENT SHEET

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WHAT IS CLAIMED IS:

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

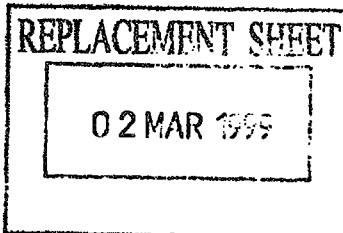
(a) forming an ethylenically unsaturated polymeric precursor terminated at one or both ends thereof with a functional group selected from the group consisting of -OH, -NH₂ and -COOH; by condensation polymerization of monomeric reactants capable of undergoing condensation polymerization, wherein at least one of said monomeric reactants contains ethylenic unsaturation, provided that if said precursor is a polyester then it is formed by condensation polymerization of an ethylenically unsaturated diacid and an ethylenically unsaturated diol; and

(b) sulfonating said ethylenically unsaturated polymeric precursor by reacting it with a sulfonating agent under conditions such that said sulfonating agent reacts with said ethylenic unsaturation and sulfonates said precursor.

2. A process according to Claim 1 wherein said sulfonating agent is selected from the group consisting of bisulfites, metabisulfites, and mixtures thereof.

3. A process according to Claim 1 or 2 wherein said ethylenically unsaturated polymeric precursor is a polyester.

4. A process according to Claim 3 wherein said ethylenically unsaturated precursor polymer is terminated at one or both ends thereof with the same



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functional group selected from the group consisting of -OH and -COOH.

5. A process according to Claim 1 or 2 wherein said ethylenically unsaturated polymeric precursor is a polyamide.

6. A process according to Claim 5 wherein said ethylenically unsaturated precursor polymer is terminated at one or both ends thereof with a functional group selected from the group consisting of -OH, -NH₂ and -COOH.

7. A process according to Claim 1 or 2 wherein said ethylenically unsaturated polymeric precursor is a polyether.

8. A process according to Claim 7 wherein said ethylenically unsaturated precursor polymer is terminated at one or both ends thereof with a functional group selected from the group consisting of -OH, -NH₂ and -COOH.

9. A process according to claim 1 or 2 wherein said ethylenically unsaturated polymeric precursor is a polyamide formed by condensation polymerization of a diacid and a diamine one or both of which are ethylenically unsaturated.



REPLACEMENT SHEET

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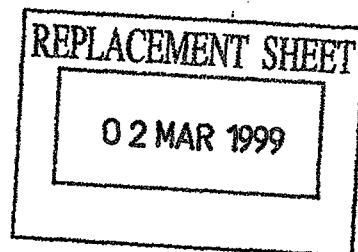
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10. A process according to Claim 1 or 2 wherein said ethylenically unsaturated polymeric precursor comprises two or more blocks, each of which is a polymer selected from the group consisting of polyesters, polyamides, and polyethers, which blocks are either bonded directly to each other or are each bonded through a $-C(O)NH-$, $-C(O)O-$ or $-O-$ linkage to an intervening moiety containing 2 to 20 carbon atoms which is saturated or contains ethylenic unsaturation; provided that blocks which are bonded directly to each other are of types different from each other.

11. A process according to Claim 10 wherein said polymeric precursor comprises a polyester block and a polyamide block.

12. A process according to Claim 10 wherein said polymeric precursor comprises a polyester block and a polyether block.

13. A process according to Claim 10 wherein said polymeric precursor comprises a polyether block and a polyamide block.



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14. A water-dispersible polymer prepared
by the process of any one claims 1-8 or 10-13.