



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US86/02742 <b>(22) International Filing Date:</b> 18 December 1986 (18.12.86)  <b>(31) Priority Application Number:</b> 812,435 <b>(32) Priority Date:</b> 23 December 1985 (23.12.85) <b>(33) Priority Country:</b> US  <b>(71) Applicant:</b> THE DOW CHEMICAL COMPANY [US/ US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). <b>(72) Inventor:</b> HOFFMAN, Dwight, K. ; 1206 Kingsbury Court, Midland, MI 48640 (US). <b>(74) Agent:</b> DAMOCLES, Nemia, C.; The Dow Chemical Company, P.O. Box 1967, Midland, MI 48641-1967 (US).		<b>(81) Designated States:</b> AT (European patent), AU, BE (Eu- ropean patent), BR, CH (European patent), DE (Eu- ropean patent), DK, FI, FR (European patent), GB (European patent), IT (European patent), JP, NL (European patent), NO, SE (European patent).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> LOW VISCOSITY, HIGH SOLIDS POLYMER POLYOLS PREPARED USING A PREFORMED DISPER- SANT  <b>(57) Abstract</b>  <p>A process for preparing a polymer polyol comprising the steps of (a) forming in a first step a dispersant by homopolymerizing a vinyl-terminated adduct, or copolymerizing said adduct with an ethylenically unsaturated monomer or mixture thereof which is not a vinyl-terminated adduct, in the presence of an active hydrogen-containing compound as a solvent under conditions such that the resulting dispersant is soluble in a base polyol, and has a Brookfield viscosity of less than 25,000 centipoises as a 20-35 wt.-% solution in an active hydrogen-containing compound, and (b) polymerizing an ethylenically unsaturated monomer or mixture thereof in the presence of said dispersant and a base polyol under conditions such that the polymerized monomer forms a plurality of particles which are stabilized against agglomeration by the dispersant. The process of this invention provides for improved stability of the dispersed polymer particles in the base polyol, and provides a polymer polyol of surprisingly low viscosity.</p>		

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LOW VISCOSITY, HIGH SOLIDS POLYMER POLYOLS PREPARED  
USING A PREFORMED DISPERSANT

5 This invention relates to polymer polyols, and particularly to polymer polyols containing high levels of dispersed polymer particles, and to a process for their production using a preformed dispersant.

10 Polymer polyols are dispersions of addition polymer particles in a continuous polyol phase. The presence of the addition polymer particles in the  
15 polyol imparts various desirable properties to polyurethanes, particularly flexible polyurethane foams, prepared from the polyol. In particular, the  
20 polymer particles act as a reinforcing filler and cell opener in the foam. The polymer particles also improve the ability of a reaction mixture containing the  
25 polymer polyol and a polyisocyanate to flow and fill a mold in the production of molded foams.

One problem with the polymer polyol is that the dispersed polymer particles tend to agglomerate and then settle out of the continuous polyol phase. It is therefore desirable to prepare the polymer polyol in

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such a way that the tendency of the particles to agglomerate is minimized. The most successful approach to date has been to employ a vinyl-unsaturated polyether which is copolymerized with the addition  
5 polymerizable monomers to form a dispersant or stabilizer.

For various reasons, it is desirable to prepare  
10 a polymer polyol having a high level of dispersed polymer particles. High levels of dispersed polymer particles provide enhanced reinforcement and cell  
15 opening. In addition, the production of high solids polymer polyols is economically advantageous, since a smaller amount is needed to obtain an equivalent amount  
20 of polymer particles. Thus, the user can purchase a smaller amount of a high solids polymer polyol and dilute it with an additional, less expensive polyol to obtain a lower overall solids level.

25 These high solids polymer polyols are especially prone to agglomeration and settling. The production of high solids polymer polyols has also been  
30 hampered by the high viscosity obtained when the solids level exceeds 30% by weight. The practical upper limit on viscosity for these polymer polyols is 12,000, (12)  
35 preferably 10,000 centipoises, (10 Pa·s) since the pumping equipment used by foamers generally cannot handle higher viscosities at an acceptable rate or with  
40 acceptable accuracy. This limit, however, is often exceeded with conventional polymer polyols having high solids.

It would therefore be desirable to provide a process whereby a polymer polyol is formed which has a low tendency for its particles to agglomerate and

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settle out. It is further desirable to provide a polymer polyol which is prepared having, at a given solids level, a viscosity which is as low as possible. More particularly, it would be desirable to provide a process whereby a polymer polyol having 35% or more solids is prepared at a useable viscosity.

This invention is such a process for preparing a polymer polyol. The process of this invention comprises the steps of:

(a) forming in a first step a dispersant by homopolymerizing a vinyl-terminated adduct, as defined herein, or copolymerizing said adduct with at least one ethylenically unsaturated monomer, as defined herein, in the presence of an active hydrogen-containing compound as a solvent under conditions such that the resulting dispersant is soluble in a base polyol and has a Brookfield viscosity of less than 25,000 centipoises (25 Pa.s) at 25°C as a 20-35 wt.-% solution of the polymer of the vinyl-terminated adduct in an active hydrogen-containing compound, and in a second step

(b) polymerizing an ethylenically unsaturated monomer or mixture thereof in the presence of said dispersant and a base polyol under conditions such that the polymerized monomer forms a plurality of particles which are stabilized against agglomeration by the dispersant.

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In a particularly notable embodiment, the vinyl-terminated adduct is homopolymerized in step (a) of the process.

5 In another aspect, this invention relates to a composition useful for stabilizing dispersed addition polymer particles in a polymer polyol against agglomeration and settling. The composition comprises  
10 a 10-90 wt.-% solution of a homopolymer of a vinyl-terminated adduct, or copolymer thereof with at least one ethylenically unsaturated monomer as defined  
15 herein, in a monol or polyol.

In another aspect, this invention relates to a process for preparing a polymer dispersion in a  
20 continuous polyol phase comprising the steps of

(a) forming a dispersant by homopolymerizing a  
25 vinyl-terminated adduct, or copolymerizing said adduct with an ethylenically unsaturated monomer or mixture thereof under conditions such that the resulting dispersant is soluble in a base polyol and has a  
30 viscosity of less than 25,000 centipoises (25 Pa.s), and then

35 (b) polymerizing an ethylenically unsaturated monomer or mixture thereof in the presence of said dispersant and a base polyol under conditions such that the polymerized monomer and said dispersant form a  
40 plurality of particles dispersed in said base polyol.

In still another aspect, this invention is a composition useful for stabilizing a polymer polyol, comprising a homopolymer of an ethylenically unsaturated adduct of a difunctional material and a monol or polyol, or a copolymer thereof with at least

one other ethylenically unsaturated monomer, wherein said dispersion has a viscosity of less than 25,000 centipoises (25 Pa·s), and said dispersion is soluble in a base polyol.

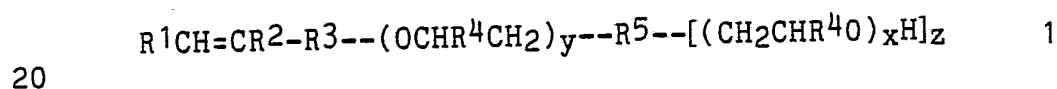
5           The process of this invention provides for improved stability of the dispersed polymer particles in the base polyol, and provides a polymer polyol of  
10           surprisingly low viscosity. Accordingly, polymer polyols having solids contents of up to 45% or more, having viscosities sufficiently low to permit their  
15           processing, can be prepared according to this invention. Another advantage of this invention is that in preparing a polymer polyol, very low amounts of  
20           relatively expensive free radical initiators are required to obtain a stable, low viscosity dispersion. A further advantage is that this process requires no  
25           volatile solvents which must be removed from the dispersant or polymer polyol prior to use.

30           The process of this invention comprises, as a first step, the preparation of a dispersant by homopolymerizing a vinyl-terminated adduct, or copolymerizing same with at least one ethylenically  
35           unsaturated monomer.

40           The vinyl-terminated adduct employed herein as a starting material is a polymer having a molecular weight of at least 200, which is soluble in the base polyol used in preparing the copolymer polyol and which contains addition polymerizable, ethylenic  
            unsaturation. Preferably, the ethylenically unsaturated monomer is capable of undergoing a free radical vinyl polymerization. More preferably, the vinyl-terminated adduct is a 300-8000 molecular weight

poly(alkylene oxide) which contains ethylenic unsaturation. Most preferably, the vinyl-terminated adduct is a 300-8000 molecular weight polymer of propylene oxide and/or ethylene oxide having a hydroxyl  
 5 functionality of 0 to 3, more preferably 1 to 2, which contains 1 vinyl group per molecule. It is preferred that polymers of the vinyl-terminated adduct having a  
 10 degree of polymerization greater than 2, more preferably greater than 4, are also soluble in a base polyol.

15           Suitable vinyl-terminated adducts are represented by the structure 1:



wherein R<sup>1</sup> is hydrogen, inertly substituted lower alkyl, nitrile, R<sup>8</sup>-OOC- or R<sup>8</sup><sub>2</sub>NCO-, wherein each R<sup>8</sup> is  
 25 independently hydrogen, inertly substituted lower alkyl, or polyoxyalkylene, R<sup>2</sup> and R<sup>4</sup> are each independently hydrogen or inertly substituted lower  
 30 alkyl, R<sup>3</sup> is a divalent radical, preferably one which activates the terminal vinyl group towards polymerization, R<sup>5</sup> is the residue of a polyhydric  
 35 initiator when x is greater than zero and the residue of a monohydric initiator bond x is zero, y is a number from 1 to 100, x is a number from 0 to 100 and z is a  
 40 number from 1 to 3. R<sup>1</sup> is preferably hydrogen or methyl, with hydrogen being most preferred. R<sup>2</sup> and R<sup>4</sup> are preferably hydrogen, methyl, ethyl, methylol or nitrile. R<sup>3</sup> is preferably phenylene, an ester linkage, a carbamate linkage, -COO(CH<sub>2</sub>)<sub>n</sub>O-, -CON(CH<sub>2</sub>)<sub>n</sub>O-,  
 -COO(CH<sub>2</sub>)<sub>n</sub>-NHCO-, or -CON(CH<sub>2</sub>)<sub>n</sub>NHCO-, -C<sub>6</sub>H<sub>5</sub>-C(CH<sub>3</sub>)<sub>2</sub>NCO-, wherein n is a number from 1 to 6. R<sup>5</sup> is



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preferably the residual radical from the polyhydric initiator used in an alkylene oxide polymerization.

5           Suitable vinyl-terminated adducts according to  
structure 1 include the reaction product of a monol or  
polyol and a difunctional material having both  
ethylenic unsaturation and a group which reacts with an  
10           active hydrogen-containing group to form a bond  
thereto. Suitable such difunctional materials include,  
for example, ethylenically unsaturated isocyanates,  
acid anhydrides, acid halides and esters. Most  
15           preferred are unsaturated isocyanates such as  
isocyanatoethylmethacrylate (IEM) and (1,1-dimethyl-1-  
isocyanatomethyl)isopropenylbenzene (TMI).

20           The monol or polyol contains one (in the case  
of the monol) or more active hydrogen-containing  
groups. Suitable active hydrogen-containing groups  
25           are those which contain at least one hydrogen atom  
which displays significant activity according to the  
Zerewitnoff test described by Kohler in the Journal of  
30           the American Chemical Society, vol. 49, p. 3181 (1927).  
Suitable active hydrogen-containing groups include  
hydroxyl, amine, mercaptan, carboxylic acid and similar  
groups. Hydroxyl and amine groups are preferred, with  
35           hydroxyl groups being most preferred. The terms  
"polyol" and "monol" are used herein to conveniently  
describe all of these active-hydrogen containing  
40           materials.

Most preferably, a polyether polyol is used to  
prepare a vinyl-terminated adduct according to  
structure 1. The polyether polyol may be the same as  
the base polyol used in preparing the polymer polyol  
or, if different, is of such a composition that the

adduct formed therefrom is soluble in the base polyol. Preferably, the polyol is a 300-8000 molecular weight hydroxyl-terminated polyether prepared in the polymerization of an alkylene oxide, preferably ethylene oxide and/or propylene oxide, in the presence of a di-, tri- or tetrahydric initiator.

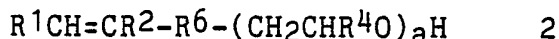
In preparing the vinyl-terminated adduct from a monol or polyol, the monol or polyol is reacted with a difunctional material as described herein under conditions such that a bond between the active hydrogen-containing group on the monol or polyol and the difunctional material is formed, and the ethylenic unsaturation of the difunctional material remains substantially unreacted. In most cases, this reaction is conducted at ambient to moderately elevated temperatures (0 to 150°C) in the substantial absence of a free radical initiator. A catalyst may be used if desired to promote the adduct-forming reaction. In particular, tertiary amines and organometallic compounds as described hereinafter are useful when an ethylenically unsaturated isocyanate is used as the difunctional material.

Most preferably, the vinyl-terminated adduct is as described in U.S. Patent Nos. 4,390,645, 4,394,491, and 4,460,715, as well as adducts formed in the reaction of a polyol and a (trialkoxyl)silyl ester of acrylic or methacrylic acid, as described in U.S. Application Serial No. 06/448,082, filed December 9, 1982.

In preparing the vinyl-terminated adduct in the reaction of a difunctional material with a monol or polyol, it is preferred to conduct the reaction so that

the majority of the adduct species formed have one vinyl group. Accordingly, the reaction of the difunctional material and the monol or polyol is conducted under conditions which promote the formation of monovinyl adducts. To obtain this level of reaction, a mole of a monol is advantageously reacted with 0.2-1.2, preferably 0.8-1.0 mole of difunctional material. When a polyol is employed, it is preferred to react 0.05 to 1.5, more preferably 0.1 to 0.8, and most preferably 0.2 to 0.6 moles of difunctional material per mole of polyol. Generally, a quantity of the monol or polyol remains unreacted and thus forms a solvent for the subsequent polymerization of the adduct. Any unreacted active hydrogens are free to react with a polyisocyanate in forming a polyurethane from the polymer polyol.

In addition, polymers having the structure 2 are also useful as the vinyl-terminated adduct:



wherein  $R^1$ ,  $R^2$  and  $R^4$  are as defined before,  $R^6$  is a divalent radical which activates the vinyl group toward polymerization and together with the terminal vinyl groups is the residue of an active hydrogen-containing initiator compound, and  $a$  is a number from 1 to 100, preferably 10 to 50.  $R^4$  is preferably hydrogen or methyl.  $R^6$  is preferably  $-COO(CH_2)_nO-$ , wherein  $n$  is a number from 1 to 6. Compounds corresponding to structure 2 include the reaction products of hydroxyethylacrylate or hydroxyethylmethacrylate with from 1 to 100 moles of an alkylene oxide.

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The vinyl-terminated adduct is then homopolymerized or copolymerized with an ethylenically unsaturated monomer to form a dispersant which is soluble in the base polyol used in preparing the polymer polyol. The relative proportions of the vinyl-terminated adduct and the ethylenically unsaturated monomer (when used) are such that the dispersant has the required solubility. Typically, 0 to 10, preferably, 0 to 0.2 parts by weight of monomer per part by weight adduct are suitable. The use of small amounts of ethylenically unsaturated monomer, particularly within the preferred ranges, is allowable as long as the dispersant remains soluble in the base polyol. The use of too much of the ethylenically unsaturated monomer can cause the formation of an insoluble dispersant, which is undesirable. In the context of this invention, the dispersant is considered to be soluble in the base polyol if it forms a clear mixture therein at both ambient temperature and at the temperature at which the polymerization of the ethylenically unsaturated monomer to form the polymer polyol is conducted. The formation of a cloudy mixture indicates a lack of solubility.

Suitable ethylenically unsaturated monomers are compounds containing ethylenic unsaturation and which contains no moiety which stabilizes polymers thereof against agglomeration when dispersed in the base polyol. Preferably, the ethylenically unsaturated monomer has a molecular weight of less than 200. More preferably, the ethylenically unsaturated monomer contains no isocyanate-reactive groups. Most preferably, the ethylenically unsaturated monomer contains no polyether moiety. Exemplary monomers

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include aliphatic conjugated dienes such as butadiene and isoprene; monovinylidene aromatic monomers such as styrene, alpha-methyl styrene, ar-chlorostyrene, ar-cyano-styrene, and ar-bromostyrene; ethylenically unsaturated carboxylic acids and esters thereof such as acrylic acid, methacrylic acid, methyl methacrylate, ethyl acrylate, 2-hydroxyethyl acrylate, butyl acrylate, itaconic acid and maleic anhydride; ethylenically unsaturated nitriles and amides such as acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, N,N-dimethyl acrylamide and N-(dimethylaminomethyl) acrylamide; vinyl esters such as vinyl acetate; vinyl ethers, vinyl ketones; vinyl and vinylidene halides, as well as a wide variety of other ethylenically unsaturated materials which are copolymerizable with the aforementioned vinyl-terminated adduct, many of which have heretofore been employed in the formation of polymer polyols as described in U.S. Patent Nos. 3,832,201 and 3,383,351. Mixtures of two or more of the foregoing monomers are also useful herein. Of the foregoing monomers, the vinyl aromatic monomers, particularly styrene, and the ethylenically unsaturated nitriles, particularly acrylonitrile, are preferred. Most preferred are styrene and mixtures thereof with acrylonitrile at a weight ratio of 99.5:0.5 to 10:90.

The polymerization of the adduct, or copolymerization of the adduct and an ethylenically unsaturated monomer to form the dispersant, is advantageously conducted at an elevated temperature in the presence of a free radical initiator. The reaction is conducted in the presence of a monol, polyol or monol/polyol mixture which is miscible with the base

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polyol. The monol and/or polyol may be material which is unreacted in the preparation of the vinyl-terminated adduct from a difunctional material and a monol or polyol and/or may comprise later-added material. The conditions of the reaction are chosen so that the resulting dispersant is soluble in the base polyol. Typically, organic peroxides, peroxyesters and the so-called azo catalysts are suitable. Such catalysts are advantageously used in an amount to achieve a rapid, yet controllable reaction rate, and to promote solubility in the dispersant. Typically, from 0.1 to 20, preferably 2 to 10, more preferably 4 to 10, weight percent based on the weight of monomers is used. The use of the generally higher levels of initiator in this step tends to cause the formation of lower molecular weight dispersants, which increases their solubility. The temperature of the polymerization reaction is advantageously 30-150°C, although optimal temperatures depend somewhat on the particular monomers and initiators employed. Suitable conditions for the polymerization of ethylenically unsaturated monomers in the production of a polymer polyol are described in U.S. Patent No. 4,460,715.

A chain transfer agent may also be employed in order to control the molecular weight of the dispersant, and therefore improve its solubility in the base polyol. Advantageously, chain transfer agents are used in conjunction with high initiator levels to control the molecular weight of the dispersant. Suitable chain transfer agents include, for example, halogenated compounds, mercaptans, sulfides, disulfides and alcohols as described in The Polymer Handbook,

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edited by J. Brandrup and E. H. Immergut, John Wiley and Sons, New York (1975).

In this process, the vinyl-terminated adduct is polymerized or copolymerized in the presence of a monol, polyol, or mixture thereof as a solvent. This monol or polyol may be present from various sources. When the vinyl-terminated adduct is prepared by reacting a monol or polyol with a difunctional monomer as described before, a quantity of unreacted monol or polyol usually remains and therefore forms a portion of the solvent. In addition, it is generally desirable for heat transfer purposes to add a quantity of a monol or polyol to the vinyl-terminated adduct prior to its polymerization. This is particularly true when the polymerization of the vinyl-terminated adduct is conducted by a continuous addition process. In such process, it is often highly desirable to add a portion of monol or polyol to the reaction vessel at the start of the reaction for heat transfer and agitation purposes. Because of the presence of the monol or polyol solvent, the dispersant is obtained as a solution of the polymerized or copolymerized vinyl-terminated adduct in the monol or polyol solvent. The polymerized adduct generally comprises 10-90, preferably 15-50, more preferably 20-40 wt.-%, most preferably 20-35 wt.-% of the dispersant. The term "dispersant" is used herein to designate a solution of the polymer of a vinyl-terminated adduct in a monol or polyol containing at least 10 wt.-% of the polymer as obtained from the polymerization reaction of the adduct.

When the viscosity of the dispersant is referred to herein, it is meant the Brookfield

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viscosity of a 20-35 wt.-% solution of the polymerized or copolymerized vinyl-terminated adduct in a monol and/or polyol. In the event that a dispersant containing a higher quantity of said polymer is prepared, the viscosity is that obtained upon dilution with additional monol or polyol to obtain a 20-35 wt.-% solution. The viscosity of a dispersant containing a lower quantity of polymer can be determined by separating the polymer from the monol and/or polyol and then, if necessary, adding additional solvent to provide a 20-35 wt.-% solution. More preferably, the viscosity of a dispersant containing less than 20 wt.-% dissolved polymer can be adequately estimated by experimentally determining the viscosities of dispersants containing varying known amounts of the polymer, and from this data setting up a calibration curve which can be used to correlate the relationship between the amount of dissolved polymer to its viscosity. The calibration curve can be used to accurately estimate what the viscosity of a dilute solution of the polymer would be if concentrated into the range of 20-35 wt.-% dissolved polymer.

When the dispersant is prepared using a volatile solvent, such solvent is removed prior to measuring the viscosity. The dispersant of this invention advantageously has a viscosity of 300 to 25,000 centipoises (0.3 to 25 Pa·s), preferably 300 to 8,000 centipoises (0.3 to 8 Pa·s), more preferably 500 to 4500 centipoises (0.5 to 4.5 Pa·s) and most preferably 500 to 2500 centipoises (0.5 to 2.5 Pa·s) at 25°C.

Inert solvents, such as volatile organic solvents, can be used in preparing the dispersant, but



are generally not necessary due to the low viscosity of the dispersant and are disadvantageous in that they must be removed before or after forming the polymer polyol. For this reason, such solvents are not  
5 preferred and are most preferably excluded.

The polymerization of the ethylenically unsaturated monomer to form the dispersant can be  
10 conducted batch-wise, but is preferably conducted by continuously adding the monomer and adduct to the reaction mixture. The use of a continuous addition  
15 process tends to give better control of the reaction and to provide a more uniform molecular weight distribution in the adduct.

20 Following the preparation of the dispersant, an additional amount of an ethylenically unsaturated monomer is polymerized in the presence of the  
25 dispersant and the base polyol to form a polymer polyol. The ethylenically unsaturated monomer used in this step may be the same or different from that used  
30 in the preparation of the dispersant. However, those monomers described herein as being useful in preparing the dispersant are also useful in preparing the polymer polyol.  
35

The base polyol is a material or mixture of materials containing a plurality of groups containing  
40 at least one active hydrogen atom. The term "base polyol" is used herein to designate the polyol or mixture thereof which constitutes the major proportion of the continuous phase of the polymer polyol. Preferably, the base polyol contains an average of from 2 to 16, more preferably 2 to 8, and most preferably 2 to 4 such groups per molecule. In addition, the base

polyol advantageously has an equivalent weight of from 70 to 4,000, preferably from 500 to 2,500. Such preferred equivalent weight polyols provide polymer polyols which are especially suitable for preparing flexible polyurethanes. In general, the preferred equivalent weight polyols exhibit a lower viscosity than higher equivalent weight polyols of the same functionality, and therefore tend to reduce the viscosity of the product polymer polyol.

Polyols which are suitable as the base polyol include those described in U.S. Patent No. 4,460,715. Preferred polyols are the polyether polyols, the polyester polyols, hydroxy-functional acrylic polymers, hydroxyl-containing epoxy resins, polyhydroxyl-terminated polyurethane polymers, polyhydroxyl-containing phosphorus compounds and alkylene oxide adducts of polyhydric thioethers. Most preferred, on the basis of cost and availability, are the polyether polyols and the polyester polyols. The most preferred polyether polyols are 500 to 2500 equivalent weight polymers of  $C_2$  to  $C_4$  alkylene oxides, especially  $C_2$ - $C_3$  alkylene oxides.

The ratios of base polyol, dispersant and monomers used to prepare the polymer polyol are chosen to provide the product with the desired solids level. Typical solids levels obtained with this invention are in the range of from 5 to 60, preferably 20 to 55, and more preferably 35 to 50% by weight of the polymer polyol. The term "solids level" means the weight percent of the composition which is in the form of polymerized ethylenically unsaturated monomers.

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Generally, 5 to 50, preferably 10 to 20 parts of dispersant are used per 100 parts of base polyol in preparing the polymer polyol. The use of the dispersant in these ranges provides the polymer polyol with excellent stability and low viscosity at reasonable cost.

Optionally, a chain transfer agent or other materials known to be useful in preparing dispersions of polymer particles in a continuous phase may be employed in the preparation of the polymer polyol. Of particular interest is the use of triiodoorganic compounds and/or inorganic iodine-releasing compounds, particularly iodine itself, as described in U. S. Patent Nos. 4,581,418 and 4,574,137. The use of these materials further aids in reducing the viscosity of the polymer polyol.

The polymerization of the monomers in preparing the polymer polyol are generally as described with respect to the preparation of the dispersant. It is generally important to agitate the reaction mixture in known manner to ensure proper particle formation. It is also preferred to use a free radical initiator in conducting the reaction. The free radical initiator can be used as a means for controlling the molecular weight of the polymerized monomers. Typically, 0.05 to 10, preferably 0.2 to 5, more preferably 0.25 to 3 and most preferably 0.25 to 1 part by weight of a free radical initiator are used per 100 parts of monomer. Use of a free radical initiator within these ranges, and especially within the preferred ranges, tends to provide for reduced viscosity in the polymer polyol. The use of a relatively low amount of free radical initiator as in the most preferred range is a

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substantial advantage of this invention, as it significantly reduces the raw material costs.

5 It is preferred to conduct the polymerization reaction of the monomers to form the polymer polyol in a continuous addition process, although a batch operation is possible. In a particularly preferred  
10 embodiment, the reaction is conducted by continuously adding, in separate streams, the monomer(s) and the dispersant to a reaction vessel which is heated to the polymerization temperature. In this embodiment, the  
15 base polyol may be all in the reaction vessel at the start of the reaction, or may be continuously added to the reactor along with the other materials. When a  
20 continuous addition process is used, it is preferred to continuously add the free radical initiator along with the dispersant and/or base polyol.

25 When the monomer, dispersant and/or base polyol are added continuously to the reaction vessel, such addition is typically conducted over a period of 10  
30 minutes to 6 hours.

After all reactants are added to the reaction vessel, it is common practice to digest the reaction  
35 mixture at the reaction temperature for a period, typically 0.5 to 3 hours, to complete the polymerization. Following the polymerization reaction,  
40 it is advantageous to remove any unreacted monomer from the polymer polyol using any suitable technique such as vacuum stripping.

The process of this invention provides a polymer polyol which, for a given solids level, exhibits a surprisingly low viscosity. Accordingly,

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this process provides a means for preparing high solids polymer polyols which have a viscosity sufficiently low for their processing into polyurethanes using conventional equipment. The particles are also well  
5 stabilized against agglomeration and settling.

If a lower solids polymer polyol is desired, the polymer polyol of this invention can be diluted  
10 with a polyol which is compatible with the base polyol. The advantages of diluting the polymer polyol are described in U.S. Patent No. 4,431,754.

15 The polymer polyol of this invention can be reacted with a polyisocyanate in conventional manner to form a polyurethane. Such reaction can be carried out  
20 in the presence of blowing agents, surfactants, catalysts, chain extenders, additional polyols, stabilizers, fillers, pigments as well as other  
25 additives which are useful in the preparation of polyurethanes.

30 Polyisocyanates suitable for use with the polymer polyol of this invention include aliphatic, aromatic and cycloaliphatic polyisocyanates. Exemplary aromatic polyisocyanates include 2,4- and/or 2,6-  
35 toluenediisocyanate (TDI), p-phenylene diisocyanate, naphthylene diisocyanate, diphenylmethanediisocyanate (MDI) and derivatives thereof. Toluene diisocyanate is  
40 most preferred.

Exemplary aliphatic and cycloaliphatic polyisocyanates include tetramethylene diisocyanate, hexamethylene diisocyanate, 1,4-cyclohexane diisocyanate, tetramethylxylene diisocyanate and isophorone

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diisocyanate, as well as the hydrogenated derivatives of the afore-mentioned aromatic polyisocyanates.

5 In addition to the foregoing, crude poly-  
isocyanates as disclosed in U.S. Patent No. 3,215,652,  
and isocyanate-terminated prepolymers and quasi-  
prepolymers prepared in the reaction of a  
10 stoichiometric excess of the polyisocyanate and a  
polyol having an equivalent weight of 31-2000 are  
useful herein.

15 In preparing a polyurethane foam with the  
polymer polyol of this invention, the polymer polyol  
may be reacted with the polyisocyanate in the presence  
of a blowing agent to form a foam. In contrast to such  
20 a "one-shot" process, the polymer polyol can be  
prereacted with a stoichiometric excess of  
polyisocyanate to form an isocyanate-terminated  
25 prepolymer which is then reacted with water to form a  
foam.

30 In addition to water, low boiling organic  
compounds, notably the halogenated alkanes, are useful  
blowing agents.

35 Any suitable urethane catalyst can be used to  
prepare polyurethanes from the polymer polyol. Notable  
are the tertiary amines and organometallic catalysts.  
Suitable such catalysts are described in U.S. Patent  
40 Nos. 4,390,645 and 2,846,408.

The foam can be used to prepare padding,  
energy-absorbing devices, balls, automobile dashboards,  
and head lights. In addition to foams, non-cellular  
elastomers can be prepared from the polymers polyol of

the inventions. The foams are characterized by having excellent load-bearing.

The following examples are provided to illustrate the invention but not to limit the scope thereof. All parts and percentages are by weight unless otherwise indicated.

10 Example 1

A. Preparation of Vinyl-terminated Adduct

15 To a three-liter, 3-necked round-bottomed flask equipped with an addition funnel, stirrer, condenser and thermocouple were added 2400 g (0.5 mole) of a 4800  
20 molecular weight ethylene oxide-capped poly(propylene oxide) triol (hereinafter Polyol A). The polyol was heated to 70°C. and 15 grams (0.1 mole) of  
25 isocyanatoethyl methacrylate (IEM) were added with stirring. Dibutyltin dilaurate catalyst (0.1 gram) was added as a catalyst, and the reaction was allowed to proceed at 70°C. until all the isocyanate groups had  
30 reacted, as determined by infrared spectroscopy. The resulting vinyl-terminated adduct was a viscous liquid.

35 B. Preparation of Dispersant

Using a reactor as described in section A of this example, with the addition of a nitrogen sparge,  
40 200 grams of Polyol A were heated to 120°C. under a nitrogen atmosphere. With stirring, a mixture of 5 g. azobisisobutyronitrile, 15 g. acrylonitrile, 35 g. styrene and 2200 g. of the vinyl-terminated adduct from Example 1-A were added with stirring over a three-hour period. The product was then stripped to remove volatile monomers and cooled to room temperature. The

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resulting dispersant had a viscosity of 1385 centipoises (cps) (1.385 Pa·s), as measured on a Brookfield Model RVF viscometer using a #2 spindle at 10 rpm. By contrast, Polyol A itself had a Brookfield  
5 viscosity of 800 cps (0.8 Pa·s) at 25°C.

#### C. Preparation of Polymer Polyol

10           Using a reactor as described in Example 1-B, 1000 g. of Polyol A and 200 g. of the dispersant prepared in Example 1-B were heated to 120°C with  
15 stirring. To the heated mixture were added, over a period of 70 minutes while maintaining the temperature at 120°C, a mixture of 6 g. azobisisobutyronitrile, 75  
20 g. acrylonitrile and 225 g. styrene. The reaction mixture was heated at 120°C. for an additional 30  
minutes following the addition of the monomers, after which the product was vacuum stripped to remove any  
25 unreacted volatile monomers. The product polymer polyol contained 20 weight-% solids and had a Brookfield viscosity of 1993 cps (1.993 Pa·s) as  
30 measured at 25°C on a Brookfield model RVF viscometer using spindle #2 at 10 rpm.

#### D. Preparation of Flexible Polyurethane Foam

35           A portion of the polymer polyol prepared in Example 1-C was diluted to 12% solids with a polyol similar to Polyol A except it contained somewhat  
40 greater EO capping. To 100 parts of the diluted polymer polyol were added 3.8 parts of water, 0.375 parts of a 33% active triethylene diamine solution, 1.7 parts diethanol amine, 1.7 parts of a silicone surfactant, 0.1 parts of an amine catalyst, 0.005 parts of an organotin catalyst and sufficient amount of an



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80/20 mixture of 2,4- and 2,6-toluene diisocyanate to provide an isocyanate index of 100. This mixture was poured into a 15" X 15" (381 mm x 381 mm) mold which was preheated to 140-145°C. and cured at that temperature for 6 minutes. The, foam was then crushed to 2.5" (63.5 mm) and then to 1.5" (38.1 mm). The resulting foam had excellent properties.

10 Example 2

A. Preparation of Vinyl-terminated Adduct

15 In a suitable reactor were placed 900 parts of a 4750 molecular weight triol prepared by reacting a trihydric initiator with a mixture of 87% propylene oxide and 13% ethylene oxide (hereinafter Polyol B). To the reactor were also added 11.82 parts isocyanatoethyl methacrylate and the resulting mixture was heated to 60-70°C. Then, 0.05 parts of an organotin catalyst were added and the mixture was permitted to react at the stated temperature for 4 hours. The resulting adduct was used in Example 2-B following.

30 B. Preparation of Dispersant

35 To a reactor equipped with a mechanical stirrer, condenser, thermocouple and addition tubes were added 600 parts of a 3100 molecular weight triol prepared by reacting a trihydric initiator with a mixture of 87% propylene oxide and 13% ethylene oxide (hereinafter Polyol C). The reactor was then heated to 125°C. and padded with nitrogen. To the reactor were simultaneously fed, over 90 minutes, a first stream containing 2597 parts of the adduct prepared in Example 2-A and 7.2 parts of azobisisobutyronitrile and a second stream containing 84 parts styrene and 36 parts

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acrylonitrile. Following the reaction, a clear solution of the dispersant in Polyol C was obtained which had a Brookfield viscosity of 2400 cps (2.4 Pa·s).

5

#### C. Preparation of Polymer Polyol

To a reactor as described in Example 2-B were added 489 parts of Polyol C and 79 parts of the dispersant of Example 2-B. This mixture was heated to 130°C. under a nitrogen sparge. To the reactor were then added a first feed stream containing 1047 parts of Polyol C, 120 parts of the dispersant and 28.5 parts of azobis-isobutyronitrile, a second stream containing 997.5 parts styrene and a third stream containing 427.5 parts acrylonitrile. Each stream was started at the same time. The monomer streams were added over 70 minutes and the first stream was added over 75 minutes. After the additions were complete, the reaction mixture was heated at 130°C for an additional hour, after which any unreacted volatile monomers were vacuum stripped. The resulting polymer polyol contained 44.3% solids and had a Brookfield viscosity of 6810 cps (6.81 Pa·s) at 25°C. The average particle size was 736 nm.

#### 35 Examples 3-5

A series of vinyl-terminated adducts were formed according to the procedure described in Example 2-A, except that the mole ratio levels of isocyanatomethacrylate (IEM) capping was varied as indicated in Table I following. Each adduct was then formed into a dispersant, and then used to prepare a polymer polyol as described in Examples 2-B and 2-C. The polymer polyols were prepared such that the IEM

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content of the copolymer polyol was the same in all cases. The viscosity of both the dispersant and the polymer polyol produced therefrom are reported in Table I. The data from Example 2 is included for comparison.

5

Table I

10	<u>Example No.</u>	<u>IEM level<sup>1</sup></u>	<u>Dispersant Viscosity<sup>2</sup></u>	<u>Polymer Polyol Viscosity<sup>2</sup></u>	<u>% Solids</u>
	2	0.4	2,400 cps (2.4 Pa·s)	6,810 cps (6.81 Pa·s)	44.3
15	3	0.2	1,050 cps (1.05 Pa·s)	11,800 cps (11.8 Pa·s)	43.8
	4	0.6	8,100 cps (8.1 Pa·s)	19,280 cps (19.28 Pa·s)	45.4
20	5	1.0	>50,000 cps (50 Pa·s)	could not form dispersion	--

<sup>1</sup>Moles IEM per mole of polyol used in preparing the vinyl-terminated adduct.

25 <sup>2</sup>All viscosities measured on a Brookfield Model RVF viscometer at 25°C.

It can be seen, therefore, that in this formulation, optimum polymer polyol viscosity was achieved when 0.4 mole of IEM was used per mole of polyol to form the dispersant. At higher IEM capping levels, the viscosity of the product increased. Similar experimentation showed that when the styrene and acrylonitrile were omitted in the preparation of the dispersant, the optimum IEM capping in the adduct level increased to 0.6-1.0 moles of IEM per mole of polyol used to form the dispersant.

Example 6

A polymer polyol was prepared in the same manner as described in Example 2, except the initiator

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level in the preparation of the polymer polyol was reduced to 5.7 parts. The product had a viscosity of 6,000 cps (6 Pa·s) at 43.9% solids. Average particle size was 706 nm. It is thus seen that the process of this invention permits the use of very low initiator levels in preparing the polymer polyol.

#### Example 7

Following the procedures described in Example 2-A, a vinyl-terminated adduct was prepared. This adduct was used to prepare a dispersant in the manner described in Example 2-B, with the exception that 7.2 parts of iodine (I) were added to the first stream. A polymer polyol was prepared using this dispersant by charging a reactor as described in Example 1-B with 489 parts of Polyol C and 79 parts of the dispersant. This mixture was heated to 130°C. under a nitrogen sparge. To the mixture were then added a first stream containing 691 parts Polyol C, 120 parts of the dispersant and 28.5 parts of azobisisobutyronitrile, a second stream containing 356 parts Polyol C and 3.6 parts iodine, a third stream containing 997.5 parts styrene and a fourth stream containing 427.5 parts acrylonitrile. Feeding of all streams was begun simultaneously, with the monomer streams being fed over 65 minutes and the first and second streams being fed over a slightly longer time. Following the additions, the reaction mixture was heated at 130°C for an additional hour. The resulting polymer polyol contained 43.8% solids and had a Brookfield viscosity of 5040 cps (5.04 Pa·s) at 25°C. Average particle size was 673 nm.

Example 8

A vinyl-terminated adduct was prepared and used to prepare a dispersant according to the method described in Example 2-A and 2-B. To a reactor were charged 69.1 parts of the stabilizer and 518.1 grams of Polyol D (a 4700 molecular weight ethylene oxide-capped poly(propylene oxide) triol. After heating to 130°C, three fed streams were simultaneously begun. The first stream contained 619 g styrene, and was added over 66 minutes. The second stream contained 210 g acrylonitrile and was added over 66.5 minutes. The third stream contained 72.9 g of the dispersant, 8.3 g of azobisisobutyronitrile and 593 grams of Polyol D. It was added over 71 minutes. After digestion and stripping as described in Example 2-C, the product copolymer polyol was recovered. The product had a Brookfield viscosity of 2450 cps (2.45 Pa·s) at 34.61% solids. This viscosity was considered excellent since a higher viscosity base polyol was used than in Examples 1-7. The copolymer polyol was useful in preparing molded polyurethane foams.

Example 9

Example 8 was repeated, except the first and second streams were replaced with a single stream containing 819 grams of styrene. The product had a Brookfield viscosity of 3620 cps (3.62 Pa·s) at 34.63% solids.

Example 10

## A. Preparation of Vinyl-terminated Adduct

5           Following the procedures described in Example 2-A, a vinyl-terminated adduct was prepared.

## B. Preparation of Dispersant

10           To a reactor equipped with mechanical stirrer, condenser, thermocouple and addition funnel was added 200 parts of polyol B. The reactor was then heated to  
15 130°C under a nitrogen blanket. To the reactor were added a solution of 2200 parts of the adduct from Example 10-A, 105 parts styrene, 45 parts  
20 acrylonitrile, 15 parts azobisisobutyronitrile and 120 parts carbon tetrachloride. The addition was complete after one hour. After an additional 0.25 hour  
25 cookdown, the mixture was stripped of volatile organics under vacuum. The final product was a clear liquid with a Brookfield viscosity of 4200 cps (4.2 Pa·s) at 25°C.

30 C. Preparation of Polymer Polyol

35           To the reactor of Experiment 10-B were added 350 parts polyol C and 75 parts of dispersant from example 10-B. This mixture was heated to 130°C under a nitrogen sparge. To the reactor was added a feed  
40 stream consisting of 420 parts styrene, 180 parts acrylonitrile, 12 parts azobisisobutyronitrile, 75 parts of dispersant from Example 10-B, and 250 parts of Polyol C. The addition was complete after one hour and after an additional 0.5 hour cookdown at 130°C the mixture was stripped of volatile organics under vacuum.

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The final product had a Brookfield viscosity of 7960 cps (7.96 Pa·s) at 25°C.

Example 11

5     A.           Preparation of Vinyl-Terminated Adduct

10               In a suitable reactor were placed 900 parts of Polyol B. To the reactor were added 17.7 parts of IEM, and the resulting mixture was heated to 60-70°C. Then 0.08 part of an organotin catalyst was added and the mixture permitted to react at the stated temperature  
15               for 4 hours.

          B.           Preparation of Dispersant

20               To a suitable reactor as described in Example 2-B were added 600 parts of Polyol C. The polyol was heated to 125°C and padded with nitrogen. To the  
25               reactor were added, over a period of 1 hour, 2640 parts of the adduct prepared in Example 11-A and 37.8 parts of azobisisobutyronitrile. Following the reaction, a  
30               clear solution was obtained which had a Brookfield viscosity of 1330 centipoises (1.33 Pa·s) at 25°C.

          C.           Preparation of Polymer Polyol

35               To a reactor as described in Example 2-C were added 512 parts of Polyol C and 56 parts of the dispersant as described in Example 11-B. This mixture  
40               was heated to 130°C under a nitrogen sparge. To the reactor were then added a first feed stream containing 1082 parts of Polyol C, 85 parts of the dispersant and 28.5 parts of azobisisobutyronitrile, a second stream containing 997.5 parts styrene and a third stream containing 427.5 parts acrylonitrile. Addition of each

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stream was started at the same time, with the first stream being added over 90 minutes and the second and third streams being added over 60 minutes. After the additions were complete, the reaction mixture was  
5 heated at 130°C for an additional hour after which any volatile impurities were vacuum stripped. The resulting polymer polyol contained 42.0 wt.-% solids  
10 and had a Brookfield viscosity at 25°C of 9,040 centipoises (9.04 Pa·s). The average particle size was 686 nanometers in diameter.

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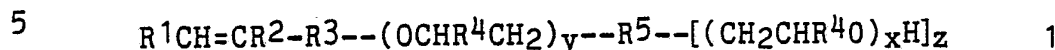
1. A process for preparing a polymer dispersion in a continuous polyol phase comprising the steps of

5 (a) forming in a first step a dispersant by homopolymerizing a vinyl-terminated adduct, or copolymerizing said adduct with at least one ethylenically unsaturated monomer, in the presence of an active hydrogen-containing compound as a solvent under conditions such  
10 that the resulting dispersant is soluble in a base polyol and has a Brookfield viscosity of less than 25,000 centipoises (25 Pa·s) at 25°C as a 20-35 wt.-% solution in an active  
15 hydrogen-containing compound, and then in a second step

(b) polymerizing an ethylenically unsaturated monomer or mixture thereof in the presence of said dispersant and a base polyol under  
20 conditions such that the polymerized monomer forms a plurality of particles which are stabilized against agglomeration by the dispersant.  
25

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2. A process as claimed in Claim 1 wherein said adduct is represented by the structure



wherein R<sup>1</sup> is hydrogen, inertly substituted lower alkyl, nitrile, R<sup>8</sup>-OOC- or R<sup>8</sup><sub>2</sub>NCO-, wherein each R<sup>8</sup> is independently hydrogen, inertly substituted lower alkyl, or polyoxyalkylene, R<sup>2</sup> and R<sup>4</sup> are each independently hydrogen or inertly substituted lower alkyl, R<sup>3</sup> is a divalent radical which activates the terminal vinyl group towards polymerization, R<sup>5</sup> is the residue of a polyhydric initiator when x is greater than zero and the residue of a monohydric initiator bond x is zero, y is a number from 1 to 100, x is a number from 0 to 100 and z is a number from 1 to 3 or



wherein R<sup>1</sup> is hydrogen, inertly substituted lower alkyl, nitrile, R<sup>8</sup>-OOC- or R<sup>8</sup><sub>2</sub>NCO-, R<sup>2</sup> and R<sup>4</sup> are each independently hydrogen or inertly substituted lower alkyl, R<sup>6</sup> is a divalent radical which activates the vinyl group toward polymerization and together with the terminal vinyl group is the residue of an active hydrogen-containing initiator compound, and a is a number from 1 to 100, preferably 10 to 50.

3. A process as claimed in Claim 1 wherein said dispersant has a viscosity of 300 to 8000 centipoises (0.3 to 8 Pa.s) and said adduct is the reaction product of a polyether polyol and 0.2-0.6

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moles of an ethylenically unsaturated isocyanate per mole of polyol.

4. A process as claimed in any of the preceding claims wherein an ethylenically unsaturated monomer is employed in step (a) and/or step (b), and such monomer comprises a monovinyl aromatic monomer, an ethylenically unsaturated nitrile, or mixture thereof.

5. A process as claimed in any of the preceding claims wherein step (a) and/or step (b) is conducted in the presence of a free radical initiator.

6. A process as claimed in any of the preceding claims wherein step (a) and/or step (b) is conducted by the continuous addition of monomer under polymerization conditions.

7. A process as claimed in any of the preceding claims wherein the polymer polyol has a viscosity of less than 10,000 cps (10 Pa·s) and a solids content of 35-50% by weight.

8. A process as claimed in Claim 5 wherein said free radical initiator is employed in step (b) in an amount of from 0.25 to 1% based on the weight of the monomer or mixture thereof.

9. A process as claimed in any of the preceding claims wherein said adduct is homopolymerized in step (a).

10. A polymer polyol prepared according to the process claimed in any of the preceding claims.

11. A composition useful for stabilizing dispersed addition polymer particles in a polymer

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polyol against agglomeration and settling comprising a 10-90 wt.-% solution of a homopolymer of a vinyl-terminated adduct, or copolymer thereof with at least one ethylenically unsaturated monomer as defined  
5 herein, in a monol and/or polyol.

12. A process for preparing a polymer  
dispersion in a continuous polyol phase comprising the  
10 steps of

(a) forming a dispersant by homopolymerizing a  
15 vinyl-terminated adduct, or copolymerizing said adduct with an ethylenically unsaturated monomer or mixture thereof under conditions such that the resulting dispersant is soluble in a base polyol and has a  
20 Brookfield viscosity of less than 25,000 centipoises (25 Pa·s), and then

(b) polymerizing an ethylenically unsaturated  
25 monomer or mixture thereof in the presence of said dispersant and a base polyol under conditions such that the polymerized monomer and said dispersant form a  
30 plurality of particles dispersed in said base polyol.

13. A dispersant composition useful for  
35 stabilizing a polymer polyol, comprising a homopolymer of an ethylenically unsaturated adduct of a difunctional material and a monol or polyol, or a copolymer thereof with at least one other ethylenically  
40 unsaturated monomer, wherein said dispersant has a viscosity of less than 25,000 centipoises (25 Pa·s), and said dispersant is soluble in a base polyol.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/US86/02742

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>3</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC (4) : C08F 2/06, 2/08, 2/14, 18/22, 118/00, 218/00; C08K 5/05, 5/06; C08L 31/00		
US CL 524/850, 853, 762, 535, 533, 377; 526/209, 301		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>4</sup>		
Classification System	Classification Symbols	
U.S.	524/850, 853, 762, 535, 533, 377 526/209, 301	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>5</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup>		
Category *	Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>
X Y	US, A, 4,148,840 (SHAH) 10 APRIL 1979. See entire document.	1, 4-13 2, 3
X	US, A, 4,460,715 (HOFFMAN) 17 JULY 1984. See entire document.	1-13
X	US, A, 4,394,491 (HOFFMAN) 19 JULY 1983. See entire document.	1-13
Y	US, A, 4,390,645 (HOFFMAN) 28 JUNE 1983. See entire document.	1-13
Y, P	US, A, 4,611,028 (PENG) 09 SEPTEMBER 1986. See entire document.	1-13
A	US, A, 3,956,225 (MURATO) 11 MAY 1976. See column 1, lines 55-64.	1-13
A	US, A, 4,500,675 (FISK) 19 FEBRUARY 1985. See Abstract.	1-13
A, P	US, A, 4,594,366 (TAYLOR) 10 JUNE 1986. See entire document.	1-13
X	US, A, 4,287,323 (TEFERTILLER) 01 SEPTEMBER 1981. See column 6, lines 7-54 and Example II.	11, 13
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: <sup>15</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search <sup>1</sup>		Date of Mailing of this International Search Report <sup>2</sup>
27 JANUARY 1987		11 FEB 1987
International Searching Authority <sup>1</sup>		Signature of Authorized Officer <sup>20</sup>
ISA/US		C. WARREN IVY

## III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No <sup>18</sup>
X	US,A, 4,140,667 (PRESTON) 20 FEBRUARY 1979. See the entire document.	11,13
X	US,A, 4,327,005 (RAMLOW) 27 APRIL 1982. See entire document.	1, 2, 4-13
&	GB,A, 2,082,601 (BASF WYANDOTTE) 10 MARCH 1982. See entire document.	1, 2, 4-13
X	US,A, 4,242,249 (VAN CLEVE) 30 DECEMBER 1980. See column 11, lines 3-11 and 47-54 and column 11, line 64 to column 12, line 11.	1-13
A	US,A, 4,463,107 (SIMROTH) 31 JULY 1984. See Table I.	1-13