

Description

This invention relates to polyol polyacrylates.

More specifically, this invention relates to polyol polyacrylates prepared from a polyol and at least one
5 acrylate monomer or polymer followed by transesterification.

In one of its more specific aspects, this invention pertains to the incorporation of a polyol polyacrylate into a polymer polyol composition for the purpose of improving the stability of dispersed vinyl polymer particles contained in the polymer polyol.

Polymer polyols containing vinyl polymer particles dispersed in a continuous polyol phase are well
10 known. Also well known is the tendency of polymer polyols to undergo phase separation if they are not stabilized. Hence, polymer polyols are generally stabilized against phase separation by incorporation of a dispersant during formation. U.S. Pat. Nos. 4,148,840 and 4,242,249 teach that certain preformed polymer polyols are suitable dispersion stabilizers. U.S. Pat. Nos. 4,327,055 and 4,334,049 teach that alkylene oxide adducts of styrene/allyl alcohol copolymers can be used as polymer polyol dispersants.

15 A more recent publication (see International Publication No. WO87/03886 and U.S. Pat. No. 4,745,153) teaches a preformed dispersant formed by homopolymerizing a vinyl-terminated adduct or copolymerizing the adduct with an ethylenically unsaturated monomer or monomer mixture in the presence of an active hydrogen-containing compound as a solvent.

Also known is the formation of graft polymers by the grafting of the potassium alkoxide derivative of
20 poly(ethylene oxide) on poly(methylmethacrylate) in homogeneous solution in toluene. [See M.A. Twark, M. Tahan, and A. Zilkha, "Grafting of Poly(ethylene oxide) on Poly(methylmethacrylate) by Transesterification," Journal of Polymer Science: Part A-1, Vol. 7, 2469-2480 (1969)].

This invention provides novel polyol polyacrylates which are particularly suitable for incorporation into polymer polyols for the purpose of stabilizing the polymer polyols against phase separation.

25 The polyol polyacrylates of this invention can be prepared by alternative methods. In one method, the in situ method, a polyacrylate graft-polyol intermediate product is first formed by polymerizing esters of acrylic and methacrylic acid in situ in a polyoxyalkylene polyether polyol followed by a transesterification reaction to produce a polyol polyacrylate. In the other method, the blend method, a homopolymer or copolymer of (meth)acrylate esters is separately prepared and blended with a polyoxyalkylene polyether
30 polyol. The resulting blend is converted into a polyol polyacrylate by a transesterification reaction.

According to this invention, there is provided a dispersant suitable for enhancing the stability of polymer polyols said dispersant being a polyol-polyacrylate formed by

(a) (i) polymerizing from 5 to 90 weight percent of at least one acrylate monomer selected from C₁-C₂₀ alkyl esters of acrylic and methacrylic acids in from 95 to 10 weight percent of polyoxyalkylene polyether
35 polyol to form a single phase homogeneous liquid intermediate reaction product containing acrylate polymer or (ii) blending from 5 to 90 weight percent of at least one acrylate polymer selected from homopolymers and copolymers of C₁-C₂₀ alkyl esters of acrylic and methacrylic acids with from 95 to 10 weight percent of a first polyoxyalkylene polyether polyol to form a single phase homogeneous liquid intermediate blend;

40 (b) optionally adding further polyoxyalkylene polyether polyol to said intermediate reaction product or blend just prior to step (c), and thereafter

(c) transesterifying from 1 to 30 mole percent of the total ester groups of the acrylate polymer of the product (i) or blend with the hydroxyl groups of the polyoxyalkylene polyether polyol.

Also according to this invention, there is provided a stable polymer polyol composition comprising a
45 continuous phase, a disperse phase within the continuous phase, and a dispersant for enhancing the stability of the polymer polyol, wherein (a) the disperse phase consists essentially of vinyl polymer particles; (b) the continuous phase consists essentially of a polyoxyalkylene polyether polyol; and (c) the dispersant is a polyol polyacrylate as defined above and is employed in an amount in the range of 0.1 to 10 percent by weight based on the total weight of continuous phase, disperse phase and dispersant. All three polyoxyal-
50 kylene polyether polyols may be the same polyol or different polyols.

According to this invention, there is also provided a method for producing the stable polymer polyols described above, which method comprises polymerizing an ethylenically unsaturated monomer or mixture of monomers (which form the disperse phase of vinyl polymer particles) in a blend of the polyoxyalkylene polyether polyol continuous phase and the polyol polyacrylate dispersant.

55 According to this invention, there is also provided a method of stabilizing a polymer polyol comprising vinyl polymer particles dispersed in a continuous polyol phase against phase separation, which method comprises incorporating into the polymer polyol composition a dispersant consisting of a polyol polyacrylate as defined above, the dispersant being employed in an amount sufficient to improve the stability of the

polymer polyol.

Polyurethanes produced using the above described polymer polyols are also provided by this invention.

In the in situ method described above, the polyacrylate graft-polyol intermediate can be prepared by polymerizing any suitable acrylate monomer or monomer mixture. Suitable acrylate monomers include the C₁ to C₂₀ alkyl esters of acrylic and methacrylic acids. Particularly suitable acrylate monomers are methyl acrylate, ethyl acrylate, propyl acrylate, N-butyl acrylate, and the like and their mixtures. Most preferred are N-butyl acrylate or a mixture of N-butyl and ethyl acrylates.

The acrylate monomer or monomer mixture is then polymerized in situ in a suitable polyol. Accordingly, the acrylate monomer must be soluble in the polyol. Polyols which can be employed include the polyoxyalkylene polyether polyols which are the polymerization products of an alkene oxide or a mixture of alkene oxides with a polyhydric alcohol. Preferably, the polyol is a 500 to 15,000 molecular weight hydroxyl terminated polyether prepared by the polymerization of an alkylene oxide in the presence of a di-, tri-, or tetra-hydric initiator. The preferred alkylene oxide is propylene oxide.

In one embodiment of this invention, the polyacrylate graft-polyol intermediate will be formed by polymerizing from 5 to 90 total weight percent, preferably from 20 to 50 total weight percent, of at least one acrylate monomer in a polyoxyalkylene polyether polyol at a reaction temperature within the range of from about 60 to about 150 °C. The intermediate product thereby formed, which is a single phase homogeneous liquid, must then undergo a transesterification reaction to form a polyol polyacrylate dispersant of this invention.

In another embodiment pertaining to the blend method for forming a polyol polyacrylate, an acrylate homopolymer or a copolymer is separately prepared and employed as a starting material to form the intermediate. Any suitable homopolymer or copolymer of (meth)acrylate esters can be used. Particularly suitable for use are the homopolymers and copolymers of the acrylate monomers listed above as being suitable for use in the in situ method for forming a polyol polyacrylate. The acrylate homopolymer or copolymer is then blended with one or more polyoxyalkylene polyether polyols as described above to give a blended intermediate product which upon transesterification gives a polyol polyacrylate dispersant of this invention. The blended intermediate product will be formed to contain from 5 to 90 weight percent acrylate polymer, preferably from 20 to 50, with the balance being polyol.

The formation of a polyol polyacrylate dispersant from either intermediate product requires a further transesterification reaction, typically, but not necessarily, carried out in additional polyoxyalkylene polyether polyol using a suitable transesterification catalyst. The polyol, if added, may be the same as or different from the polyol used to form the intermediate. After transesterification, the weight percent acrylate polymer in the polyol polyacrylate should be from 5 to 30, preferably 10 to 25. Accordingly, depending on the weight percent acrylate polymer in the intermediate, it may or may not be desirable to use additional polyol in the transesterification reaction. The transesterification reaction occurs between the terminal hydroxyl groups of the polyol and the ester groups of the acrylate polymer. From 1 to 30 mole percent, preferably from 5 to 25 mole percent of the total ester groups of the acrylate polymer react with the hydroxyl groups of the polyol.

The transesterification catalysts are such as are conventionally employed. Among the catalysts which can be employed are alkali metal oxides, hydroxides or alkoxides, particularly those of potassium or sodium; oxides, alkyls, carboxylates, halides and alkoxides of transition metals such as tin, zinc, zirconium, titanium, aluminum, and manganese; sulfuric acid; hydrochloric acid, and alkyl or aryl sulfonic acids. Solid acids such as Nafion® resin, Amberlyst® resin, and zeolites and other molecular sieves can also be used and the like.

The polymer polyols of this invention will be formed by polymerizing an ethylenically unsaturated monomer or mixture of monomers in a polyol mixture comprising at least one polyoxyalkylene polyol and a polyol polyacrylate dispersant in the presence of a free radical initiator at a temperature from about 60 °C. to about 150 °C.

Any conventional process for preparing polymer polyols can be employed including batch, semi-batch, and continuous processes. The preferred process is a semi-batch process in which all or at least a major amount of the polyol polyacrylate dispersant is added in the reactor charge and the major amount of polyol is added in the feed charge. It is most preferred to add all of the dispersant in the reactor charge. If a plurality of continuous stirred tank reactors (CSTR) in series is employed, the charge to the first CSTR preferably includes all or at least the major amount of dispersant. To the second CSTR, in addition to the product feed from the first CSTR, will be added the feed charge containing the major amount of polyol.

The amount of the polyol polyacrylate dispersant employed to produce the polymer polyol will be within the weight percent range of from 0.1 to 10, preferably from 0.3 to 5 based on the total amount of monomer polyol, and dispersant employed. The weight ratio of total monomer or monomer mixture (or disperse phase) to polyol (or continuous phase) will be from 1:19 to 1:1.

The preferred ethylenically unsaturated monomers employed to produce polymer polyols of the present invention are both styrene and acrylonitrile to make a copolymer. The copolymer will contain in weight percent 20 to 100 styrene with the balance being acrylonitrile. Other suitable monomers include, but are not limited to, butadiene, isoprene, 1,4-pentadiene, 1,6-hexadiene, 1,7-octadiene, acrylonitrile, methacrylonitrile, α -methylstyrene, methylstyrene, 2,4-dimethylstyrene, ethyl styrene, isopropylstyrene, butylstyrene, substituted styrenes, such as cyanostyrene, phenylstyrene, cyclohexylstyrene, benzylstyrene, substituted styrenes such as cyanostyrene, nitrostyrene, N,N-dimethylaminostyrene, acetoxystyrene, methyl 4-vinylbenzoate, phenoxystyrene, p-vinyl diphenyl sulfide, p-vinylphenyl phenyl oxide, acrylic and substituted acrylic monomers such as acrylic acid, methacrylic acid, methyl acrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, methyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, isopropyl methacrylate, octyl methacrylate, ethyl α -ethoxyacrylate, methyl α -acetoaminoacrylate, butyl acrylate, 2-ethylhexyl acrylate, phenyl acrylate, phenyl methacrylate, N,N-dimethylacrylamide, N,N-dibenzylacrylamide, N-butylacrylamide, methacrylyl formamide, vinyl esters, vinyl ethers, vinyl ketones, vinyl acetate, vinyl alcohol, vinyl butyrate, isopropenylacetate, vinyl formate, vinyl acrylate, vinyl methacrylate, vinyl methoxy acetate, vinyl benzoate, vinyl toluene, vinyl naphthalene, vinyl methyl ether, vinyl ethyl ether, vinyl propyl ethers, vinyl butyl ethers, vinyl 2-ethylhexyl ether, vinyl phenyl ether, vinyl 2-methoxyethyl ether, methoxybutadiene, vinyl 2-butoxyethyl ether, 3,4-dihydro-1,2-pyran, 2-butoxy-2'-vinyl ether, vinyl 2-ethylmercaptoethyl ether, vinyl methyl ketone, vinyl ethyl ketone, vinyl phenyl ketone, vinyl ethyl sulfide, vinyl ethyl sulfone, N-methyl-N-vinyl acetamide, N-vinylpyrrolidone, vinyl imidazole, divinyl sulfide, divinyl sulfoxide, divinyl sulfone, sodium vinyl sulfonate, methyl vinyl sulfonate, N-vinyl pyrrole, dimethyl fumarate, dimethyl maleate, maleic acid, crotonic acid fumaric acid, itaconic acid, monomethyl itaconate, t-butylaminoethyl methacrylate, dimethylaminoethyl methacrylate, glycidyl acrylate, allyl alcohol, glycol monoesters of itaconic acid, vinyl pyridine, maleic anhydride, maleimide, N-substituted maleimides, such as N-phenylmaleimide and the like.

The polymerization initiator may be any suitable initiator for the particular monomers employed. Suitable catalytic initiators useful in producing the polymer polyol compositions of this invention are the free radical type of vinyl polymerization catalysts, such as the peroxides, persulfates, perborates, percarbonates, azo compounds, and the like. Specific examples include, but are not limited to, 2,2'-azo-bis-isobutyronitrile (AIBN), dibenzoyl peroxide, lauroyl peroxide, di-t-butyl peroxide, diisopropyl peroxide carbonate, t-butyl peroxy- ω -ethylhexanoate, t-butylperpivalate, 2,5-dimethyl-hexane-2,5-di-per-2-ethyl hexoate, t-butylperneodecanoate, t-butylperbenzoate, t-butyl percrotonate, t-butyl perisobutyrate, di-t-butyl perphthalate, 2,2'-azo-bis(2-methylbutanenitrile) for example. Other suitable catalysts may be employed, of course. The concentration of initiator is not critical and can vary within wide limits of from about 0.1 to about 5.0 weight percent based on the total feed to the reactor.

The polyols most suitable for use in this invention are polyoxyalkylene polyether polyols or mixtures thereof which are the polymerization products of an alkylene oxide or a mixture of alkylene oxides with a polyhydric alcohol. The polyol may contain small amounts of unsaturation. The molecular weight of the polyol will be within the range of from 500 to 15,000, preferably from 2,000 to 10,000. Although typically the polyols selected for the preparation of the intermediate, the transesterification reaction, and the polymer polyol will be identical, they may all be different polyoxyalkylene polyether polyols. As discussed above, depending on the weight percent acrylate polymer in the intermediate, a third addition of polyol may not be required.

Polymer polyols according to this invention will be formed by polymerizing from 5 to less than 50 weight percent, preferably 10 to 45 weight percent, of the ethylenically unsaturated monomer or monomer mixture, based on the total weight of the monomer and polyol, in from 95 to 50 or more weight percent, preferably 90 to 55 weight percent, of at least one polyoxyalkylene polyether polyol in the presence of a polyol polyacrylate dispersant of the invention.

The following examples further demonstrate the preparation of intermediate products, polyol polyacrylate dispersants, polymer polyols incorporating the polyol polyacrylate dispersants, and polyurethanes made using the polymer polyols.

EXAMPLES 1-2

Two polyacrylate graft-polyol intermediate products were separately prepared using the following procedure and the amounts, materials, and process conditions identified in following Table 1.

Into a 3-liter reactor fitted with a stirrer, a condenser, a thermometer, and an addition tube and under a blanket of nitrogen was charged 100 grams of base polyol.

The reactor charge was then heated to the temperature indicated, and the specified feed charge of acrylate monomers, initiator, and additional base polyol was added.

Upon the completion of the feed charge, the in situ polymerization product of each example was held at the reaction temperature for from about 1/2 to one hour and then stripped of residual monomers for one hour at from 115 to 125°C. and about 666.5 Pa (5mm Hg). The product of Example 1 was a 38 weight percent ethyl acrylate/n-butyl acrylate copolymer in ARCOL® 1130 polyol. The product of Example 2 was a 38 weight percent n-butyl acrylate homopolymer in ARCOL® 1130 polyol.

TABLE 1

POLYACRYLATE GRAFT-POLYOL INTERMEDIATE PRODUCTS

<u>Example No</u>	<u>1</u>	<u>2</u>
Monomer Composition	Ethyl Acrylate/ n-Butyl Acrylate	n-Butyl Acrylate
Monomer Weight Ratio	50/50	100
Base Polyol	ARCOL® 1130 ¹	ARCOL® 1130
Reaction Temp., °C.	123	120
Initiator Conc., Wt. %	1.0	1.0
Feed, Addition Time, h	1.5	1.5
<u>Reactor Charge, g</u>		
Base Polyol	100	100
<u>Feed Charge, g</u>		
Monomers	400	400
VAZO® 67 ²	10.0	10.0
Base Polyol	500	500
Monomer Conv., %	94	96
Viscosity Pas (cps), 5/sec	2.95 (2950)	1.81 (1810)

¹ARCOL® 1130 polyol - a glycerine initiated polyether of propylene oxide and ethylene oxide having a hydroxyl number of 48 and containing essentially secondary hydroxyl groups available from ARCO Chemical Company.

²VAZO® 67 - 2,2'-azobis(2-methylbutanenitrile) polymerization catalyst available from E. I. DuPont de Nemours & Co.

EXAMPLE 3

This example demonstrates the preparation of poly(n-butyl acrylate) for use in the blend method for forming a polyol polyacrylate. Substantially the procedure described in Example 2 was used with the following changes.

An equivalent amount of xylene was substituted for the base polyol, and only 7.5 g. of the VAZO® 67 initiator was used. After stripping residual monomer and solvent, the resulting product, poly(n-butyl acrylate), had a viscosity of 12.1 Pas (12,100 cps).

EXAMPLE 4

This example demonstrates the preparation of a polyol polyacrylate dispersant of this invention by the further transesterification reaction of the polyacrylate graft-polyol intermediate of Example 1.

To a reactor fitted with an overhead stirrer and connected to a cold trap and a vacuum pump were added 100 grams of the polyacrylate graft-polyol of Example 1, an additional 100 grams of Arcol 1130 polyol, and 1.0 gram of transesterification catalyst (potassium methoxide).

The reaction mixture was subjected to a vacuum of about 5 torr and heated at about 110°C., i.e., until the viscosity of the reaction mixture was about 35 Pas (35,000 cps.) at 25°C.

The resulting transesterification reaction product was allowed to cool and then flushed with nitrogen, diluted with tetrahydrofuran solvent and blended with 10 grams of Magnesol® magnesium silicate.

The resulting product, a polyol polyacrylate dispersant, was isolated by filtration and solvent stripping. The dispersant had a viscosity of about 26.9 Pas (26,900 cps.) at 25°C.

EXAMPLE 5

This example demonstrates the preparation of a polyol polyacrylate dispersant of this invention by the further transesterification of the polyacrylate graft-polyol product formed in Example 1.

To a reactor fitted with an overhead stirrer and connected to a cold trap and a vacuum pump were added 100 grams of the polyacrylate polyol of Example 1, an additional 100 grams of Arcol® 1130 polyol, and 1.0 gram of transesterification catalyst (potassium methoxide).

The reaction mixture was subjected to a vacuum of about 666.5 Pa (5 torr) and heated at about 110°C. i.e., until the viscosity of the reaction mixture was within the range of about 30 Pas (30,000 cps.) at 25°C.

The resulting transesterification reaction product was allowed to cool and then flushed with nitrogen, diluted with tetrahydrofuran solvent and blended with 10 grams of Magnesol® magnesium silicate.

The resulting polyol polyacrylate dispersant was isolated by filtration and solvent stripping. It had a viscosity of about 23.4 Pas (23,400 cps.) at 25°C.

EXAMPLE 6

Following substantially the procedure of Example 4, but using 100 grams of the polyacrylate graft-polyol product of Example 2, another polyol polyacrylate dispersant was prepared.

The resulting polyol polyacrylate dispersant had a viscosity of 25.4 Pas (25,400 cps.) at 25°C.

EXAMPLE 7

This example demonstrates the preparation of a polyol polyacrylate dispersant of this invention.

To a reactor fitted with an overhead stirrer and connected to a cold trap and vacuum pump were added 150 grams of Arcol® 1130 polyol and 10.7 ml. of 1 N. aqueous potassium hydroxide (transesterification catalyst). The mixture was heated to 100-110°C. for one hour under a pressure of 666.5 Pa (5 torr) and then cooled to room temperature. Next, 76.0 grams of the polyacrylate graft-polyol of Example 2 was added.

This mixture was heated to 50-55°C. under a pressure of 5 torr for about 2 hours, and the resulting transesterification reaction product was cooled, flushed with nitrogen diluted with tetrahydrofuran solvent, and blended with 10 grams of Magnesol® magnesium silicate.

The polyol polyacrylate dispersant was isolated by filtration and solvent stripping and found to have a viscosity of 9.44 Pas (9440 cps.) at 25°C.

EXAMPLE 8

This example demonstrates the preparation of a polyol polyacrylate dispersant of this invention.

To a reactor fitted with an overhead stirrer and connected to a cold trap and vacuum pump were added
 5 100 grams of ARCOL® 1130 polyol and 5.3 ml. of 1 N-aqueous sodium hydroxide (transesterification catalyst). The mixture was heated to 110°C. for 1.5 hours under a pressure of 666.5 Pa (5 torr) and then cooled to room temperature. Next, 100 grams of the polyacrylate graft-polyol product of Example 2 were added. This mixture was heated to 100-110°C. for 7 hours at 400 - 666.5 Pa (3-5 torr) and the resulting transesterification reaction product was cooled, flushed with nitrogen, diluted with tetrahydrofuran, and
 10 blended with 10 grams of Magnesol® magnesium silicate.

The polyol polyacrylate dispersant was isolated by filtration and solvent stripping and found to have a viscosity of 7.08 Pas (7080 cps.) at 25°C.

EXAMPLE 9

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This example demonstrates the preparation of a polyol polyacrylate dispersant of this invention.

To a reactor fitted with an overhead stirrer and connected to a cold trap and vacuum pump were added
 150 grams of ARCOL® 1130 polyol and 10.7 ml. of 1 N-aqueous potassium hydroxide (transesterification catalyst). The mixture was heated to 100-110°C. for one hour under a pressure of 666.5 Pa (5 torr) and
 20 then cooled to room temperature. Next, a blend of 45.0 grams of ARCOL® 1130 and 30.0 grams of poly(n-butyl acrylate) prepared according to Example 3 were added. This mixture was heated to 100°C. for 3.6 hours, then 110-116°C. for 6.0 hours under a pressure of 666.5 Pa (5 torr), and the resulting transesterification reaction product was cooled, flushed with nitrogen diluted with tetrahydrofuran solvent, and blended with 20 grams of Magnesol® magnesium silicate.

25 The polyol polyacrylate dispersant was isolated by filtration and solvent stripping and found to have a viscosity of 6 Pas (6000 cps.) at 25°C.

EXAMPLES 10-27

30 Eighteen polymer polyols were made each employing one of the polyol polyacrylate dispersants prepared in Examples 4-9 and the following procedure.

Into a 3-liter, 4-neck resin kettle equipped with a stirrer, condenser, thermometer, addition tube, and under a blanket of nitrogen were charged the amounts of base polyol and polyol polyacrylate dispersant identified under the heading "Reactor Charge" in following Table 2.

35 After the kettle was heated to the specified reaction temperature the amounts of monomers, initiator, and base polyol identified under the heading "Feed Charge" were added over a two-hour time period. All products were milk-white dispersions.

All dispersions were held at the reaction temperature for about 1/2 to 1 hour and then stripped for 1 to 1-1/2 hours at 90-120°C. and less than 666.5 Pa (5 mm Hg). Table 2 contains the properties of the
 40 resultant polymer polyols of this invention made with polyol polyacrylate dispersants.

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55 50 45 40 35 30 25 20 15 10 5

TABLE 2

Polymer Polyols Incorporating Polyol Polyacrylate Dispersants

<u>Example No.</u>	<u>10</u>	<u>11</u>	<u>12</u>	<u>13</u>	<u>14</u>	<u>15</u>	<u>16</u>	<u>17</u>	<u>18</u>
Monomer Charge, Wt %	20	20	20	20	20	20	20	20	20
SAN Weight Ratio	70/30	70/30	70/30	70/30	75/25	80/20	90/10	100/0	70/30
Base Polyol	Arcol 1130								
Polyol Polyacrylate Dispersant of Example No.	4	4	4	6	6	6	6	6	6
% Dispersant (based on total reactants less initiator)	2.5	1.25	0.8	0.4	1.2	0.8	0.8	4.0	0.8
% of Total Polyol in Feed	94	94	94	94	94	94	94	90	80
Reaction Temp., °C.	120	120	120	120	120	120	120	120	120
Initiator Conc., Wt. %	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Feed, Addition Time, h	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
<u>Reactor Charge, g</u>									
Base Polyol	50	75	84	92	76	84	84	40	304
Dispersant	50	25	16	8	24	16	16	40	16
<u>Feed Charge, g</u>									
Styrene	280	280	280	280	300	320	360	200	280
Acrylonitrile	120	120	120	120	120	80	40	--	120
Initiator (VAZO 67)	10.0	10.0	10.0	10.0	10.0	10.0	10.0	5.0	10.0
Base Polyol	1500	1500	1500	1500	1500	1500	1500	720	1280
<u>Dispersion Properties</u>									
Conversion % Overall	94	93	94	94	91	92	85	79	94
Viscosity, Pas (cps) 20/sec.	1.34 (1340)	1.26 (1260)	1.17 (1170)	1.21 (1220)	1.17 (1170)	1.08 (1080)	1.03 (1030)	1.24 (1240)	1.31 (1330)
Particle Size, μ (IPA)	.58	.66	.62	.78	.58	.76	1.51	1.3	.61
Centrifugable Solids, Wt. %	1.7	1.5	1.6	1.8	1.5	1.6	6.3	12.7	1.8

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TABLE 2 (cont'd)
Polymer Polyols Incorporating Polyol Polyacrylate Dispersants

Example No.	19	20	21	22	23	24	25	26	27
Monomer Charge, Wt %	40	40	40	40	40	40	42	40	40
SAN Weight Ratio	70/30	75/25	75/25	75/25	70/30	75/25	75/25	75/25	75/25
Base Polyol	Arcol 1130								
Polyol Polyacrylate Dispersant of Example No.	5	5	5	6	6	7	7	8	9
% Dispersant	3.0	3.0	1.5	1.2	1.2	1.8	2.3	2.4	2.4
(based on total reactants less initiator)									
% of Total Polyol in Feed	92	92	92	92	92	92	92	92	92
Reaction Temp., °C.	120	120	120	120	120	120	120	120	120
Initiator Conc., Wt. %	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Feed, Addition Time, h	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Reactor Charge, g	40	40	64	76	76	64	53.8	52	52
Base Polyol	60	60	36	24	24	36	46.4	48	48
Dispersant									
Feed Charge, g									
Styrene	560	600	600	600	560	600	630	600	600
Acrylonitrile	240	200	200	200	240	200	210	200	200
Initiator (VAZO 67)	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0
Base Polyol	1100	1100	1100	1100	1100	1100	1060	1100	1100
Dispersion Properties									
Conversion % Overall	97	96	97	96	97	96	96	96	96
Viscosity, Pas (cps) 20/sec.	6.65 (6630)	6.37 (6370)	4.39 (4390)	4.3 (4300)	7.16 (7160)	4.23 (4230)	5.56 (5560)	4.71 (4710)	4.23 (4230)
Particle Size, μ (IPA)	.60	.67	.72	.82	.75	.86	.78	.82	.82
Centrifugable Solids, Wt. %	3.6	3.8	3.4	3.7	6.5	3.9	4.7	3.6	4.0

From the above data, it will be seen that the polyol polyacrylate dispersants of this invention are effective in achieving stable dispersions at high solids contents. Moreover, the particle sizes, viscosities, and centrifugable solids of the polymer polyols produced using the polyol polyacrylate dispersants are excellent.

Polyurethanes may be made by reacting the polymer polyols described above with an organic polyisocyanate in the presence of a polyurethane formation catalyst. If a foam is desired, a blowing agent such as a halocarbon (trichlorofluoromethane, for example), water, or carbon dioxide may also be present.

The polyurethane formation catalysts are typically tin catalysts or tertiary amine compounds. Other conventional additives such as silicone surfactants, fire retardant additives (melamine, for example), etc. may also be present. For more information in preparing polyurethanes, particularly flexible polyurethanes, see U.S. Pat. Nos. 4,338,408, 4,342,687, and 4,381,353, incorporated herein by reference. The foams made using the polymer polyols described herein have excellent physical properties. Flexible carpet underlay foam and molded automobile foam may be prepared using the polymer polyols and techniques described herein.

A typical slab polyurethane foam is prepared by first charging polymer polyol, water, catalyst, and silicone surfactant into a vessel while stirring vigorously. Next, the polyisocyanate is added to the vessel with stirring, and the resulting mixture is immediately poured into a cardboard cakebox; and the polyurethane foam allowed to rise and cure at room temperature.

Using substantially the procedure described above, a slab polyurethane foam suitable for use as carpet underlayment was prepared from the following amounts of ingredients.

Ingredient	Amount (parts by wt.)
Polymer Polyol of Example 22	100
Water	2.2
L-6202 silicon surfactant ¹	0.8
Amine ²	0.3
T-10 Organo Tin Catalyst (50% Active) ³	0.4
Toluene Diisocyanate	29.6

¹Available from Union Carbide Corporation.

²Prepared by blending 2 parts B11 and 1 part 33LV, both available from Air Products and Chemicals, Inc., and 3 parts Thanol® F3020, available from ARCO Chemical Company.

³Available from Air Products and Chemicals, Inc.

The foam reactivity was acceptable, and the resulting foam possessed excellent physical properties.

It will be evident from the foregoing that various modifications can be made to this invention. Such, however, are considered as being within the scope of the invention.

Claims

1. A dispersant suitable for enhancing the stability of polymer polyols said dispersant being a polyol-polyacrylate formed by
 - (a) (i) polymerizing from 5 to 90 weight percent of at least one acrylate monomer selected from C₁-C₂₀ alkyl esters of acrylic and methacrylic acids in from 95 to 10 weight percent of polyoxyalkylene polyether polyol to form a single phase homogeneous liquid intermediate reaction product containing acrylate polymer or (ii) blending from 5 to 90 weight percent of at least one acrylate polymer selected from homopolymers and copolymers of C₁-C₂₀ alkyl esters of acrylic and methacrylic acids with from 95 to 10 weight percent of a polyoxyalkylene polyether polyol to form a single phase homogeneous liquid intermediate blend;
 - (b) optionally adding further polyoxyalkylene polyether polyol to said intermediate reaction product or blend just prior to step (c), and thereafter
 - (c) transesterifying from 1 to 30 mole percent of the total ester groups of the acrylate polymer of the product (i) or blend with the hydroxyl groups of the polyoxyalkylene polyether polyol.
2. A dispersant as claimed in claim 1 in which in step (b) the same polyoxyalkylene polyether polyol is added as is employed in step (a).
3. A dispersant as claimed in claim 1 or claim 2 in which in step (b) a polyoxyalkylene polyether polyol is added which is different from the polyoxyalkylene polyether polyol employed in step (a).
4. A dispersant as claimed in any one of claims 1 to 3 in which in step (a) from 20 to 50 weight percent of the at least one acrylate monomer is polymerised in from 80 to 50 weight percent of the polyol.



The polyurethane formation catalysts are typically tin catalysts or tertiary amine compounds. Other conventional additives such as silicone surfactants, fire retardant additives (melamine, for example), etc. may also be present. For more information in preparing polyurethanes, particularly flexible polyurethanes, see U.S. Pat. Nos. 4,338,408, 4,342,687, and 4,381,353, incorporated herein by reference. The foams made using the polymer polyols described herein have excellent physical properties. Flexible carpet underlay foam and molded automobile foam may be prepared using the polymer polyols and techniques described herein.

A typical slab polyurethane foam is prepared by first charging polymer polyol, water, catalyst, and silicone surfactant into a vessel while stirring vigorously. Next, the polyisocyanate is added to the vessel with stirring, and the resulting mixture is immediately poured into a cardboard cakebox; and the polyurethane foam allowed to rise and cure at room temperature.

Using substantially the procedure described above, a slab polyurethane foam suitable for use as carpet underlayment was prepared from the following amounts of ingredients.

Ingredient	Amount (parts by wt.)
Polymer Polyol of Example 22	100
Water	2.2
L-6202 silicon surfactant ¹	0.8
Amine ²	0.3
T-10 Organo Tin Catalyst (50% Active) ³	0.4
Toluene Diisocyanate	29.6

¹Available from Union Carbide Corporation.

²Prepared by blending 2 parts B11 and 1 part 33LV, both available from Air Products and Chemicals, Inc., and 3 parts Thanol® F3020, available from ARCO Chemical Company.

³Available from Air Products and Chemicals, Inc.

The foam reactivity was acceptable, and the resulting foam possessed excellent physical properties.

It will be evident from the foregoing that various modifications can be made to this invention. Such, however, are considered as being within the scope of the invention.

Claims

1. A dispersant suitable for enhancing the stability of polymer polyols said dispersant being a polyol-polyacrylate formed by
 - (a) (i) polymerizing from 5 to 90 weight percent of at least one acrylate monomer selected from C₁-C₂₀ alkyl esters of acrylic and methacrylic acids in from 95 to 10 weight percent of polyoxyalkylene polyether polyol to form a single phase homogeneous liquid intermediate reaction product containing acrylate polymer or (ii) blending from 5 to 90 weight percent of at least one acrylate polymer selected from homopolymers and copolymers of C₁-C₂₀ alkyl esters of acrylic and methacrylic acids with from 95 to 10 weight percent of a polyoxyalkylene polyether polyol to form a single phase homogeneous liquid intermediate blend;
 - (b) optionally adding further polyoxyalkylene polyether polyol to said intermediate reaction product or blend just prior to step (c), and thereafter
 - (c) transesterifying from 1 to 30 mole percent of the total ester groups of the acrylate polymer of the product (i) or blend with the hydroxyl groups of the polyoxyalkylene polyether polyol.
2. A dispersant as claimed in claim 1 in which in step (b) the same polyoxyalkylene polyether polyol is added as is employed in step (a).
3. A dispersant as claimed in claim 1 or claim 2 in which in step (b) a polyoxyalkylene polyether polyol is added which is different from the polyoxyalkylene polyether polyol employed in step (a).
4. A dispersant as claimed in any one of claims 1 to 3 in which in step (a) from 20 to 50 weight percent of the at least one acrylate monomer is polymerised in from 80 to 50 weight percent of the polyol.



5. A dispersant as claimed in any one of claims 1 to 3 in which in step (a) from 20 to 50 weight percent of the at least one acrylate polymer is blended in from 80 to 50 weight percent of the polyol.
6. A stable polymer polyol composition comprising a continuous phase, a disperse phase within the continuous phase, and a dispersant for enhancing the stability of the polymer polyol, wherein
 5 the disperse phase consists essentially of polyoxyalkylene polyether polyol;
 the continuous phase consists essentially of polyoxyalkylene polyether polyol; and
 the dispersant is a polyol polyacrylate as claimed in any one of claims 1 to 5, said dispersant being
 10 employed in an amount in the range of 0.1 to 10 percent by weight based on the total weight of
 continuous phase, disperse phase and dispersant.
7. A polymer polyol composition as claimed in claim 6 in which said dispersant is employed in an amount
 15 within the range of from 0.3 to 5 weight percent based on the total weight of continuous phase,
 disperse phase and dispersant.
8. A polymer polyol composition as claimed in claim 6 or claim 7 in which the polyoxyalkylene polyether
 polyol of the continuous phase and the polyoxyalkylene polyether polyol used in step (a) of the
 formation of the dispersant have the same composition.
9. The polymer polyol composition as claimed in claim 6 or claim 7 in which the polyoxyalkylene
 20 polyether polyol of the continuous phase and the polyoxyalkylene polyether polyol used in step (a) of
 the formation of the dispersant have different compositions.
10. A polymer polyol composition as claimed in any one of claims 6 to 9 in which said disperse phase is
 25 selected from (1) polystyrene particles, (2) styrene/acrylonitrile copolymer particles, (3) styrene/N-
 phenylmaleimide copolymer particles, and (4) styrene/N-phenylmaleimide/acrylonitrile copolymer par-
 ticles.
11. A polymer polyol composition as claimed in any one of claims 6 to 10 in which said continuous phase
 30 is a polyoxyalkylene polyether polyol having a molecular weight within the range of from 500 to 15,000.
12. A polymer polyol composition as claimed in any one of claims 6 to 10 in which said continuous phase
 is a polyoxyalkylene polyether polyol having a molecular weight within the range of from 2,000 to
 10,000.
13. A polymer polyol composition as claimed in any one of claims 6 to 12 in which the weight ratio of the
 35 disperse phase (a) to the continuous phase (b) is within the range of from 1:19 to 1:1.
14. A method for producing a stable polymer polyol as claimed in any one of claims 6 to 13 which
 40 comprises polymerizing an ethylenically unsaturated monomer or mixture of monomers to form the
 vinyl polymer particles in a blend of the continuous phase and the polyol polyacrylate dispersant.
15. A method of stabilizing a polymer polyol comprising vinyl polymer particles dispersed in a continuous
 45 polyether polyol phase against phase separation, the method comprising incorporating into the polymer
 polyol composition a polyol polyacrylate dispersant as claimed in any one of claims 1 to 5.
16. A polyurethane product made by a process comprising reacting a polymer polyol of any of claims 6 to
 13 or made by the method of claim 14 or claim 15 with an organic polyisocyanate in the presence of a
 polyurethane catalyst.

Patentansprüche

1. Dispergiermittel, das sich zur Verbesserung der Stabilität von Polymerpolyolen eignet und ein Polyol-
 Polyacrylat ist, das gebildet wird durch
 55 a) (i) Polymerisation von 5 bis 90 Gew.% mindestens eines aus C₁-C₂₀-Alkylestern von Acryl- und
 Methacrylsäuren ausgewählten Acrylatmonomeren in 95 bis 10 Gew.% Polyoxyalkylenpolyetherpoly-
 ol, um ein aus einer einphasigen homogenen Flüssigkeit bestehendes Zwischenprodukt zu bilden,
 das Acrylatpolymer enthält, oder durch (ii) Vermischen von 5 bis 90 Gew.% mindestens eines aus



- Homopolymeren und Copolymeren von C₁-C₂₀-Alkylestern von Acryl- und Methacrylsäuren ausgewählten Acrylatpolymeren mit 95 bis 10 Gew.% eines Polyoxyalkylenpolyetherpolyols, um eine aus einer einphasigen, homogenen Flüssigkeit bestehende Zwischenmischung herzustellen, wobei man:
- b) diesem Zwischenprodukt bzw. der Zwischenmischung unmittelbar vor Schritt c) wahlweise weiteres Polyoxyalkylenpolyetherpolyol zusetzt und danach
- c) 1 bis 30 Mol% der Gesamtestergruppen des Acrylatpolymeren des Produkts (i) oder der Mischung mit den Hydroxylgruppen des Polyoxyalkylenpolyetherpolyols umestert.
2. Dispergiermittel nach Anspruch 1, bei dem in Schritt b) das gleiche Polyoxyalkylenpolyetherpolyol wie in Schritt a) zugesetzt wird.
 3. Dispergiermittel nach Anspruch 1 oder 2, bei dem in Schritt b) ein anderes Polyoxyalkylenpolyetherpolyol als in Schritt a) zugesetzt wird.
 4. Dispergiermittel nach einem der Ansprüche 1 bis 3, bei dem in Schritt a) 20 bis 50 Gew.% mindestens eines Acrylatmonomeren in 80 bis 50 Gew.% des Polyols polymerisiert werden.
 5. Dispergiermittel nach einem der Ansprüche 1 bis 3, bei dem in Schritt a) 20 bis 50 Gew.% mindestens eines Acrylatpolymeren in 80 bis 50 Gew.% des Polyols vermischt werden.
 6. Stabile Polymerpolyolzusammensetzung, die eine zusammenhängende Phase, eine disperse Phase innerhalb der zusammenhängenden Phase sowie ein Dispergiermittel zur Verbesserung der Stabilität des Polymerpolyols umfaßt, in der die disperse Phase im wesentlichen aus Polyetherpolyol aus Vinylpolymerteilchen besteht; die zusammenhängende Phase im wesentlichen aus Polyoxyalkylenpolyetherpolyol besteht und das Dispergiermittel ein Polyolacrylat nach einem der Ansprüche 1 bis 5 ist, das in einer Menge von 0,1 bis 10 Gew.% bezogen auf das Gesamtgewicht der zusammenhängenden Phase, der dispersen Phase und des Dispergiermittels verwendet wird.
 7. Polymerpolyolzusammensetzung nach Anspruch 6, in der das Dispergiermittel in einer Menge im Bereich von 0,3 bis 5 Gew.% bezogen auf das Gesamtgewicht der zusammenhängenden Phase, der dispersen Phase und des Dispergiermittels verwendet wird.
 8. Polymerpolyolzusammensetzung nach Anspruch 6 oder 7, in der das Polyoxyalkylenpolyetherpolyol der zusammenhängenden Phase und das in Schritt a) der Erzeugung des Dispergiermittels verwendete Polyoxyalkylenpolyetherpolyol die gleiche Zusammensetzung aufweisen.
 9. Polymerpolyolzusammensetzung nach Anspruch 6 oder 7, in der das Polyoxyalkylenpolyetherpolyol der zusammenhängenden Phase und das in Schritt a) der Erzeugung des Dispergiermittels verwendete Polyoxyalkylenpolyetherpolyol verschiedene Zusammensetzungen aufweisen.
 10. Polymerpolyolzusammensetzung nach einem der Ansprüche 6 bis 9, in der die disperse Phase aus (1) Polystyrolteilchen, (2) Styrol/Acrylnitril-Copolymerteilchen, (3) Styrol/N-Phenylmaleinimid-Copolymerteilchen und (4) Styrol/N-Phenylmaleinimid/Acrylnitril-Copolymerteilchen ausgewählt ist.
 11. Polymerpolyolzusammensetzung nach einem der Ansprüche 6 bis 10, in der die zusammenhängende Phase ein Polyoxyalkylenpolyetherpolyol mit einem Molekulargewicht im Bereich von 500 bis 5.000 ist.
 12. Polymerpolyolzusammensetzung nach einem der Ansprüche 6 bis 10, in der die zusammenhängende Phase ein Polyoxyalkylenpolyetherpolyol mit einem Molekulargewicht im Bereich von 2.000 bis 10.000 ist.
 13. Polymerpolyolzusammensetzung nach einem der Ansprüche 6 bis 12, in der das Gewichtsverhältnis der dispersen Phase (a) zur zusammenhängenden Phase (b) im Bereich von 1 : 19 bis 1 : 1 liegt.
 14. Verfahren zur Herstellung eines stabilen Polymerpolyols nach einem der Ansprüche 6 bis 13, bei dem ein ethylenisch ungesättigtes Monomer oder eine Mischung von Monomeren polymerisiert wird, um die Vinylpolymerteilchen in einer Mischung aus der zusammenhängenden Phase und dem Polyolpolyacry-



lat-Dispergiermittel zu erzeugen.

15. Verfahren zur Stabilisierung eines Polymerpolyols, das in einer zusammenhängenden Polyetherpolyolphase dispergierte Vinylpolymerteilchen enthält, bei dem man in die Polymerpolyolzusammensetzung ein Polyolpolyacrylat-Dispergiermittel nach einem der Ansprüche 1 bis 5 inkorporiert.
16. Polyurethanprodukt, das durch ein Verfahren, bei dem man ein Polymerpolyol nach einem der Ansprüche 6 bis 13 zur Umsetzung bringt, oder durch das Verfahren nach Anspruch 14 oder 15 mit einem organischen Polyisocyanat in Gegenwart eines Polyurethankatalysators hergestellt wird.

Revendications

1. Dispersant convenable pour augmenter la stabilité de polymère polyols, ce dispersant étant un polyol-polyacrylate formé par
 - (a) (i) la polymérisation de 5 à 90% en poids d'au moins un monomère acrylique choisi parmi des esters alkyliques en C_{1-20} d'acide acrylique et d'acide méthacrylique, dans 95 à 10% en poids de polyoxyalkylène polyéther polyol, pour former un produit réactionnel intermédiaire liquide homogène à phase unique contenant un polymère acrylique, ou (ii) le mélange de 5 à 90% en poids d'au moins un polymère acrylique choisi parmi les homopolymères et les copolymères d'esters alkyliques en C_{1-20} d'acide acrylique et d'acide méthacrylique, avec 95 à 10% en poids d'un polyoxyalkylène polyéther polyol pour former un mélange intermédiaire liquide homogène à phase unique;
 - (b) l'addition éventuelle d'une quantité supplémentaire de polyoxyalkylène polyéther polyol à ce produit réactionnel ou à ce mélange intermédiaire juste avant l'étape (c), et ensuite
 - (c) la transestérification de 1 à 30% en moles du total des groupes ester du polymère acrylique du produit (i) ou du mélange (ii) avec les groupes hydroxy du polyoxyalkylène polyéther polyol.
2. Dispersant suivant la revendication 1, dans lequel, dans l'étape (b), il est utilisé le même polyoxyalkylène polyéther polyol que dans l'étape (a).
3. Dispersant suivant les revendications 1 ou 2, dans lequel, dans l'étape (b), il est ajouté un polyoxyalkylène polyéther polyol qui est différent du polyoxyalkylène polyéther polyol employé dans l'étape (a).
4. Dispersant suivant l'une quelconque des revendications 1 à 3, dans lequel, dans l'étape (a), 20 à 50% en poids du monomère acrylique au moins présent sont polymérisés avec de 80 à 50% en poids du polyol.
5. Dispersant suivant l'une quelconque des revendications 1 à 3, dans lequel, dans l'étape (a), 20 à 50% en poids du monomère acrylique au moins présent sont mélangés avec de 80 à 50% en poids du polyol.
6. Composition de polymère polyol stable comprenant une phase continue, une phase dispersée à l'intérieur de la phase continue et un dispersant pour augmenter la stabilité du polymère polyol, dans laquelle :
 - la phase dispersée consiste essentiellement en particules de polymère vinylique;
 - la phase continue consiste essentiellement en polyoxyalkylène polyéther polyol; et
 - le dispersant est un polyol polyacrylate suivant l'une quelconque des revendications 1 à 5, ce dispersant étant employé en une quantité comprise dans la gamme de 0,1 à 10% en poids par rapport au poids total de la phase continue, de la phase dispersée et du dispersant.
7. Composition de polymère polyol suivant la revendication 6, dans laquelle ce dispersant est employé en une quantité comprise dans la gamme de 0,3 à 5% en poids par rapport au poids total de la phase continue, de la phase dispersée et du dispersant.
8. Composition de polymère polyol suivant les revendications 6 ou 7, dans laquelle le polyoxyalkylène polyéther polyol de la phase continue et le polyoxyalkylène polyéther polyol utilisé dans l'étape (a) de la formation du dispersant, ont la même composition.



9. Composition de polymère polyol suivant les revendications 6 ou 7, dans laquelle le polyoxyalkylène polyéther polyol de la phase continue et le polyoxyalkylène polyéther polyol utilisé dans l'étape (a) de la formation du dispersant, ont des compositions différentes.
- 5 10. Composition de polymère polyol suivant l'une quelconque des revendications 6 à 9, dans laquelle cette phase dispersée est choisie parmi (1) des particules de polystyrène, (2) des particules de copolymère styrène/acrylonitrile, (3) des particules de copolymère styrène/N-phénylmaléimide et (4) des particules de copolymère de styrène/N-phénylmaléimide/acrylonitrile.
- 10 11. Composition de polymère polyol suivant l'une quelconque des revendications 6 à 10, dans laquelle cette phase continue est un polyoxyalkylène polyéther polyol ayant un poids moléculaire dans la gamme de 500 à 15.000.
- 15 12. Composition de polymère polyol suivant l'une quelconque des revendications 6 à 10, dans laquelle cette phase continue est un polyoxyalkylène polyéther polyol ayant un poids moléculaire dans la gamme de 2.000 à 10.000.
- 20 13. Composition de polymère polyol suivant l'une quelconque des revendications 6 à 12, dans laquelle le rapport en poids de la phase dispersée (a) à la phase continue (b) est compris dans la gamme de 1:19 à 1:1.
- 25 14. Procédé pour la production d'un polymère polyol stable suivant l'une quelconque des revendications 6 à 13, qui comprend la polymérisation d'un monomère ou d'un mélange de monomères éthyléniquement insaturés pour former les particules de polymère vinylique dans un mélange de la phase continue et du dispersant de type polyol polyacrylate.
- 30 15. Procédé pour stabiliser vis-à-vis d'une séparation de phases, un polymère polyol comprenant des particules de polymère vinylique dispersées dans une phase continue de polyéther polyol, comprenant l'incorporation dans la composition de polymère polyol d'un dispersant de type polyol polyacrylate suivant l'une quelconque des revendications 1 à 5.
- 35 16. Polyuréthane produit par un procédé comprenant la réaction d'un polymère polyol suivant l'une quelconque des revendications 6 à 13, ou préparé suivant le procédé des revendications 14 ou 15, avec un polyisocyanate organique en présence d'un catalyseur de polyuréthane.