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(54) POLYMER/POLYOL COMPOSITIONS AND PROCESS FOR
 PRODUCTION THEREOF/

(71) We, UNION CARBIDE CORPORATION, a Corporation organised and existing under the laws of the State of New York, United States of America, of 270 Park Avenue, New York, State of New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to liquid polymer/polyol compositions and their preparation, and to the use of these compositions in the production of polyurethanes.

Polymer/polyol compositions suitable for use in producing polyurethane foams, elastomers and other similar material are known materials. These compositions can be produced by polymerizing one or more olefinically unsaturated monomer dissolved or dispersed in a polyol in the presence of a free radical catalyst. These polymer/polyol compositions have the valuable property of imparting to, for example, polyurethane foams produced therefrom higher load-bearing properties than are imparted by unmodified polyols.

The polymer/polyol compositions that found initial commercial acceptance were primarily compositions produced from polyols and acrylonitrile and, to some extent, acrylonitrile-methyl-methacrylate mixtures. These compositions were at least primarily used commercially in producing foams under conditions such that the heat generated during foaming is readily dissipated (e.g.—the foams are of a relatively thin cross-section) or under conditions such that relatively little heat is generated during foaming.

More recently, polymer/polyol compositions produced from polyols and acrylonitrile or acrylonitrile-styrene mixtures have been used commercially. However, the severe discolora-

tion (scorch) of the resulting foams has presented some problems, particularly when the polymer composition contains acrylonitrile contents that comprise more than 50 per cent of the polymer.

British Patent Specification No. 1,412,797 provides an improved process for forming polymer/polyols which includes, in general, maintaining a low monomer concentration throughout the reaction mixture during the process. The polymer/polyols produced can be converted to low density, water-blown polyurethane foams having reduced scorch.

Still further, British Patent Specification No. 1,516,385 discloses additional and substantial improvements in forming polymer/polyols. This allows the optimization of the polymer content and the usable monomer ratios for a given polyol.

Reference can also be made to the disclosures of United States Patents No. 3,823,201 and 3,418,354.

Despite these improvements, and while polymer/polyol compositions can be produced from widely varying polymer contents and monomer mixtures, practical quality control restrictions such as stability and filterability have resulted in commercial limitations insofar as the usable maximum styrene content, the maximum polymer content and the minimum molecular weight for the polyol are concerned.

Some patents in the polymer/polyol field disclose the interchangeable use of azo and peroxide catalysts. Thus, for example, among several catalysts set forth, British Patent Specification No. 1,412,797 lists the half-life for *t*-butylperoxypivalate and *t*-butylperoxybutyrate. No examples using these catalysts are, however, included. Indeed, the only specific example of a process for forming a polymer/polyol which utilizes a peroxyester, peroxide-type catalyst of which applicants are aware is shown in

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British Patent Specification No. 1,321,679 which discloses in the specification a continuous process for forming an 80/20 acrylonitrile/styrene polymer/polyol with a polyether polyol having a molecular weight of 4,000 and a catalyst of azodiisobutyronitrile or tertiary butyl peroctoate. However, in all the working Examples, including one corresponding to this process, an azo catalyst was used.

The use of azo-type catalysts presents processing difficulties due to the solid nature of the catalysts. Also, a toxic, by-product residue is formed. And, as has been described herein, there are limitations which restrict in a practical, commercial sense the polymer/polyol compositions which can be provided.

It has been theorized that the stability of polymer/polyols requires the presence of a minor amount of a graft copolymer formed from the polymer and polyol. And, a number of literature references have observed large differences in grafting efficiency between the use of peroxides such as benzoyl peroxide and azobis-isobutyronitrile in certain monomer-polymer systems while others have noted no marked difference.

In the *Journal of Cellular Plastics*, March 1966, entitled "Polymer/Polyols; A New Class of Polyurethane Intermediates by Kuryla *et al*", there is reported a series of precipitation experiments run to determine any marked differences in the polymer/polyols produced by either benzoyl peroxide or azobis-isobutyronitrile when used as the initiators in the *in situ* polymerization of acrylonitrile in a propylene oxide triol having a theoretical number average molecular weight of about 3000. The data indicated no significant differences between the polymers isolated and no marked "initiator effect" was observed.

Indeed, it was reported that the azo catalyzed polymer/polyols were found to be much more reactive, and processed better in the making of urethane flexible foams, than those polymer/polyols which were made using a peroxide catalyst. It was observed that apparently residual peroxides remaining in the refined polymer/polyol "poison" the foaming catalysts.

Accordingly, despite the handling difficulties associated with using azo-type catalysts as has been described herein, virtually all of the commercial polymer/polyol compositions have been produced using this type of catalyst. There has been no recognition in the polymer/polyol field that any superior results could be achieved using a peroxide-type catalyst.

Polymer/polyols have been commercially accepted for various applications; however, there has been little or no acceptance in other applications such as, for example, slab stock foam where virtually scorch-free products are demanded, which necessitate the use of acrylonitrile/styrene polymer/polyols with low acrylonitrile/styrene ration, or elastomers

where relatively low molecular weight polyols are typically utilized to provide the requisite product stiffness. Still other applications could desirably utilize polyurethane foams with even higher load-bearing capacities than can be currently provided.

In accordance with one aspect of the present invention there is provided a liquid polymer/polyol composition consisting essentially of: (1) from 40 to 90 weight per cent of a polyoxypropylene polyol having a molecular weight of at least 5000 and (2) from 60 to 10 weight per cent of an acrylonitrile homopolymer or a copolymer of acrylonitrile and styrene wherein the acrylonitrile/styrene weight ration is from 100/0 to 20/80, wherein the homopolymer or copolymer is in the form of particles which are stably dispersed in the polyol, and the composition contains sufficient polymer particles with diameters of less than 30 microns to provide at least 20% filterability (as hereinafter defined), and wherein the composition is provided by the polymerization of acrylonitrile and, when present, styrene in the polyol; the polyol molecular weight, the weight per cent of the monomer or monomers (based on the total weight of monomer plus polyol) and the acrylonitrile/styrene ratio in the monomer or monomers being such as to fall within the limits defined by the areas A to N of Figures 1 to 14 of the accompanying drawings, the said composition having been produced in the presence of a *t*-alkyl peroxyester free radical catalyst.

In accordance with another aspect of the present invention there is provided a liquid polymer/polyol composition consisting essentially of: (1) from 40 to 90 weight per cent of a polyoxypropylene polyol having a molecular weight of at least 5000 and (2) from 60 to 10 weight per cent of an acrylonitrile homopolymer or a copolymer of acrylonitrile and styrene wherein the acrylonitrile/styrene weight ratio is from 100/0 to 20/80, wherein the homopolymer or copolymer is in the form of particles which are stably dispersed in the polyol, and the composition contains sufficient polymer particles with diameters of less than 30 microns to provide at least 20% filterability (as hereinafter defined), and wherein the composition is produced by the polymerization of acrylonitrile and, when present, styrene in the polyol; the polyol molecular weight, the weight per cent of the monomer or monomers (based on the total weight of monomer plus polyol) and the acrylonitrile/styrene ratio in the monomer or monomers being such as to fall within the limits defined by the areas A to N of Figures 1 to 14 of the accompanying drawings, the said polyol being either a propylene oxide or a propylene oxide and ethylene oxide adduct of a polyhydroxy alkane.

The present invention also provides a polyurethane when produced from a liquid

polymer/polyol composition of the present invention.

Preferably the polymerization is conducted in a continuous operation whilst maintaining a sufficiently low monomer to polyol ratio throughout the reaction mixture during the polymerization such as to produce a polymer consisting substantially wholly of polymer particles having diameters less than 1 micron.

Preferably the polyol in composition B has a molecular weight in the range of from 5000 to 8000. Also it is preferred that the acrylonitrile/styrene ratio of the compositions is less than 50/50, e.g. from 30/70 to 50/50.

In the accompanying drawings:—

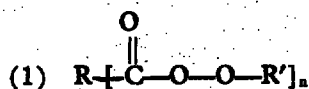
Figure 1 is a graph of the per cent monomer in the feed versus the acrylonitrile/styrene ratio of the monomer in the feed for polymer/polyol compositions formed with a polyol (Polyol I) having a theoretical number average molecular weight of 5,000;

Figures 2 to 9 are graphs of the monomer content versus the molecular weight of the polyol for acrylonitrile/styrene monomer ratios ranging from all acrylonitrile to 30/70 and illustrating the preferred polymer/polyol compositions which can be achieved using the present invention which cannot be formed using an azo catalyst (at least when the continuous process described herein is employed); and

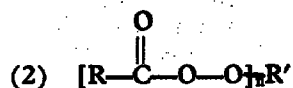
Figures 10 to 14 are graphs of the polyol molecular weight versus the acrylonitrile/styrene monomer ratios for monomer contents ranging from 10 to 50 weight per cent and showing the preferred polymer/polyol compositions achieved using the present invention that cannot be formed with an azo catalyst (at least when the continuous process described herein is employed).

In the accompanying drawings, reference to "acceptable" and "unacceptable" products are to be interpreted in terms of whether or not the products so formed meet a preferred characteristic of the invention, namely 100% filterability through a 700 mesh screen; and not whether or not they fall within the scope of the accompanying drawing.

In general, the present invention is predicated on the discovery that polymer/polyol compositions exhibiting outstanding properties for various commercial applications can be made by utilizing, in the formation of the polymer/polyols, a specific type of peroxide catalyst, namely *t*-alkyl peroxyester catalysts. More specifically, the usable catalysts can be characterized by the following formulae:



and



where R' is an alkyl group usually containing from 4 to 20 carbon atoms, preferably 4 to 8, and the carbon atom or atoms adjacent the oxygen bond are tertiary, *n* is 1 or 2, and R is an alkyl group usually containing from 3 to 12 carbon atoms or an aromatic group; with the proviso that when *n* is 2 R' in formula (2) is an alkylene group. The preferred catalysts are *t*-butyl peroxy-2-ethylhexanoate, *t*-butylperpivalate, 2—5 dimethyl-hexane-2, 5-di-per-2-ethyl hexoate, *t*-butyl-perneodecanoate, *t*-butylperbenzoate, *t*-butylpercrotonate, *t*-butyl isobutyrate or di-*t*-butylphthalate.

The aliphatic diesteres are described in United States Patent Specification No. 3,264,274 may also be employed as can the aryl peresters as described in United States Patent Specification No. 2,567,615. By the utilization of this specific type of catalyst, polymer/polyols can be produced on a commercial basis with outstanding properties such as filterability in processing yet which can relax the specific parameters that have been previously used so that either the polymer or the styrene content can be increased. Also, polymer/polyols on a commercial scale with outstanding properties can be produced with polyols having a molecular weight lower than have been heretofore used.

The compositions of the present invention are distinct from prior art compositions in that the present compositions are produced using a *t*-alkyl peroxide catalyst and/or, in a specific embodiment, are produced from polyols consisting of the propylene oxide or propylene oxide and ethylene oxide adducts of polyhydroxy-alkanes.

In general, the ratio of acrylonitrile to styrene can suitably range from 100/0 to 20/80, and the monomer content in the feed can comprise up to 60 per cent by weight of the polymer/polyol. The ratio of acrylonitrile to styrene monomer in the feed that may be employed to form polymer/polyol compositions according to the present invention will depend upon the specific polyol being used and the proportion of the monomer in the feed. The greatest latitude is achieved with the highest molecular weight polyols; and the breadth of the usable acrylonitrile/styrene ratio for a given polyol will, in turn, depend upon the level of the polymer content. Generally, as the polymer content increases, the usable acrylonitrile/styrene range will become narrower. The maximum polymer content (or monomer content in the feed) for any given polyol and acrylonitrile/styrene ratio is that polymer content (or monomer content) above which the resulting product will not pass the requisite filtration test as will be described in detail hereinafter. The actual polymer content and the acrylonitrile/styrene ratio that are used will, of course, be dependent to a large extent on the requirements needed for the intended end

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use application. As an example, when the polymer/polyol compositions are to be used for forming scorch-free, slab stock foam, it is preferred that the styrene monomer content be at least equal to the acrylonitrile content and, more preferably the acrylonitrile/styrene ratio should be between 45/55 and 30/70.

While the present invention is directed to the use of an acrylonitrile/styrene monomer system, it should be appreciated that minor amounts of an additional monomer or monomers may be employed. However, in this event, the relative amount of acrylonitrile should remain within the limits previously set forth herein.

By way of illustration, the following interrelationships apply to a polyol having a theoretical number average molecular weight of 5,000.

For a glycerol-started triol consisting of 86 weight per cent oxypropylene groups and 14 weight per cent oxyethylene groups and having a molecular weight of about 5,000, the usable acrylonitrile to styrene weight ratio may vary between about 100:0 and 30:70 when the polymer content is no higher than about 18 weight per cent with a preferred monomer range of 100:0 to 40:60. With no more than 25 weight per cent polymer, the usable acrylonitrile to styrene range with such a triol is between 100:0 and 36:64 with a preferred range of 90:10 to 45:55. Employing no more than 35 weight per cent polymer, the usable acrylonitrile to styrene range is between 88:12 and 47:53. With no more than 45 weight per cent polymer, the usable acrylonitrile to styrene range is between 87:13 and 71:29. At an acrylonitrile to styrene weight ratio of 80:20, a polymer/polyol can be made as high as 50 per cent polymer or above with this triol.

With respect to the polyol constituent, this comprises poly(oxypropylene) glycols, triols and higher functionality polyols. These polyols include poly(oxypropylene-oxyethylene)-polyols; however, desirably, the oxyethylene content should comprise less than 50 per cent of the total. The ethylene oxide can be incorporated in any fashion along the polymer chain. Stated another way, the ethylene oxide can be either incorporated in internal blocks, as terminal blocks, or may be randomly distributed along the polymer chain. As is well known in the art, the preferred polyols herein do contain varying amounts of unsaturation. The extent of unsaturation does not affect in any adverse way the formation of the polymer/polyols in accordance with the present invention.

For the purposes of this invention, the polyol should have a number average molecular weight of 5,000 or greater, the number average being used herein being the theoretical value. The true number average molecular weight may be somewhat less, depending upon the extent

to which the true molecular functionality is below the starting or theoretical functionality. It should be appreciated that the stability of the polymer/polyol compositions decreases with decreasing molecular weight of the polyol employed. However, in accordance with the present invention, even when a polyol with a molecular weight of 1,000 has been used, the shelf life in terms of settling tendencies may be as much as at least three months.

The polyols employed can have hydroxyl numbers which vary over a wide range. In general, the hydroxyl numbers of the polyols employed in the invention can range from 20 and lower, to 150 and higher. The hydroxyl number is defined as the number of milligrams of potassium hydroxide required for the complete hydrolysis of the fully acetylated derivative prepared from 1 gram of polyol. The hydroxyl number can also be defined by the equation:

$$\text{OH} = \frac{56.1 \times 1000 \times f}{\text{m.w.}}$$

where

OH = hydroxyl number of the polyol

f = functionality, that is, average number of hydroxyl groups per molecule of polyol.

m.w. = molecular weight of the polyol.

The exact polyol employed depends upon the end-use of the polyurethane product to be produced. The molecular weight or the hydroxyl number is selected properly to result in flexible or semi-flexible foams or elastomers when the polymer/polyol produced from the polyol is converted to a polyurethane. The polyols preferably possess a hydroxyl number of from 50 to 150 for semi-flexible foams and from 20 to 70 for flexible foams. These limits are not intended to be restrictive, but are merely illustrative of the large number of possible combinations of the above polyol co-reactants.

While not preferred, any other type of known polyols may also be used. Amongst the polyols which can be employed are one or more polyols from the following classes, known to those skilled in the polyurethane art:

- (a) Alkylene oxide adducts of non-reducing sugars and sugar derivatives, at least a portion of the alkylene oxide being propylene oxide;
- (b) Alkylene oxide adducts of phosphorus and polyphosphorus acids, at least a portion of the alkylene oxide being propylene oxide;
- (c) Alkylene oxide adducts thereof of polyphenols, at least a portion of the alkylene oxide being propylene oxide;
- (d) The polyols from natural oils such as castor oil, at least a portion of the polyol being derived from propylene oxide;

(e) Alkylene oxide adducts of polyhydroxyalkanes other than those already described herein, at least a portion of the alkylene oxide being propylene oxide.

5 Examples of suitable alkylene oxide adducts of the polyhydroxyalkanes include, amongst others, the alkylene oxide adducts of 1,3-dihydroxypropane, 1,3-dihydroxybutane, 1,4-dihydroxybutane, 1,4-, 1,5- and 1,6-dihydroxyhexane, 1,2-, 1,3-, 1,4-, 1,6-, and 1,8-dihydroxyoctane, 1,10-dihydroxydecane, glycerol, 10 1,2,4-trihydroxybutane, 1,2,6-trihydroxyhexane, 1,1,1-trimethylolethane, 1,1,1-trimethylolpropane, pentaerythritol, caprolactone, polycaprolactone, xylitol, arabitol, sorbitol and mannitol.

15 A further class of polyol which can be employed is the class of alkylene oxide adducts of the non-reducing sugars, wherein the alkylene oxides may contain from 2 to 4 carbon atoms, in addition to propylene oxide. Amongst the non-reducing sugars and sugar derivatives contemplated are sucrose, alkyl glycosides such as methyl glucoside and ethyl glucoside, glycol glycosides such as ethylene glycol glucoside, propylene glycol glucoside, glycerol glucoside and 1,2,6-hexanetriol glucoside, as well as the alkylene oxide adducts of the alkyl glycosides as described in United States Patent Specification No. 3,073,788.

20 A still further useful class of polyol is the class of polyphenols, and preferably the alkylene oxide adducts thereof wherein the alkylene oxides may contain from 2 to 4 carbon atoms, in addition to propylene oxide. Amongst the polyphenols which are contemplated are, for example, bisphenol A, bisphenol F, the condensation products of phenol and formaldehyde, the novolac resins; the condensation products of various phenolic compounds and acrolein; the simplest member of this class being the 1,1,3-tris(hydroxyphenyl)propanes, and the condensation products of various phenolic compounds and glyoxal, glutaraldehyde, and other dialdehydes, the simplest members of this class being the 1,1,2,2-tetrakis (hydroxyphenol) ethanes.

25 The alkylene oxide adducts of phosphorus and polyphosphorus acids are another useful class of polyol. Ethylene oxide, 1,2-epoxypropane, the epoxybutanes and 3-chloro-1,2-epoxypropane are preferred alkylene oxides. Phosphoric acid, phosphorus acid, the polyphosphoric acids such as tripolyphosphoric acid and the polymetaphosphoric acids are desirable for use in this connection.

30 It should be appreciated that blends or mixtures of various useful polyols may be used if desired. With polyols other than the preferred type, the useful monomer contents and acrylonitrile/styrene ratio may vary somewhat.

35 In accordance with the present invention, the free radical catalyst employed in the present

invention comprises a *t*-alkyl peroxyester as previously described herein. Useful catalysts must have a satisfactory half-life within the temperature ranges used in forming the polymer/polyol compositions, i.e.—the half-life should preferably be about 25 per cent or less of the residence time in the reactor at a given temperature. With half-lives which are unduly long at the given temperature, an excessive amount of catalyst would be required to obtain an acceptable reaction rate which would in turn result in large amounts of undecomposed catalyst being left in the product. This excess peroxide would lead to development of odor in the product and also be harmful during the subsequent polyurethane foaming reaction. Desirably, the catalysts used should provide a polymer/polyol with as low an acid number as possible, preferably less than about 0.5. Still further, useful catalysts should preferably be in the liquid state and not be unduly sensitive to shock.

40 Representative examples of useful catalyst species include *t*-butyl peroxy-2-ethylhexanoate, *t*-butylperpivalate, 2,5 dimethyl-hexane-2,5-di-per-2-ethyl hexoate, *t*-butylperneodecanoate, *t*-butylperbenzoate, *t*-butyl percrotonate, *t*-butyl isobutyrate and di-*t*-butylphthalate. It is particularly preferred to utilize *t*-butyl-peroxy-2-ethylhexanoate inasmuch as this species can be safely stored as a blend in a diluent at a temperature of about 65° F., for example, when stored as a 50 weight per cent blend with dioctylphthalate, as compared with the lower temperatures required for other species, (e.g.—30° F.), and results in polymer/polyol compositions having acid numbers only slightly higher than compositions formed from an azo catalyst.

45 The catalyst concentration is not critical and can be varied within wide limits. As a representative range, the concentration can vary from 0.1 to 1.0 weight per cent, based upon the total feed to the reactor. Up to a certain point, increases in the catalyst concentration result in increased monomer conversion but further increases do not substantially increase conversion. On the other hand, increasing catalyst concentration increasingly improves product stability. The catalyst concentration selected will usually be an optimum value considering all factors, including costs.

50 It should be appreciated that, while the present invention is directed to the formation of polymer/polyol compositions utilizing the described peroxyester catalysts, certain amounts of other types of free radical catalysts such as an azo catalyst may also be incorporated with the peroxyester catalyst being utilized. Of course, the amount of the peroxyester catalyst used should be sufficient to allow production of polymer/polyol compositions in accordance with the present invention.

55 The polymer/polyols of the present invention

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are produced by utilizing the process set forth in British Patent Specification No. 1,412,797. In accordance with that process, a low monomer to polyol ratio is maintained throughout the reaction mixture during the process. This is achieved by employing process conditions that provide rapid conversion of monomer to polymer. In practice, a low monomer to polyol ratio is maintained, in the case of semi-batch and continuous operation, by control of the temperature and mixing conditions and, in the case of semi-batch operation, also by slowly adding the monomers to the polyol.

The polymerization can also be carried out with an inert organic solvent present that does not dissolve the polymer. Examples thereof are toluene, benzene, acetonitrile, ethyl acetate, hexane, heptane, dicyclohexane, dioxane, acetone, N,N-dimethylformamide, and N,N-dimethylacetamide, including those known in the art as being suitable solvents for the polymerization of vinyl monomers. The only requirement in the selection of the solvent and the polyol is that they do not interfere with the monomer's polymerization reaction. When an inert organic solvent is used, it is generally removed from the reaction mixture by conventional means before the polymer/polyol is used to produce polyurethane foams.

The temperature range is not critical and may vary from 100° C. to 150° C. or perhaps greater, the preferred range being from 115° C. to 135° C. As has been noted herein, the catalyst and temperature should be selected so that the catalyst has a reasonable rate of decomposition with respect to the hold-up time in the reactor for a continuous flow reactor or the feed time for a semi-batch reactor.

The mixing conditions employed are those attained using a back mixed reactor (e.g.—a stirred flask or stirred autoclave). Reactors of this type keep the reaction mixture relatively homogeneous and so prevent localized high monomer to polyol ratios such as occur in certain tubular reactors, (e.g.—in the first stages of "Marco" (Registered Trade Mark) reactors when these reactors are operated with all the monomer added to the first stage).

The process of this invention produces polymer/polyol compositions which are characterized by relatively high polymer contents, small particle size, freedom from scrap and seeds and convertibility to useful high modulus polyurethane elastomers and foams. More particularly, with a given polyol, the present invention allows the ratio of styrene to acrylonitrile, or the polymer content, to be increased, yet still providing stable products. Also, stable polymer/polyols may be made with lower molecular weight polyols than can be accomplished by prior processes.

The polymer/polyols of the present invention comprise dispersions in which the polymer particles (the same being either individual

particles or agglomerates of individual particles) are relatively small in size and, in the preferred embodiment are all essentially less than 30 microns. Thus, in the preferred embodiment, essentially all of the product (viz.—about 99 per cent or more) will pass through the filter employed in the filtration test that will be described in conjunction with the Examples. This ensures that the polymer/polyol products can be successfully processed in all types of the relatively sophisticated machine systems now in use for large volume production of polyurethane products, including those employing impingement-type mixing which necessitate the use of filters that cannot tolerate any significant amount of relatively large particles. Less rigorous applications are satisfied when about 50 per cent of the product passes through the filter. Some applications may also find useful products in which only about 20 per cent passes through. Accordingly, the polymer/polyols of the present invention contemplate products in which at least 20 per cent pass through the filter, preferably at least 50 per cent, and most preferably essentially all.

The polymer/polyols formed pursuant to this invention may also be distinguished by the characteristic ester odor and by the substantial freedom from trace amounts of the tetramethylsuccinonitrile formed as a residue when an azo catalyst is used. By "substantial freedom" it is meant that the resulting polymer/polyol will contain less than the typical level of this toxic residue present when solely an azo catalyst is used. No residue will be present when only a peroxyester catalyst is used but trace amounts will be present when small amounts of an azo catalyst is used with the peroxyester catalysts employed in this invention.

With respect to the preferred polymer/polyol compositions within the scope of the present invention, the usable monomer contents, polyol molecular weights and acrylonitrile/styrene monomer ratios can be determined from the figures. In each figure, the preferred compositions achievable with the present invention but not by using an azo catalyst have been cross-hatched and lettered.

More particularly, the preferred polymer/polyol compositions of this invention are defined by a volume in which the three dimensions comprise monomer content, polyol molecular weight and acrylonitrile/styrene monomer ratio. The individual figures represent various cross-sections taken through this volume in each of the three dimensions.

The determination of whether a particular polymer/polyol composition is within the present invention is easily determined in those situations wherein any one of the three parameters corresponds to any one of the pre-selected parameters set forth in the figures. Thus, for example, when the polyol molecular

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weight is 5,000, the usable combinations of monomer content and acrylonitrile/styrene monomer ratio are shown by Area A of FIG. 1. As a further example, of the acrylonitrile/styrene monomer ratio is 40/60, the usable polyol molecular weights and monomer content are defined by Area H of FIG. 8.

In those situations wherein none of the three parameters correspond to any one of the pre-selected parameters set forth in the figures, the usable parameters are determined by co-ordination of any two of the figures having the closest parameters and with linear interpolation between the figures. In cases wherein an interpolation must be made, it is preferred to utilize those figures which minimize the interpolation required.

The present invention also provides a method for producing polyurethane products by reacting: (a) a polymer/polyol composition of this invention, (b) an organic polyisocyanate, and (c) a catalyst for the reaction of (a) and (b) to produce the polyurethane product, and, when a foam is being prepared, a blowing agent and a foam stabilizer. The reaction and foaming operations can be performed in any suitable manner, preferably by the one-shot technique.

The organic polyisocyanates that are useful in producing polyurethane products in accordance with this invention are organic compounds that contain at least two isocyanato groups. These compounds are well known in the art. Suitable organic polyisocyanates include the hydrocarbon diisocyanates, (e.g., the alkylene diisocyanates and the arylene diisocyanates) as well as known triisocyanates. Examples of suitable polyisocyanates are: 1,2-diisocyanatoethane, 1,3-diisocyanatopropane, 1,2-diisocyanatopropane, 1,4-diisocyanatobutane, 1,5-diisocyanatopentane, 1,6-diisocyanatohexane, bis(3-isocyanatopropyl)ether, bis(3-isocyanatopropyl)sulfide, 1,7-diisocyanatoheptane, 1,5-diisocyanato-2,2-dimethylpentane, 1,6-diisocyanato-3-methoxyhexane, 1,8-diisocyanato-octane, 1,5-diisocyanato-2,2,4-trimethylpentane, 1,9-diisocyanatononane, 1,10-diisocyanatodecane, 1,11-diisocyanatoundecane, 1,12-diisocyanatododecane bis(isocyanatohexyl)sulfide, 1,4-diisocyanatobenzene, 2,4-diisocyanatotoluene, 2,6-diisocyanato tolylene, 1,3-diisocyanato-*o*-xylene, 1,3-diisocyanato-*m*-xylene, 1,3-diisocyanato-*p*-xylene, 2,4-diisocyanato-1-chlorobenzene, 2,4-diisocyanato-1-nitrobenzene, and 2,5-diisocyanato-1-nitrobenzene and mixtures thereof.

The catalysts that are useful in producing polyurethanes in accordance with this invention include: (a) tertiary amines such as bis(dimethylaminoethyl)ether, trimethylamine, triethylamine, N-methylmorpholine, N-ethylmorpholine, N,N-dimethylbenzylamine, N,N-dimethylethanolamine, N,N,N',N'-tetramethyl-1,3-butanediamine, triethanolamine, 1,4-diaza-

bicyclo[2.2.2]octane, and pyridine oxide; (b) tertiary phosphines such as trialkylphosphines and dialkylbenzylphosphines; (c) strong bases such as alkali and alkaline earth metal hydroxides, alkoxides, and phenoxides; (d) acidic metal salts of strong acids such as ferric chloride, stannic chloride, stannous chloride, antimony trichloride and bismuth nitrate and chloride; (e) chelates of various metals such as those which can be obtained from acetylacetone, benzoylacetone, trifluoroacetylacetone, ethyl acetoacetate, salicylaldehyde, cyclopentanone-2-carboxylate, acetyl-acetoneimine, bis-acetylacetonealkylene-diimines and salicylaldehydeimine, with various metals such as Be, Mg, Zn, Cd, Pb, Ti, Zr, Sn, As, Bi, Cr, Mo, Mn, Fe, Co, Ni, or such ions as MoO_4^{++} ; UO_2^{++} ; (f) alcoholates and phenolates of various metals such as $\text{Ti}(\text{OR})_3$, $\text{Sn}(\text{OR})_2$ and $\text{Al}(\text{OR})_3$, wherein R is an alkyl or aryl group, and the reaction products of alcoholates with carboxylic acids, betadiketones, and 2-(N,N-dialkylamino)alkanols, such as the well known chelates of titanium obtained by these or equivalent procedures; (g) salts of organic acids with a variety of metals such as alkali metals, alkaline earth metals, Al, Sn, Pb, Mn, Co, Ni, and Cu, including, for example, sodium acetate, potassium laurate, calcium hexanoate, stannous acetate, stannous octoate, stannous oleate, lead octoate, and metallic driers such as manganese and cobalt naphthenate; and (h) organometallic derivatives of tetravalent tin, trivalent and pentavalent As, Sb, and Bi, and metal carbonyls or iron and cobalt.

Among the organotin compounds that deserve particular mention are dialkyltin salts of carboxylic acids, e.g. dibutyltin diacetate, dibutyltin dilaurate, dibutyltin maleate, dilauryltin diacetate, dioctyltin diacetate, dibutyltin-bis(4-methylaminobenzoate) and dibutyltin-bis(6-methylaminocaproate). Similarly a trialkyltin hydroxide, dialkyltin oxide, dialkyltin dialkoxide, or dialkyltin dichloride may be used. Examples of these compounds include trimethyltin hydroxide, tributyltin hydroxide, trioctyltin hydroxide, dibutyltin oxide, dioctyltin oxide, dilauryltin oxide, dibutyltin-bis(isopropoxide), dibutyltinbis(2-dimethylaminopentylate), dibutyltin dichloride and dioctyltin dichloride.

The tertiary amines may be used as primary catalysts for accelerating the reactive hydrogen/isocyanate reaction or as secondary catalysts in combination with one or more of the above noted metal catalysts. Metal catalysts or combinations of metal catalysts, may also be employed as the accelerating agents, without the use of amines. The catalysts are employed in small amounts, for example, from 0.001 per cent to 5 per cent, based on weight of the reaction mixture.

When the product being formed is a polyurethane foam, this may be accomplished by

15

employing a small amount of a polyurethane blowing agent, such as water, in the reaction mixture (for example, from 0.5 to 5 weight per cent of water, based upon total weight of the polymer/polyol composition), or through the use of blowing agents which are vaporized by the exotherm of the reaction, or by a combination of the two methods. Examples of polyurethane blowing agents are halogenated hydrocarbons such as trichloromonofluoromethane, dichlorodifluoromethane, dichloromonofluoromethane, dichloromethane, trichloromethane, 1,1-dichloro-1-fluoroethane, 1,1,2-trichloro - 1,2,2 - trifluoromethane, hexafluorocyclobutane and octafluorocyclobutane. Another class of blowing agents include thermally unstable compounds which liberate gases upon heating, such as N,N'-dimethyl-N,N'-dinitrosoterephthalamide. The generally preferred method of foaming for producing flexible foams is the use of water or a combination of water plus a fluorocarbon blowing agent such as trichloromonofluoromethane. The quantity of blowing agent employed will vary with factors such as the density desired in the foamed product. The anti-scorch properties of the foams produced using polymer/polyol compositions are most evident when at least some of the blowing agent is water and the water is used in an amount that results in a foam having a density less than 1.75 pounds per cubic foot. Generally, the use of water in an amount of at least 3.0 per cent by weight based on the total weight of the polymer/polyol composition results in a foam having a density of less than 1.75 pounds per cubic foot.

It is also within the scope of the invention to employ small amounts, e.g., about 0.001 per cent to 5.0 per cent by weight, based on the total reaction mixture, of a foam stabilizer such as a "hydrolyzable" polysiloxane-polyoxyalkylene block copolymer such as the block copolymers described in United States Patent Specifications Nos. 2,834,748 and 2,917,480. Another useful class of foam stabilizers are the "non-hydrolyzable" polysiloxane-polyoxyalkylene block copolymers such as the block copolymers described in United States Patent Specification No. 3,505,377; and in British Patent Specification Nos. 1,341,028 and 1,220,471. The latter class of copolymers differs from the above-mentioned polysiloxane-polyoxyalkylene block copolymers in that the polysiloxane moiety is bonded to polyoxyalkylene moiety through direct carbon-to-silicon bonds, rather than through carbon-to-oxygen-to-silicon bonds. These various polysiloxane-polyoxyalkylene block copolymers preferably contain from 5 to 50 weight per cent of polysiloxane polymer with the remainder being polyoxyalkylene polymer.

The polyurethanes produced in accordance with this invention may be advantageously employed in various applications. For example,

the present invention allows the production of polyurethane foams from polymer/polyols in which the polymer composition contains less than about 50 per cent by weight acrylonitrile. These foams may be desirably employed in the slab foam market where the cross-sections are relatively large and where a relatively large exotherm is employed. In these situations, polyurethane foams produced in accordance with this invention result in essentially white products wherein virtually no scorch can be detected. Still further, the polymer/polyols of this invention may be used to form polyurethane elastomers in which relatively low molecular weight polyols must be used to provide the requisite. Also, polymer/polyols pursuant to this invention may be employed to form polyurethane products for applications where maximum load-bearing characteristics are required.

The following Examples are illustrative, but not in limitation of, the present invention.

DEFINITIONS

As used in the Examples appearing below, the following designations, symbols, terms and abbreviations have the indicated meanings:

"Theoretical molecular weight" of a polyol denotes a molecular weight calculated using the equation set forth previously based on the functionality of the starter used to produce the polyol and the experimentally determined hydroxyl number of the polyol.

"Molecular weights" of polyols are number average molecular weights.

"Triol" or "Diol" denotes the nominal functionality of a polyol based on the functionality of the starter. Actual polyol functionalities are somewhat lower (3 to 20 per cent lower) than with nominal functionality because of the presence of some amount of lower functionality material produced by side reactions. These side reactions are more significant the higher the molecular weight of the polyol being produced.

"Polyol I"—A polyalkylene oxide triol produced from propylene and ethylene oxides and glycerine and having theoretical number average molecular weight of 5,000. The alkylene oxide units are present primarily in blocks and the primary OH content is about 75 per cent. The ethylene oxide is used to "cap" the triol. Based on its alkylene oxide content this triol contains 85 weight per cent C_2H_4O and 15 weight per cent C_3H_6O .

"A/S" or "A:S" denotes the weight ratio of acrylonitrile to styrene.

"Calc" denotes calculated.

"cps" denotes centipoises.

"gm" denotes grams.

"hr" denotes hour.

"Parts" denotes parts by weight.

"Poly A" denotes polyacrylonitrile.

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"Poly S" denotes polystyrene.

"ppm" denotes parts by weight per million parts by weight.

"wt-%" denotes per cent by weight.

5 "VAZO-64" or "VAZO" denotes 2,2'-azobis-isobutyronitrile.

"%" denotes percentage by weight unless otherwise stated.

10 "Esperox 31M" denotes tertiary-butyl per-pivalate.

"USP 245" denotes 2,5 dimethylhexane-2,5-diper 2-ethyl hexoate.

"Esperox 10" denotes tertiary-butyl perbenzoate.

15 "DTBPP" denotes di-t-butyl diperoxy-phthalate.

"ESPEROX 33M" denotes ter.-butylperneodecanoate.

FILTERABILITY

20 The preferred compositions of this invention are essentially free of polymer particles having diameters over 30 microns. A composition meets this criteria if over 99 weight per cent of the composition passes successively through a 150-mesh screen and a 700 mesh screen in the following test. A 470 gram sample of the composition being tested is diluted with 940 grams of isopropanol to reduce viscosity effects. The diluted sample is passed through a 2.4 square inch 150 mesh screen and then through a 2.4 square inch 700 mesh screen. (The screens are cleaned, dried and weighed before the test.) Then the screens are washed with isopropanol to remove any polyol, dried and weighed. The difference between the final and initial screen weights corresponds to the amount of polymer that did not pass through the screens. The 150-mesh screen has a square mesh with average mesh opening of 105 microns and it is a "Standard Tyler" 150 square mesh screen. The 700-mesh screen is made with a Dutch twill weave having average mesh openings of 30 microns and is described in Bulletin 46267-R of the Ronningen-Petter Company of Kalamazoo, Michigan.

Example 1.

50 To illustrate the relatively low acid number which can be achieved using the preferred peroxyester catalyst of the present invention, a

polymer/polyol was prepared using a semi-batch process. To a 1-liter flask provided with a stirrer, thermometer, feed inlet, reflux condenser and nitrogen atmosphere, 320 grams of polyol I was charged. This polyol was heated to 115° C. under nitrogen. Then, over a period of about 80 minutes, a mixture of 60 grams of acrylonitrile and 60 grams of styrene in 160 grams of polyol I containing 18 micromoles of tertiary-butyl peroxy 2-ethylhexanoate initiator was added. The temperature was maintained at 115° C. during the addition and during a subsequent cookout of 40 minutes duration. The reaction product was then stripped at 100° C. and 1-5 mm. mercury pressure for four hours.

The resulting polymer/polyol had a viscosity (Brookfield) of 3350 cps. at 25° C. and an acid number (mg.KOH per gm. sample) of 0.06.

Example 2.

For purposes of comparison, the semi-batch process of Example 1 was repeated to form a polymer/polyol using a "Vazo" catalyst. The resulting stripped polymer/polyol had a viscosity of 2730 cps. at 25° C. and an acid number of 0.04.

Examples 3-18.

These Examples illustrate the upper limits for forming preferred polymer/polyols with Polyol I and *t*-butyl peroxy 2-ethylhexoate.

A continuous process was used in these Examples.

A tank reactor fitted with baffles and an impeller was used. The feed components were pumped to the reactor after going through an inline mixer to assure complete mixing of the feed components before entering the reactor. The internal temperature of the reactor was controlled to within one degree Centigrade by controlled heating or cooling to the outside of the reactor. The product from the reactor flowed out of the reactor to a back pressure regulator adjusted to some positive back pressure and then through a water cooled tubular heat exchanger to a product receiver. Portions of the crude product were vacuum stripped at 2 millimeters pressure and 120 to 130° C. for testing.

Table I below presents the experimental conditions and results in tabular form.

(17)

TABLE I

Example	3	4	5	6	7	8	9	10
Monomer Content in Feed, Wt. %	25.1	35.3	23.4	30.7	35.3	30.5	35.5	40.9
Ratio of Acrylonitrile to Styrene	30/70	30/70	40/60	40/60	40/60	50/50	50/50	50/50
Reaction Temperature, °C	130	130	130	130	130	130	130	130
Catalyst Concentration, wt. % in Feed	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Polyol Feed Rate, gm/hr	2076	1203	2143	1928	1193	1942	1199	1084
Monomer Feed Rate, gm/hr.	696	656	654	852	652	852	657	749
Polymer in Product By Calc. — Poly A, %	6.9	10.0	8.5	11.2	13.5	14.0	16.7	19.2
— Poly S, %	16.1	23.6	13.3	17.6	20.7	14.9	17.4	20.4
Total %	23.0	33.6	21.8	28.8	34.2	28.9	34.1	39.6
Product Properties								
Viscosity (Brookfield) at 25°C., cps.	7060	25,750	2870	5230	9600	4100	7720	14,150
Filterability — % thru 700 Mesh	49.3	0.9	100	53.0	0.4	100	100	4.7

TABLE I (Continued)

Example	11	12	13	14	15	16	17	18
Monomer Content in Feed, Wt. %	30.3	35.5	46.2	59.7	30.0	35.0	25.4	29.9
Ratio of Acrylonitrile to Styrene	60/40	70/30	70/30	80/20	90/10	90/10	100/0	100/0
Reaction Temperature, °C	130	130	130	130	130	130	130	130
Catalyst Concentration, wt. % in Feed	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Polyol Feed Rate, gm/hr	1944	1196	744		1944		2020	1956
Monomer Feed Rate, gm/hr	846	657	640		834		686	834
Polymer in Product By Calc. - Poly A, %	16.7	23.5	31.2		25.0		22.8	
- Poly S, %	11.9	10.5	14.0		3.0		-	
Total %	28.6	34.0	45.2		28.0		22.8	
Product Properties								
Viscosity (Brookfield) at 25°C., cps.	3910	5860	15,500		17,200		5940	
Filterability - % thru 700 Mesh	100	100	4.7		100		100	

The polymer contents (wt. % monomers in feed) and acrylonitrile to styrene ratios of the compositions of these Examples are set forth in FIGURE 1. The numbers beside the data points refer to compositions produced in the correspondingly numbered Examples. Preferred polymer/polyols in accordance with this invention are identified by a square while products which do not meet the requisites of the

preferred embodiment are denoted by a solid square.

An exclusion curve represented by a dotted line is set forth in the figure to define the boundary between preferred polymer/polyol compositions and those which do not pass the requisite filtration test. As will be appreciated, the exclusion curve should not be considered as a rigid boundary but, rather, as a

reasonable guideline based upon the data included. As can be seen, a wide range of useful polymer/polyol compositions can be made even with this relatively low molecular weight polyol.

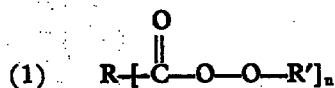
As can be seen in FIG. 1 the use of the present invention achieves formation of polymer/polyol compositions meeting the requisite filtration test that are unattainable with an azo catalyst under these conditions.

Related liquid polymer/polyol compositions are described and claimed in copending application No. 01741/79 (Serial No. 1,559,123).

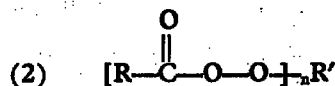
WHAT WE CLAIM IS:—

1. A liquid polymer/polyol composition consisting of: (1) from 40 to 90 weight per cent of a polyoxypropylene polyol having a molecular weight of at least 5,000 and (2) from 60 to 10 weight percent of an acrylonitrile homopolymer or a copolymer of acrylonitrile and styrene wherein the acrylonitrile/styrene weight ratio is from 100/0 to 20/80, wherein the homopolymer or copolymer is in the form of particles which are stably dispersed in the polyol, and the composition contains sufficient polymer particles with diameters of less than 30 microns to provide at least 20% filterability (as hereinbefore defined), and wherein the composition is produced by the polymerization of acrylonitrile and, when present, styrene in the polyol; the polyol molecular weight, the weight per cent of the monomer or monomers (based on the total weight of monomer plus polyol) and the acrylonitrile/styrene ratio in the monomer or monomers being such as to fall within the limits defined by the areas A to N of Figures 1 to 14 of the accompanying drawings, the said composition having been produced in the presence of a *t*-alkyl peroxyester free radical catalyst.

2. A composition as claimed in claim 1 wherein the catalyst is a compound having the general formula:—



or



wherein *n* is 1 or 2, *R'* is an alkyl group containing from 4 to 20 carbon atoms in which the carbon atom or atoms adjacent the oxygen bond are tertiary atoms, and *R* is an alkyl group containing from 3 to 12 carbon atoms or an aromatic group; with the proviso that when *n* is 2 *R'* is formula (2) above is an alkylene group.

3. A composition as claimed in claim 2

wherein the catalyst is *t*-butyl peroxy-2-ethylhexanoate, *t*-butylperpivalate, 2—5 dimethylhexane-2, 5-di-per-2-ethyl hexoate, *t*-butylperneodecanoate, *t*-butylperbenzoate, *t*-butylpercrotonate, *t*-butyl isobutyrate or di-*t*-butylphthalate.

4. A composition as claimed in any one of the preceding claims wherein the polymerization is conducted in a continuous operation whilst maintaining a sufficiently low monomer to polyol ratio throughout the reaction mixture during the polymerization such as to produce a polymer consisting substantially wholly of polymer particles having diameters less than 1 micron.

5. A composition as claimed in any one of the preceding claims containing sufficient polymer particles with diameters of less than 30 microns to provide at least 50% filterability (as hereinbefore defined).

6. A composition as claimed in claim 5 containing sufficient polymer particles with diameters of less than 30 microns to provide at least 99% filterability (as hereinbefore defined).

7. A composition as claimed in any one of the preceding claims wherein essentially all of the homopolymer or copolymer particles have diameters less than 30 microns.

8. A composition as claimed in any one of the preceding claims wherein the acrylonitrile/styrene ratio is less than 50/50.

9. A composition as claimed in any one of the preceding claims wherein the molecular weight of the polyol is from 5,000 to 8,000.

10. A liquid polymer/polyol composition consisting essentially of: (1) from 40 to 90 weight percent of a polyoxypropylene polyol having a molecular weight of at least 5,000 and (2) from 60 to 10 weight per cent of an acrylonitrile homopolymer or a copolymer of acrylonitrile and styrene wherein the acrylonitrile/styrene weight ratio is from 100/0 to 20/80, wherein the homopolymer or copolymer is in the form of particles which are stably dispersed in the polyol and the composition contains sufficient polymer particles with diameters of less than 30 microns to provide at least 20% filterability (as hereinbefore defined), and wherein the composition is produced by the polymerization of acrylonitrile and, when present, styrene in the polyol; the polyol molecular weight, the weight per cent of the monomer or monomers (based in the total weight of monomer plus polyol) and the acrylonitrile/styrene ratio in the monomer or monomers being such as to fall within the limits defined by the areas A to N of Figures 1 to 14 of the accompanying drawings, the said polyol being either a propylene oxide or a propylene oxide and ethylene oxide adduct of a polyhydroxy alkane.

11. A composition as claimed in claim 10 containing sufficient polymer particles with di-

reasonable guideline based upon the data included. As can be seen, a wide range of useful polymer/polyol compositions can be made even with this relatively low molecular weight polyol.

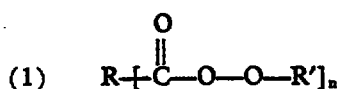
As can be seen in FIG. 1 the use of the present invention achieves formation of polymer/polyol compositions meeting the requisite filtration test that are unattainable with an azo catalyst under these conditions.

Related liquid polymer/polyol compositions are described and claimed in copending application No. 01741/79 (Serial No. 1,559,123).

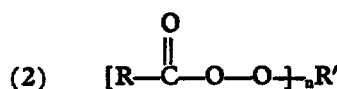
WHAT WE CLAIM IS:—

1. A liquid polymer/polyol composition consisting of: (1) from 40 to 90 weight per cent of a polyoxypropylene polyol having a molecular weight of at least 5,000 and (2) from 60 to 10 weight percent of an acrylonitrile homopolymer or a copolymer of acrylonitrile and styrene wherein the acrylonitrile/styrene weight ratio is from 100/0 to 20/80, wherein the homopolymer or copolymer is in the form of particles which are stably dispersed in the polyol, and the composition contains sufficient polymer particles with diameters of less than 30 microns to provide at least 20% filterability (as hereinbefore defined), and wherein the composition is produced by the polymerization of acrylonitrile and, when present, styrene in the polyol; the polyol molecular weight, the weight per cent of the monomer or monomers (based on the total weight of monomer plus polyol) and the acrylonitrile/styrene ratio in the monomer or monomers being such as to fall within the limits defined by the areas A to N of Figures 1 to 14 of the accompanying drawings, the said composition having been produced in the presence of a *t*-alkyl peroxyester free radical catalyst.

2. A composition as claimed in claim 1 wherein the catalyst is a compound having the general formula:—



or



wherein *n* is 1 or 2, *R'* is an alkyl group containing from 4 to 20 carbon atoms in which the carbon atom or atoms adjacent the oxygen bond are tertiary atoms, and *R* is an alkyl group containing from 3 to 12 carbon atoms or an aromatic group; with the proviso that when *n* is 2 *R'* is formula (2) above is an alkylene group.

3. A composition as claimed in claim 2

wherein the catalyst is *t*-butyl peroxy-2-ethylhexanoate, *t*-butylperpivalate, 2—5 dimethylhexane-2, 5-di-per-2-ethyl hexoate, *t*-butylperneodecanoate, *t*-butylperbenzoate, *t*-butylpercrotonate, *t*-butyl isobutyrate or di-*t*-butylphthalate.

4. A composition as claimed in any one of the preceding claims wherein the polymerization is conducted in a continuous operation whilst maintaining a sufficiently low monomer to polyol ratio throughout the reaction mixture during the polymerization such as to produce a polymer consisting substantially wholly of polymer particles having diameters less than 1 micron.

5. A composition as claimed in any one of the preceding claims containing sufficient polymer particles with diameters of less than 30 microns to provide at least 50% filterability (as hereinbefore defined).

6. A composition as claimed in claim 5 containing sufficient polymer particles with diameters of less than 30 microns to provide at least 99% filterability (as hereinbefore defined).

7. A composition as claimed in any one of the preceding claims wherein essentially all of the homopolymer or copolymer particles have diameters less than 30 microns.

8. A composition as claimed in any one of the preceding claims wherein the acrylonitrile/styrene ratio is less than 50/50.

9. A composition as claimed in any one of the preceding claims wherein the molecular weight of the polyol is from 5,000 to 8,000.

10. A liquid polymer/polyol composition consisting essentially of: (1) from 40 to 90 weight percent of a polyoxypropylene polyol having a molecular weight of at least 5,000 and (2) from 60 to 10 weight per cent of an acrylonitrile homopolymer or a copolymer of acrylonitrile and styrene wherein the acrylonitrile/styrene weight ratio is from 100/0 to 20/80, wherein the homopolymer or copolymer is in the form of particles which are stably dispersed in the polyol and the composition contains sufficient polymer particles with diameters of less than 30 microns to provide at least 20% filterability (as hereinbefore defined), and wherein the composition is produced by the polymerization of acrylonitrile and, when present, styrene in the polyol; the polyol molecular weight, the weight per cent of the monomer or monomers (based in the total weight of monomer plus polyol) and the acrylonitrile/styrene ratio in the monomer or monomers being such as to fall within the limits defined by the areas A to N of Figures 1 to 14 of the accompanying drawings, the said polyol being either a propylene oxide or a propylene oxide and ethylene oxide adduct of a polyhydroxy alkane.

11. A composition as claimed in claim 10 containing sufficient polymer particles with di-



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ameters of less than 30 microns to provide at least 50% filterability (as hereinbefore defined).

5 12. A composition as claimed in claim 11 containing sufficient polymer particles with diameters of less than 30 microns to provide at least 99% filterability (as hereinbefore defined).

10 13. A composition as claimed in any one of claims 10 to 12 wherein essentially all of the polymer particles have diameters less than 30 microns.

15 14. A composition as claimed in any one of claims 10 to 13 wherein the acrylonitrile/styrene ratio is less than 50/50.

20 15. A composition as claimed in any one of claims 10 to 14 wherein the polymerization is conducted in a continuous operation, in the presence of a *t*-alkyl peroxyester free radical catalyst and whilst maintaining a sufficiently low monomer to polyol ratio throughout the reaction mixture during the polymerization such as to produce a polymer consisting substantially wholly of polymer particles having diameters less than 1 micron.

25 16. A composition as claimed in claim 15 wherein the peroxyester catalyst is *t*-butyl peroxy 2-ethylhexoate.

30 17. A composition as claimed in any one of claims 10 to 16 wherein the molecular weight

of the polyol is from 5,000 to 8,000.

18. A composition as claimed in claim 1 or claim 10 substantially as hereinbefore described.

19. A composition as claimed in claim 1 or claim 10 substantially as hereinbefore described in any one of Examples 1, 5, 8, 9, 11, 12, 15 or 17. 35

20. A process for producing a liquid polymer/polyol composition as claimed in any one of the preceding claims substantially as hereinbefore described. 40

21. A method of producing a polyurethane which comprises reacting an organic polyisocyanate with a liquid polymer/polyol composition as claimed in any one of claims 1 to 19 in the presence of a catalyst for the urethane-forming reaction. 45

22. A method as claimed in claim 21 wherein the reaction is effected in the presence of a blowing agent and a foam stabiliser. 50

23. A method as claimed in claim 21 substantially as hereinbefore described.

24. A polyurethane when produced by a method as claimed in any one of claims 21 to 23. 55

BOULT, WADE & TENNANT,

Chartered Patent Agents,

34 Cursitor Street, London, EC4A 1PQ.

