

**APPARATUS AND PROCESS FOR DISPERSING ISOCYANATE
TERMINATED POLYURETHANE PREPOLYMERS**

5 Cross Reference to Related Application

 This application is a continuation-in-part of Copending application
Serial No. 08/528936, filed September 15, 1995.

Field Of The Invention

**10 This invention relates to an apparatus and process for dispersing
isocyanate-terminated polyurethane prepolymers in water.**

Background Of The Invention

**15 It is known that dynamic mixers, which have a pitched blade turbine
within a draft tube to generate axial flow, are useful for continuously
emulsifying, homogenizing and dispersing materials. References describing
such mixers include:**

**20 Japanese Utility Model Patent No. 1148021 (Canan KK) discloses
turbine dynamic mixers which are designed to generate axial flow within the
vessel.**

**25 A product brochure entitled, "T.K. Homomic Line Flow" from
Tokushu Kika Kogyo Co., Ltd, (Osaka, Japan) describes turbine dynamic
mixers which are useful for emulsifying, homogenizing and dispersing
materials which are transferable by metering feed pumps. The mixers are also
described as being useful for continuously dissolving several kinds of resin
solutions in solvent. The reference fails to disclose the use of said mixers for
dispersing isocyanate terminated polyurethane prepolymers in water.**

**30 Generally, water dispersible isocyanate-terminated polyurethane
prepolymers are formed by reacting a stoichiometric excess of polyisocyanate
with compounds containing active hydrogen atoms such as polyols and
polyamines. The prepolymers are dispersed in water using mechanical**

agitation and then reacted with compounds such as water soluble amines. The resulting product is a water-based polyurethane-urea polymer.

The apparatus most often used to disperse these prepolymers are stator-rotor and pin dynamic mixers. Such mixers are designed to rapidly disperse the prepolymers in water using a high energy per unit volume input and short residence times. For example, U.S. Pat. No. 4,742,095, Mobay Corporation (Pittsburg, PA) describes stator-rotor and pins dynamic mixers operating at a speed of about 500 revolutions per minute (rpm) to 8,000 rpm, a mixing wattage of about 0.3 watts/cu.cm. to 10.0 watts/cu.cm. and a mixing volume of at least about 0.1 liters. The average residence time in said mixers being from about 1-second to 30-seconds.

Other related patents, which fail to disclose the apparatus and process of the present invention, include British Pat. No. 1,414,930, Pat. No. 1,432,112, Pat. No. 1,428,907 and German Offenlegungsschrift Pat. No. 2,347,299.

A disadvantage with these dynamic mixers is that reduced residence times may not generate a uniform particle dispersion, and a high energy per unit volume input can cause shear induced destabilization generating increased sedimentation.

To enhance the performance characteristics of water-based polyurethane-urea polymers, it is often necessary to form isocyanate-terminated polyurethane prepolymers which are characterized as having increased hydrophobicity, crystallinity and viscosities. Such prepolymers are not easily dispersed in water, require extended residence times, and lower energy per unit volume input to generate uniform particle dispersions which are substantially free of sedimentation.

Therefore, there remains a need for an apparatus and process which can disperse isocyanate-terminated polyurethane prepolymers in water using extended residence times and a lower energy per unit volume input.

Summary Of The Invention

The present invention is directed to an apparatus and process for dispersing isocyanate-terminated polyurethane prepolymers in water. The apparatus comprises:

- 5 a) at least one reaction vessel containing a water dispersible NCO-terminated polyurethane prepolymer which is the reaction product of;
 - 1) at least one polyisocyanate; and
 - 2) at least one polyol and/or polyamine component which
10 may be substituted with at least one hydrophilic moiety;
- b) at least one supply vessel containing at least one compound such as water, organic materials and inorganic materials;
- c) at least one dynamic mixer, which has a pitched blade turbine within a draft tube to generate axial flow, configured to
15 provide:
 - 1) a mixing zone volume greater than about 0.1 liters;
 - 2) an average tip speed greater than about 100 meters/min.;
 - 3) an average power per unit volume input less than about
0.60 watts/cu.cm.;
 - 20 4) an average residence time of at least about 10-seconds; with
 - 5) an average of at least about 5-passes through the mixing zone; and
- d) at least one finishing vessel wherein the dispersion is further
25 reacted to form a water-based polyurethane-urea polymer.

The invention is further characterized by a process for dispersing NCO-terminated polyurethane prepolymers, comprising the steps of:

- a) combining an aqueous solution of organic and inorganic ingredients with at least one water dispersible isocyanate-terminated polyurethane prepolymer to form a materials
30 mixture;



5

- b) feeding the materials mixture into at least one axial flow dynamic mixer and utilizing a dispersing process comprising;
- 1) an average tip speed greater than about 100 meters/min.;
 - 2) an average power per unit volume input less than about 0.60 watts/cu.cm.;
 - 3) an average residence time of at least about 10-seconds; with
 - 4) an average of at least about 5-passes through the mixing zone;
 - 5) an average flow rate greater than about 30 liters/hours; and
- c) transferring the dispersion to at least one finishing vessel and completing the isocyanate reaction to form a water-based polyurethane-urea polymer.

10

15

Surprisingly, the inventive apparatus and process generates uniform prepolymer dispersions using extended residence times and lower energy per unit volume input.

Brief Description Of The Drawings

20

Figure 1 is a side fragmentary view, in partial cross-section, of a axial flow dynamic mixer used in the apparatus and process of the invention.

Figure 2 is a schematic diagram of an apparatus of the invention.

Detailed Description Of The Invention

25

The present invention is directed to an apparatus and process for dispersing NCO-terminated polyurethane prepolymers. The apparatus is a turbine mixer which has a pitched blade turbine within a draft tube. The turbine mixers, which generate axial flow within the mixing vessel, can be configured to provide a lower energy per unit volume, extended residence times and multiple passes through the mixing zone. Such mixers have proven

30

useful for processing prepolymers which are difficult to disperse in water.



Suitable dynamic mixers are commercially available from Tokushu Kika Kogyo Co., Ltd., Osaka, Japan under the product name T.K. Homomic Line Flow. Such mixers can be configured to provide:

- 1) a mixing zone volume greater than from about 0.1 liters;
- 5 2) a tip speed of about 100 meters/min. to about 5,000 meters/min., and more preferably from about 250 meters/min. to about 1500 meters/min.;
- 3) a power per unit volume input from about 0.01 watts/cu.cm. to about 0.60 watts/cu.cm., and more preferably from about 0.10
10 watts/cu.cm. to about 0.30 watts/cu.cm.;
- 4) an average residence time from about 10-seconds to about 120-seconds, and more preferably from about 10-seconds to about 60-seconds; with
- 5) an average number of passes through the mixing zone from
15 about 2-passes to about 150-passes, and more preferably from about 10-passes to about 60-passes; and
- 6) a flow-out rate greater than about 100 liters/hr.

The average residence time and the average number of passes through the mixing zone can be varied with the material feed rates and the tip speed. If
20 desired, greater quantities of dispersion may be produced per unit time by using more than one mixer at a time.

Figure 1 illustrates a dynamic mixer of the type used in the apparatus and process of the invention. The mixer includes a motor 12 mounted to a motor base 14 which is connected to a bearing case 16. The bearing case 16
25 mounts the motor on the vessel lid 18.

A mixing vessel 20 is removably mounted to lid 18. Pitched blade turbine 26 and draft tube 28 define a mixing zone. The blade is mounted to a shaft 32 operatively connected to the motor shaft via a mechanical seal 34. The vessel is double chambered having a central mixing chamber 21, a
30 recirculation zone 22 and a smaller annular exit chamber 24. An inlet 36 provides feed access to the mixing chamber 21 while outlet 38 provides for exit of the dispersed product emerging from the mixing chamber.

In Figure 1, the direction of flow is indicated by the arrows. Material entering the vessel via inlet 36 is directed through the mixing zone 21 and cycles through the draft tube 28 and the recirculation zone 22 in an axial flow. The dispersed material exits from the recirculation zone through outlet 38.

5 Figure 2 is a schematic representation of an apparatus in accordance with the invention. A water dispersible isocyanate-terminated polyurethane prepolymer is prepared in reaction vessel 100 and fed via metering pump 110 into dynamic mixer 300. The contents of supply vessel 200 is fed to mixer 300 via meter pump 210, which joins conduit 110 to provide a single feed line into mixer 300. The prepolymer dispersion exiting mixer 300 is fed via
10 conduit 310 to a stirred finishing vessel 500. The contents of supply vessel 400 can be added to the dispersion in several locations. For example, the supply vessel contents can be fed into the mixing vessel 300 via meter pumped conduit 410 or into conduit 310 via meter pumped conduit 420 or into the
15 finishing vessel 500 via meter pumped conduit 430. Alternatively, supply vessel 400, conduit 410, 420 and 430 can be omitted. Once the components are within the finishing vessel 500, the prepolymer dispersion is stirred to complete the isocyanate reaction and form a water-based polyurethane-urea polymer.

20 At least one reaction vessel is used in the apparatus and process of the invention. If desired, multiple reaction vessels may be used. Such vessels may contain isocyanate-terminated polyurethane prepolymers of different composition.

25 At least one axial flow turbine mixer, which is mounted in a draft tube, is used in the invention. The term "draft tube" refers to an open cylinder which separates the mixing zone from the recirculation zone. The draft tube generates axial flow and allows recirculation through the mixing vessel. If desired, multiple mixers may be used to disperse large quantities of prepolymer thus increasing the total volume of dispersion produced per unit
30 time.

At least one supply vessel is used. The vessel contains at least one component which may include amines, antioxidants, biocides, coalescing aids,

coloring agents, defoamers, dispersed pigments, emulsifiable waxes, fillers, fire retardant agents, fungicides, ionic and/or nonionic emulsifiers, natural polymer dispersions, non-polyurethane based emulsifiable synthetic resins, organic co-solvents, perfume-like materials, plasticizers, sequestering agents, UV stabilizers, water, wetting agents and their mixtures.

The isocyanate-terminated polyurethane prepolymers and the supply vessel contents can be transferred using metering pumps which may include centrifugal pumps, diaphragm pumps, gear pumps, piston pumps, peristaltic pumps, progressive cavity pumps, lobe pumps, screw pumps and vane pumps. Alternatively, said materials may be transferred using gravity feed and/or compressed gasses including nitrogen which may require the use of control valves. Preferably, a conduit system comprising pipes or tubes is used to channel the materials throughout the apparatus of the invention.

At least one finishing vessel is used and is preferably equipped with mechanical agitation. Also, multiple finishing vessels may be used to react the prepolymer dispersions with dissimilar compounds having active hydrogen atoms. Such a process is used to generate water-based polyurethane-urea polymers which differ in composition.

To enhance the performance characteristics of water-based polyurethane-urea polymers, it is often necessary to form isocyanate-terminated polyurethane prepolymers having properties such as increased hydrophobicity, crystallinity and viscosity. Examples include the hydrophobic prepolymers described in U.S. Pat. No. 5,354,807 (H.B. Fuller Company) and the crystalline polymers described in copending application Serial No. 08/528936, incorporated herein by reference. Said prepolymers can have viscosities ranging from about 10,000 m.Pas to about 100,000 m.Pas, and more preferably from about 15,000 m.Pas to about 50,000 m.Pas. These prepolymers are more likely to develop a uniform particle dispersion when extended residence times and lower energy per unit volume inputs are utilized.

The prepolymers are prepared by reacting a stoichiometric excess of polyisocyanate with at least one polyol and/or polyamine compound which may be substituted with at least one hydrophilic moiety. The materials can be

reacted at a temperature in a range from about 25°C to about 100°C, and more preferably from about 60°C to about 90°C. The percent isocyanate, present in the finished prepolymer, can be in a range from about 1.0% by weight to about 15.0% by weight, and more preferably from about 4.0% by weight to about 8.0% by weight, based on total prepolymer solids.

The prepolymers are preferably dispersed using distilled and/or deionized water. The water temperature is greater than 0°C and preferably in a range from about 5°C to about 100°C, and more preferably from about 25°C to about 50°C.

The water-based polymers of the present invention can have a solids content in the range from about 20.0% by weight to about 80.0% by weight, and preferably from about 30.0% by weight to about 50.0% by weight.

Once the isocyanate-terminated polyurethane prepolymer has been dispersed and transferred to a finishing vessel, the dispersion may be charged with the contents of a second supply vessel, which may contain de-ionized water and water soluble amines, to form a dispersion mixture. Said mixture may or may not be agitated and can be reacted at a temperature from about 5°C to about 100°C, and preferably from about 25°C to about 65°C.

The following description of compositions is illustrative of the types of dispersible products which are advantageously prepared using the apparatus and process of the present invention. Those skilled in the art will recognize that alternative products may be formed using other reactants.

The polyisocyanates may be linear aliphatic, cyclic aliphatic, aromatic, and mixtures thereof. The polyisocyanate is preferably a mixture including hindered polyisocyanate and non-hindered polyisocyanate. The term "hindered polyisocyanate" is defined as an isocyanate moiety which is less sensitive to the water-isocyanate reaction due to the proximity of adjacent aliphatic character. The hindered polyisocyanate may be present in the polyisocyanate mixture in a range from about 1 part to about 95 parts, and more preferably from about 25 parts to about 75 parts, based on 100 parts total polyisocyanates. Examples of commercially available hindered polyisocyanates include Vestanat® IPDI which is 3-isocyanatomethyl-3,5,5-

trimethylcyclohexyl isocyanate from HULS America, Inc. (Piscataway, NJ) and TMXDI[®] which is 1,3-bis (1-isocyanato-1-methylethyl) benzene from Cyanamid (Wayne, NJ). Examples of commercially available non-hindered polyisocyanates include Luxate[®] HM which is 1,6-hexamethylene diisocyanate from Olin Corporation (Stamford, CT), diphenylmethane diisocyanate from Upjohn Polymer chemicals (Kalamazoo, MI), Desmodur[®] W which is Dicyclohexylmethane- 4,4'-diisocyanate from Mobay Corporation (Pittsburgh, PA) and toluene diisocyanate (TDI).

The presence of a hindered polyisocyanate is preferred in the process of the invention. It is surmised such sterically hindered polyisocyanates are less likely to be completely reacted during prepolymer synthesis. The resulting isocyanate-terminated polyurethane prepolymers, which are less sensitive to the isocyanate/water reaction, can be dispersed in water allowing further reaction with amines.

If desired, the water dispersible isocyanate-terminated polyurethane prepolymers may be subjected to complete hydrolysis. Such prepolymers, which are preferably based on sulfonate character, generate polyurethane-urea polymers having enhanced properties such as water- resistance and heat resistance and are described in the above mentioned copending application Serial No. 08/528936.

Other polyisocyanates which may be used include modified polyisocyanates prepared from hexamethylene diisocyanate, isophorone diisocyanate and toluylene diisocyanate. The modified diisocyanates can have functionalities such as urethanes, uretdiones, isocyanurates, biurets and mixtures thereof.

Examples of small molecular weight polyols which may be used in the preparation of the water dispersible isocyanate-terminated polyurethane prepolymers can have hydroxyl numbers, as determined by ASTM designation E-222-67 (Method B), in a range from about 130 to about 1250, and preferably from about 950 to about 1250. Examples of preferred small molecular weight polyols include trimethylolpropane, diethylene glycol, 1,4-butanediol, 1,6-hexanediol, glycerol and the aliphatic diols described in U.S. Pat. No.

5,039,732, Sherwin-Williams Company (Baltimore, MD), incorporated herein by reference.

The prepolymer of the invention may be rendered water dispersible by the chemical incorporation of anionic moieties, non-ionic moieties, cationic moieties and mixtures thereof. Anionic polyurethane-urea polymers are preferred and prepolymers containing a combination of sulfonate and carboxylate groups are most preferred. Examples of ionic moieties which may be incorporated into the prepolymer include dimethylpropionic acid and 1,4-dihydroxybutane sulfonic acid described in U.S. Pat No. 3,412,054 and U.S. Pat No. 4,108,814, incorporated herein by reference.

The anionic groups can be neutralized with bases such as alkali metal hydroxides, organic tertiary amines, ammonia and mixtures thereof. Conversion of the anionic groups to ionic groups (salts) may be accomplished before, during or after the prepolymer has been dispersed in water.

Polymeric diols used in the preparation of the prepolymers can have hydroxyl numbers, as determined by ASTM designation E-222-67 (Method B), in a range from about 20 to about 140, and preferably from about 55 to about 110. The polymeric polyols can have melting temperatures from about 10°C to about 200°C, and more preferably from about 25°C to about 95°C. The polyols can be selected from the group consisting of polyester polyols, polyether polyols, polycarbonate polyols, polyurethane polyols, polyacetal polyols, polyacrylate polyols, polycaprolactone polyols, polyesteramide polyols, polythioether polyols, and mixtures thereof. The preferred polymeric polyols are those described in the above mentioned copending application Serial No. 08/528936 and U.S. Pat No. 5,334,690 (Hoechst Aktiengesellschaft, Fed.), incorporated herein by reference.

The inventive process generates water-based polyurethane-urea polymers which are characterized as having enhanced properties including heat and water resistance. Said process is also useful in the preparation of water-based polyurethane-urea polymer blends and hybrids containing polyacrylic and/or polyvinyl polymers. Examples include the compositions

described in copending U.S. application 08/561197, filed November 21, 1995, H.B. Fuller Company (St. Paul, MN) incorporated herein by reference.

The invention is illustrated by the following non-limiting examples.

5

Example 1

Example 1 describes the preparation of a highly crystalline water-based polyurethane-urea polymer.

To a reaction vessel was charged 45.39 kgs. (44.5 hydroxyl
10 equivalence) Rucoflex[®] XS-5483-55 which is a sulfonated polyester polyol from Ruco Polymer Corporation (Hicksville, NY), 2.13 kgs. (15.9 hydroxyl equivalence) dimethylolpropionic acid, 2.39 kgs. (53.0 hydroxyl equivalence) 1,4-butanediol, 6.60 kgs. (59.4 isocyanate equivalence) isophorone diisocyanate, 9.99 kgs. (118.8 isocyanate equivalence) hexamethylene
15 diisocyanate and 4.24 kgs. anhydrous acetone. The mixture was mildly agitated and heated to 70°C for approximately 2.5-hours then charged with 1.27 kgs. triethylamine and stirred an additional 15-minutes before dispersing.

The prepolymer (80°C) and de-ionized water (60°C) were combined in-line and transferred to a T.K. Homonic Line Flow model 100S axial flow
20 dynamic mixer from Tokushu Kika Kogyo Co., Ltd. (Osaka, Japan). The prepolymer was transferred from the reaction vessel using a gear pump set at a rate of 3.60 kgs. per minute while the water was transferred from a supply vessel using a progressive gravity pump set at a rate of 6.40 kgs. per minute. The mixer was configured to provide an average residence time of 61-seconds
25 using a shaft speed of 3,600 rpm and a tip speed of 1,000 meters/min.

The dispersion was transferred to a finishing vessel equipped with a turbine agitator and run at a circulation rate of about 10 min⁻¹ for approximately 20 minutes. To the dispersion was charged a mixture containing ethylene diamine in de-ionized water. The dispersion was stirred
30 an additional 30-minutes at 60°C to generate a water-based polyurethane-urea polymer. The polymers properties are described below:

pH = 7.9

Solids = 31.38%

Mean diameter article size = 189 nm.

Viscosity = 40 m.Pas

5

Example 2

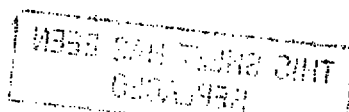
Example 2 describes the preparation of a hydrophobic water-based polyurethane-urea polymer.

10 To a reaction vessel was charged 28.53 kgs. (56.0 hydroxyl equivalence) Rucoflex® S-102-10 which is a polyester polyol from Ruco Polymer Corporation (Hicksville, NY), 0.348 kgs. (7.8 hydroxyl equivalence) trimethylolpropane, 3.48 kgs. (50.0 hydroxyl equivalence) dimethylolpropionic acid, 30.18 kgs. TMXDI® which is tetramethylxylene diisocyanate from Cyanamid (Wayne, NJ), 0.362 kgs. Irganox® 1076 which is
15 a hindered phenol antioxidant from Ciba-Giegy Corporation (Hawthorne, NY) and 2.50 kgs. triethylamine. The mixture was mildly agitated and heated to 90°C for 2-hours.

The pre-prepolymer was charged with 6.60 kgs. (47.0 amine equivalence) Tomah®-14 which is isodecyloxypropyl-1,3-diaminopropane
20 from Tomah Products (Milton, WI). The amine was charged to the reactor over a 1- hour period keeping the temperature below 90°C.

The prepolymer, which had a viscosity of approximately 15,000 m.Pas at 90°C, was processed as similarly described in Example 1. The exception
25 being the prepolymer was metered at 4.4 kgs./min., the water (62°C) was metered at a rate of 7.0 kgs./min., the turbine tip speed was 1,000 meters/sec. and the average residence time was 53-seconds.

The dispersion was transferred to a finishing vessel equipped with a turbine agitator and run at a circulation rate of about 10 min⁻¹ for
30 approximately 20-minutes. To the dispersion was charged a chain extender solution consisting of 12.65% diethylene triamine, 39.62% ethylene diamine and water. The dispersion was stirred an additional 30-minutes to generate a



water-based polyurethane-urea polymer. The polymers properties are described below:

pH = 9.12

Solids = 36.7%

5 Viscosity = 20 m.Pas

10

15

20

25

30



THIS SHEET HAS BEEN
REPLACED

WO 97/10273

PCT/US96/14445

Claims

1. An apparatus for dispersing isocyanate-terminated polyurethane prepolymers comprising:
 - a) at least one reaction vessel containing a water dispersible isocyanate-terminated polyurethane prepolymer;
 - b) at least one supply vessel;
 - c) at least one supply conduit system;
 - d) at least one dynamic mixer which has a pitched blade turbine within a draft tube; and
 - e) at least one finishing vessel.
2. A reaction vessel as described in Claim 1, wherein said water dispersible isocyanate-terminated polyurethane prepolymer is the reaction product of:
 - a) at least one polyisocyanate; and
 - b) at least one isocyanate reactive component which may be substituted with at least one hydrophilic moiety.
3. A water dispersible isocyanate-terminated polyurethane prepolymer as described in Claim 2 wherein said polyisocyanate is selected from the group consisting of aliphatic polyisocyanates, cyclic aliphatic polyisocyanates, aromatic polyisocyanates and mixtures thereof.
4. A polyisocyanate mixture as described in Claim 2, comprising a hindered polyisocyanate.
5. A hindered polyisocyanate as described in Claim 4, including isophorone diisocyanate, tetramethylxylene diisocyanate and mixtures thereof.
6. An apparatus as described in Claim 1, wherein said supply vessel contains at least one compound selected from the group consisting of amines, antioxidants, biocides, coalescing aids, coloring agents, defoamers, dispersed pigments, emulsifiable waxes, fillers, fire retardant agents, fungicides, ionic and/or nonionic emulsifiers, natural polymer dispersions, non-polyurethane based emulsifiable synthetic resins, organic co-solvents, perfume-like materials, plasticizers,





WO 97/10273

PCT/US96/14445

sequestering agents, UV stabilizers, water, wetting agents and their mixtures thereof.

7. An apparatus as described in Claim 1, wherein said supply conduit is comprised of pipes.

5 8. An apparatus as described in Claim 6, wherein said materials can be transferred with at least one pump selected from the group consisting of piston pumps, gear pumps, centrifugal pumps, diaphragm pumps, lobe pumps, progressive cavity pumps, peristaltic pumps, screw pumps and vane pumps.

10 9. A process for the preparation of water-based polyurethane-urea polymers with dynamic mixers, comprising the steps of:

15 a) combining an aqueous solution comprising at least one compound selected from the group consisting of amines, antioxidants, biocides, coalescing aids, coloring agents, defoamers, dispersed pigments, emulsifiable waxes, fillers, fire retardant agents, fungicides, ionic and/or nonionic emulsifiers, natural polymer dispersions, non-polyurethane based emulsifiable synthetic resins, organic co-solvents, perfume-like materials, plasticizers, sequestering agents, UV stabilizers and wetting agents with at least one water dispersible isocyanate-terminated polyurethane prepolymer to form a materials mixture;

20 b) feeding said materials mixture into a dynamic mixer to form a dispersion;

25 c) transferring said dispersion into a finishing vessel to complete the formation of a water-based polyurethane-urea polymer; wherein said dynamic mixers have a pitched blade turbine within a draft tube, use a lower energy per unit volume input, have extended residence times and multiple passes through the mixing zone.

30

THIS SHEET HAS BEEN
REPLACED

10. A Mixer as described in Claim 1 or Claim 9, wherein said mixer is configured to provide an average tip speed greater than about 100 meters per minute.





WO 97/10273

PCT/US96/14445

11. A mixer as described in Claim 1 or Claim 9, wherein said mixer is configured to provide an average power per unit volume input less than about 0.60 watts per cubic centimeter.
12. A mixer as described in Claim 1 or Claim 9, wherein said mixer is configured to provide an average residence time of at least about 10-seconds.
13. A mixer as described in Claim 1 or Claim 9, wherein said mixer is configured to provide greater than about 5-passes through the mixing zone.
14. A mixer as described in Claim 1 or Claim 9, wherein said mixer is configured to provide an average flow rate greater than about 30 liters per hour.
15. A process as described in Claim 9, wherein said materials are transferred with at least one pump selected from the group consisting of centrifugal pumps, diaphragm pumps, lobe pumps, gear pumps, peristaltic pumps, piston pumps and progressive cavity pumps, screw pumps and vane pumps.

THIS SHEET HAS BEEN
REPLACED

