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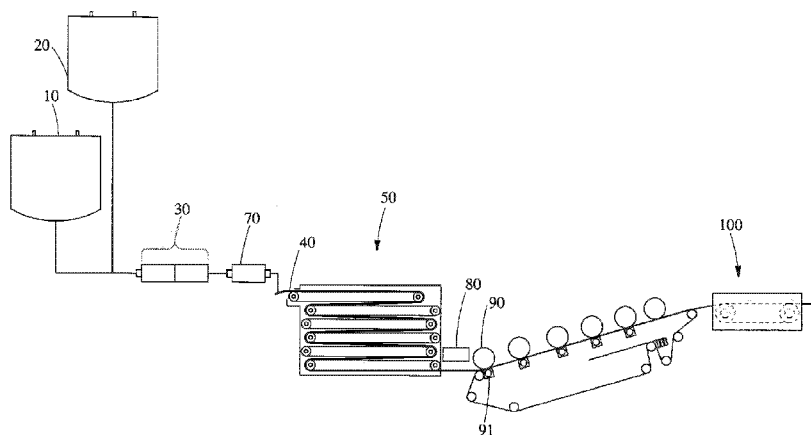


Fig. 1

(57) Abstract: A High Internal Phase Emulsion (HIPE) foam having low levels of unpolymerized monomer.



WO 2011/081987 A1

HIGH INTERNAL PHASE EMULSION FOAM HAVING LOW LEVELS OF UNPOLYMERIZED MONOMERS

FIELD OF THE INVENTION

This application relates to a High Internal Phase Emulsion (HIPE) foam having low levels of unpolymerized monomers

BACKGROUND OF THE INVENTION

An emulsion is a dispersion of one liquid in another liquid and generally is in the form of a water-in-oil mixture having an aqueous or water phase dispersed within a substantially immiscible continuous oil phase. Water-in-oil (or oil in water) emulsions having a high ratio of dispersed aqueous phase to continuous oil phase are known in the art as High Internal Phase Emulsions, also referred to as "HIPE" or HIPEs. At relatively high dispersed aqueous phase to continuous oil phase ratios the continuous oil phase becomes essentially a thin film separating and coating the droplet-like structures of the internal, dispersed aqueous phase. In one embodiment the continuous oil phase of a water-in-oil HIPE comprises one or more polymerizable monomers. These monomers can be polymerized, forming a cellular structure, for example a foam, having a cell size distribution defined by the size distribution of the dispersed, aqueous phase droplets.

Polymerization of the monomers starts upon the activation of an initiator and continues during the curing process. The curing process is often at the end or near the end of the foam forming process; after which the HIPE foam is prepared for its future uses. However, after the addition of initiator and the curing process not all of the monomers are polymerized. These residual unpolymerized monomers can cause problems both in the HIPE foam and the process used to prepare the HIPE foams. If unreacted monomers are present in the HIPE foam they may pose a safety concern at certain levels, adversely affect the desired HIPE foam properties or interfere with the further HIPE foam processing steps, such as cutting or the application of other components to the HIPE foam. In addition, the monomers also have a tendency to adhere to surfaces which can cause processing problems both in batch processes where the monomers may adhere to the mold cavity requiring cleaning of the molds or in the case of a continuous process requiring the cleaning of the surface upon which a HIPE is deposited onto.

Accordingly, there is a need for HIPE foams having low levels of unpolymerized monomers and a method that reduces the amount of unpolymerized monomer in HIPE foams.

SUMMARY OF THE INVENTION

A High Internal Phase Emulsion foam formed by polymerizing a High Internal Phase Emulsion is provided that comprises an oil phase having monomer, cross-linking agent, emulsifier; photoinitiator; and an aqueous phase; wherein the High Internal Phase Emulsion foam comprises less than 400 ppm unpolymerized monomer.

A High Internal Phase Emulsion foam formed by polymerizing a High Internal Phase Emulsion is provided that comprises a first layer having an oil phase which includes monomer, cross-linking agent, emulsifier; photoinitiator; and an aqueous phase. The High Internal Phase Emulsion also includes a second layer having an oil phase which includes monomer, cross-linking agent, emulsifier; photoinitiator; and an aqueous phase; wherein the High Internal Phase Emulsion foam comprises less than 400 ppm unpolymerized monomer.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a process flow diagram of the present invention.

FIG. 2 is a process flow diagram of the present invention.

FIG. 3 is a graph showing monomer reduction.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a High Internal Phase Emulsion (HIPE) foam having low levels of unpolymerized monomer. HIPEs of the present invention comprising a continuous oil phase containing monomers and an aqueous phase are produced using a continuous process, for example by having a HIPE deposited on a belt, such as an endless belt. While on the belt the HIPE are moved to a heating zone, where the monomers are polymerized to form a HIPE foam. Following the heating zone the HIPE foam is moved to a UV light zone, wherein the unpolymerized monomers are exposed to UV light which polymerizes them.

A High Internal Phase Emulsion (HIPE) comprises two phases. One phase is a continuous oil phase comprising monomers that are polymerized to form a HIPE foam and an emulsifier to help stabilize the HIPE. The oil phase may also include one or more photoinitiators. The monomer

component, may be present in an amount of from about 80% to about 99%, and in certain embodiments from about 85% to about 95% by weight of the oil phase. The emulsifier component, which is soluble in the oil phase and suitable for forming a stable water-in-oil emulsion may be present in the oil phase in an amount of from about 1% to about 20% by weight of the oil phase. The emulsion may be formed at an emulsification temperature of from about 10° C to about 130° C and in certain embodiments from about 50° C to about 100° C.

In general, the monomers will include from about 20% to about 97% by weight of the oil phase at least one substantially water-insoluble monofunctional alkyl acrylate or alkyl methacrylate. For example, monomers of this type may include C₄-C₁₈ alkyl acrylates and C₂-C₁₈ methacrylates, such as ethylhexyl acrylate, butyl acrylate, hexyl acrylate, octyl acrylate, nonyl acrylate, decyl acrylate, isodecyl acrylate, tetradecyl acrylate, benzyl acrylate, nonyl phenyl acrylate, hexyl methacrylate, 2-ethylhexyl methacrylate, octyl methacrylate, nonyl methacrylate, decyl methacrylate, isodecyl methacrylate, dodecyl methacrylate, tetradecyl methacrylate, and octadecyl methacrylate.

The oil phase may also comprise from about 2% to about 40%, and in certain embodiments from about 10% to about 30%, by weight of the oil phase, a substantially water-insoluble, polyfunctional crosslinking alkyl acrylate or methacrylate. This crosslinking comonomer, or crosslinker, is added to confer strength and resilience to the resulting HIPE foam. Examples of crosslinking monomers of this type comprise monomers containing two or more activated acrylate, methacrylate groups, or combinations thereof. Nonlimiting examples of this group include 1,6-hexanedioldiacrylate, 1,4-butanedioldimethacrylate, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, 1,1 2-dodecyldimethacrylate, 1,14-tetradecanedioldimethacrylate, ethylene glycol dimethacrylate, neopentyl glycol diacrylate (2,2-dimethylpropanediol diacrylate), hexanediol acrylate methacrylate, glucose pentaacrylate, sorbitan pentaacrylate, and the like. Other examples of crosslinkers contain a mixture of acrylate and methacrylate moieties, such as ethylene glycol acrylate-methacrylate and neopentyl glycol acrylate-methacrylate. The ratio of methacrylate:acrylate group in the mixed crosslinker may be varied from 50:50 to any other ratio as needed.

Any third substantially water-insoluble comonomer may be added to the oil phase in weight percentages of from about 0% to about 15% by weight of the oil phase, in certain embodiments

from about 2% to about 8%, to modify properties of the HIPE foams. In certain cases, "toughening" monomers may be desired which impart toughness to the resulting HIPE foam. These include monomers such as styrene, vinyl chloride, vinylidene chloride, isoprene, and chloroprene. Without being bound by theory, it is believed that such monomers aid in stabilizing the HIPE during polymerization (also known as "curing") to provide a more homogeneous and better formed HIPE foam which results in better toughness, tensile strength, abrasion resistance, and the like. Monomers may also be added to confer flame retardancy as disclosed in U.S. Pat. No. 6,160,028 (Dyer) issued Dec. 12, 2000. Monomers may be added to confer color, for example vinyl ferrocene, fluorescent properties, radiation resistance, opacity to radiation, for example lead tetraacrylate, to disperse charge, to reflect incident infrared light, to absorb radio waves, to form a wettable surface on the HIPE foam struts, or for any other desired property in a HIPE foam. In some cases, these additional monomers may slow the overall process of conversion of HIPE to HIPE foam, the tradeoff being necessary if the desired property is to be conferred. Thus, such monomers can be used to slow down the polymerization rate of a HIPE. Examples of monomers of this type comprise styrene and vinyl chloride.

The oil phase may further contain an emulsifier used for stabilizing the HIPE. Emulsifiers used in a HIPE can include: (a) sorbitan monoesters of branched C₁₆-C₂₄ fatty acids; linear unsaturated C₁₆-C₂₂ fatty acids; and linear saturated C₁₂-C₁₄ fatty acids, such as sorbitan monooleate, sorbitan monomyristate, and sorbitan monoesters, sorbitan monolaurate diglycerol monooleate (DGMO), polyglycerol monoisostearate (PGMIS), and polyglycerol monomyristate (PGMM); (b) polyglycerol monoesters of -branched C₁₆-C₂₄ fatty acids, linear unsaturated C₁₆-C₂₂ fatty acids, or linear saturated C₁₂-C₁₄ fatty acids, such as diglycerol monooleate (for example diglycerol monoesters of C₁₈:1 fatty acids), diglycerol monomyristate, diglycerol monoisostearate, and diglycerol monoesters; (c) diglycerol monoaliphatic ethers of -branched C₁₆-C₂₄ alcohols, linear unsaturated C₁₆-C₂₂ alcohols, and linear saturated C₁₂-C₁₄ alcohols, and mixtures of these emulsifiers. See U.S. Pat. No. 5,287,207 (Dyer et al.), issued Feb. 7, 1995 and U.S. Pat. No. 5,500,451 (Goldman et al.) issued Mar. 19, 1996. Another emulsifier that may be used is polyglycerol succinate (PGS), which is formed from an alkyl succinate, glycerol, and triglycerol.

Such emulsifiers, and combinations thereof, may be added to the oil phase so that they comprise between about 1% and about 20%, in certain embodiments from about 2% to about 15%, and in certain other embodiments from about 3% to about 12% by weight of the oil phase. In certain

embodiments, coemulsifiers may also be used to provide additional control of cell size, cell size distribution, and emulsion stability, particularly at higher temperatures, for example greater than about 65° C. Examples of coemulsifiers include phosphatidyl cholines and phosphatidyl choline-containing compositions, aliphatic betaines, long chain C₁₂-C₂₂ dialiphatic quaternary ammonium salts, short chain C₁-C₄ dialiphatic quaternary ammonium salts, long chain C₁₂-C₂₂ dialkoyl(alkenoyl)-2-hydroxyethyl, short chain C₁-C₄ dialiphatic quaternary ammonium salts, long chain C₁₂-C₂₂ dialiphatic imidazolinium quaternary ammonium salts, short chain C₁-C₄ dialiphatic imidazolinium quaternary ammonium salts, long chain C₁₂-C₂₂ monoaliphatic benzyl quaternary ammonium salts, long chain C₁₂-C₂₂ dialkoyl(alkenoyl)-2-aminoethyl, short chain C₁-C₄ monoaliphatic benzyl quaternary ammonium salts, short chain C₁-C₄ monohydroxyaliphatic quaternary ammonium salts. In certain embodiments, ditallow dimethyl ammonium methyl sulfate (DTDAMMS) may be used as a coemulsifier.

Photoinitiators may comprise between about 0.05% and about 10%, and in certain embodiments between about 0.2% and about 10% by weight of the oil phase. Lower amounts of photoinitiator allow light to better penetrate the HIPE foam, which can provide for polymerization deeper into the HIPE foam. However, if polymerization is done in an oxygen-containing environment, there should be enough photoinitiator to initiate the polymerization and overcome oxygen inhibition. Photoinitiators can respond rapidly and efficiently to a light source with the production of radicals, cations, and other species that are capable of initiating a polymerization reaction. The photoinitiators used in the present invention may absorb UV light at wavelengths of about 200 nanometers (nm) to about 800 nm, in certain embodiments about 250 nm to about 450 nm. If the photoinitiator is in the oil phase, suitable types of oil-soluble photoinitiators include benzyl ketals, α -hydroxyalkyl phenones, α -amino alkyl phenones, and acylphosphine oxides. Examples of photoinitiators include 2,4,6-[trimethylbenzoyldiphosphine] oxide in combination with 2-hydroxy-2-methyl-1-phenylpropan-1-one (50:50 blend of the two is sold by Ciba Speciality Chemicals, Ludwigshafen, Germany as DAROCUR® 4265); benzyl dimethyl ketal (sold by Ciba Geigy as IRGACURE 651); α , α -dimethoxy- α -hydroxy acetophenone (sold by Ciba Speciality Chemicals as DAROCUR® 1173); 2-methyl-1-[4-(methyl thio) phenyl]-2-morpholino-propan-1-one (sold by Ciba Speciality Chemicals as IRGACURE® 907); 1-hydroxycyclohexyl-phenyl ketone (sold by Ciba Speciality Chemicals as IRGACURE® 184); bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (sold by Ciba Speciality Chemicals as IRGACURE 819); diethoxyacetophenone, and 4-(2-hydroxyethoxy)phenyl-(2-hydroxy-2-methylpropyl) ketone

(sold by Ciba Speciality Chemicals as IRGACURE® 2959); and Oligo [2-hydroxy-2-methyl-1-[4-(1-methylvinyl) phenyl]propanone] (sold by Lamberti spa, Gallarate, Italy as ESACURE® KIP EM).

The dispersed aqueous phase of a HIPE comprises water, and may also comprise one or more components, such as initiator, photoinitiator, or electrolyte, wherein in certain embodiments, the one or more components are at least partially water soluble.

One component of the aqueous phase may be a water-soluble electrolyte. The water phase may contain from about 0.2% to about 40%, in certain embodiments from about 2% to about 20%, by weight of the aqueous phase of a water-soluble electrolyte. The electrolyte minimizes the tendency of monomers, comonomers, and crosslinkers that are primarily oil soluble to also dissolve in the aqueous phase. Examples of electrolytes include chlorides or sulfates of alkaline earth metals such as calcium or magnesium and chlorides or sulfates of alkali earth metals such as sodium. Such electrolyte can include a buffering agent for the control of pH during the polymerization, including such inorganic counterions as phosphate, borate, and carbonate, and mixtures thereof. Water soluble monomers may also be used in the aqueous phase, examples being acrylic acid and vinyl acetate.

Another component that may be present in the aqueous phase is a water-soluble free-radical initiator. The initiator can be present at up to about 20 mole percent based on the total moles of polymerizable monomers present in the oil phase. In certain embodiments, the initiator is present in an amount of from about 0.001 to about 10 mole percent based on the total moles of polymerizable monomers in the oil phase. Suitable initiators include hydrogen peroxide, lauryl peroxide, t-butyl hydrogen peroxide, other suitable peroxides, ammonium persulfate, sodium persulfate, potassium persulfate, 2,2'-azobis(N,N'-dimethyleneisobutyramidine)dihydrochloride, and other suitable azo initiators, redox couples such as persulfate-bisulfate, persulfate-ascorbic acid and others. In certain embodiments, to reduce the potential for premature polymerization which may clog the emulsification system, addition of the initiator may be just after or near the end of emulsification. In certain embodiments a small amount of inhibitor may be added to inhibit polymerization during emulsification.

Photoinitiators present in the aqueous phase may be at least partially water soluble and may comprise between about 0.05% and about 10%, and in certain embodiments between about 0.2% and about 10% by weight of the oil phase. Lower amounts of photoinitiator allow light to better penetrate the HIPE foam, which can provide for polymerization deeper into the HIPE foam. However, if polymerization is done in an oxygen-containing environment, there should be enough photoinitiator to initiate the polymerization and overcome oxygen inhibition. Photoinitiators can respond rapidly and efficiently to a light source with the production of radicals, cations, and other species that are capable of initiating a polymerization reaction. The photoinitiators used in the present invention may absorb UV light at wavelengths of from about 200 nanometers (nm) to about 800 nm, in certain embodiments from about 200 nm to about 350 nm, and in certain embodiments from about 350 nm to about 450 nm. If the photoinitiator is in the aqueous phase, suitable types of water-soluble photoinitiators include benzophenones, benzils, and thioxanones. Examples of photoinitiators include 2,2'-Azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride; 2,2'-Azobis[2-(2-imidazolin-2-yl)propane]disulfate dehydrate; 2,2'-Azobis(1-imino-1-pyrrolidino-2-ethylpropane)dihydrochloride; 2,2'-Azobis[2-methyl-N-(2-hydroxyethyl)propionamide]; 2,2'-Azobis(2-methylpropionamidine)dihydrochloride; 2,2'-dicarboxymethoxydibenzalacetone, 4,4'-dicarboxymethoxydibenzalacetone, 4,4'-dicarboxymethoxydibenzalicyclohexanone, 4-dimethylamino-4'-carboxymethoxydibenzalacetone; and 4,4'-disulphoxymethoxydibenzalacetone. Other suitable photoinitiators that can be used in the present invention are listed in U.S. Pat. No. 4,824,765 (Sperry et al.) issued Apr. 25, 1989.

In addition to the previously described components other components may be included in either the aqueous or oil phase of a HIPE. Examples include antioxidants, for example hindered phenolics, hindered amine light stabilizers; plasticizers, for example dioctyl phthalate, dinonyl sebacate; flame retardants, for example halogenated hydrocarbons, phosphates, borates, inorganic salts such as antimony trioxide or ammonium phosphate or magnesium hydroxide; dyes and pigments; fluorescers; filler particles, for example starch, titanium dioxide, carbon black, or calcium carbonate; fibers; chain transfer agents; odor absorbers, for example activated carbon particulates; dissolved polymers; dissolved oligomers; and the like.

HIPE foam is produced from the polymerization of the monomers comprising the continuous oil phase of a HIPE. In certain embodiments, HIPE foams may have one or more layers, and may be either homogeneous or heterogeneous polymeric open-celled foams. Homogeneity and

heterogeneity relate to distinct layers within the same HIPE foam, which are similar in the case of homogeneous HIPE foams or which differ in the case of heterogeneous HIPE foams. A heterogeneous HIPE foam may contain at least two distinct layers that differ with regard to their chemical composition, physical properties, or both; for example layers may differ with regard to one or more of foam density, polymer composition, specific surface area, or pore size (also referred to as cell size). For example, for a HIPE foam if the difference relates to pore size, the average pore size in each layer may differ by at least about 20%, in certain embodiments by at least about 35%, and in still other embodiments by at least about 50%. In another example, if the differences in the layers of a HIPE foam relate to density, the densities of the layers may differ by at least about 20%, in certain embodiments by at least about 35%, and in still other embodiments by at least about 50%. For instance, if one layer of a HIPE foam has a density of 0.020 g/cc, another layer may have a density of at least about 0.024 g/cc or less than about 0.016 g/cc, in certain embodiments at least about 0.027 g/cc or less than about 0.013 g/cc, and in still other embodiments at least about 0.030 g/cc or less than about 0.010 g/cc. If the differences between the layers are related to the chemical composition of the HIPE or HIPE foam, the differences may reflect a relative amount difference in at least one monomer component, for example by at least about 20%, in certain embodiments by at least about 35%, and in still further embodiments by at least about 50%. For instance, if one layer of a HIPE or HIPE foam is composed of about 10% styrene in its formulation, another layer of the HIPE or HIPE foam should be composed of at least about 12%, and in certain embodiments of at least about 15%.

A HIPE foam having separate layers formed from differing HIPEs, as explained in more detail below, provides a HIPE foam with a range of desired performance characteristics. For example, a HIPE foam comprising a first and second foam layer, wherein the first foam layer has a relatively larger pore or cell size, than the second layer, when used in an absorbent article may more quickly absorb incoming fluids than the second layer. By way of example when used in an absorbent article the first foam layer may be layered over the second foam layer having relatively smaller pore sizes, as compared to the first foam layer, which exert more capillary pressure and drain the acquired fluid from the first foam layer, restoring the first foam layer's ability to acquire more fluid. HIPE foam pore sizes may range from 1 to 200 μm and in certain embodiments may be less than 100 μm . HIPE foams of the present invention having two major parallel surfaces may be from 0.05 to 10 mm thick, and in certain embodiments 2 mm to 8 mm.

The desired thickness of a HIPE will depend on the materials used to form the HIPE, the speed at which a HIPE is deposited on a belt, and the intended use of the resulting HIPE foam

The HIPE foams of the present invention are relatively open-celled. This refers to the individual cells or pores of the HIPE foam being in substantially unobstructed communication with adjoining cells. The cells in such substantially open-celled HIPE foam structures have intercellular openings or windows that are large enough to permit ready fluid transfer from one cell to another within the HIPE foam structure. For purpose of the present invention, a HIPE foam is considered "open-celled" if at least about 80% of the cells in the HIPE foam that are at least 1 μ m in size are in fluid communication with at least one adjoining cell.

In addition to being open-celled, in certain embodiments HIPE foams are sufficiently hydrophilic to permit the HIPE foam to absorb aqueous fluids, for example the internal surfaces of a HIPE foam may be rendered hydrophilic by residual hydrophilizing surfactants or salts left in the HIPE foam following polymerization, by selected post-polymerization HIPE foam treatment procedures (as described hereafter), or combinations of both.

In certain embodiments, for example when used in certain absorbent articles, a HIPE foam may be flexible and exhibit an appropriate glass transition temperature (T_g). The T_g represents the midpoint of the transition between the glassy and rubbery states of the polymer. In general, HIPE foams that have a higher T_g than the temperature of use can be very strong but will also be very rigid and potentially prone to fracture. In certain embodiments, regions of the HIPE foams of the current invention which exhibit either a relatively high T_g or excessive brittleness will be discontinuous. Since these discontinuous regions will also generally exhibit high strength, they can be prepared at lower densities without compromising the overall strength of the HIPE foam.

HIPE foams intended for applications requiring flexibility should contain at least one continuous region having a T_g as low as possible, so long as the overall HIPE foam has acceptable strength at in-use temperatures. In certain embodiments, the T_g of this region will be less than about 30° C for foams used at about ambient temperature conditions, in certain other embodiments less than about 20° C. For HIPE foams used in applications wherein the use temperature is higher or lower than ambient, the T_g of the continuous region may be no more than 10° C greater than the use temperature, in certain embodiments the same as use temperature, and in further

embodiments about 10° C less than use temperature wherein flexibility is desired. Accordingly, monomers are selected as much as possible that provide corresponding polymers having lower Tg's.

The HIPE foams of the present invention may be used as absorbent core materials in absorbent articles, such as feminine hygiene articles, for example pads, pantliners, and tampons; disposable diapers; incontinence articles, for example pads, adult diapers; homecare articles, for example wipes, pads, towels; and beauty care articles, for example pads, wipes, and skin care articles, such as used for pore cleaning.

To produce a HIPE using the above, and shown in FIG.1, an aqueous phase 10 and an oil phase 20 are combined in a ratio between about 8:1 and 140:1. In certain embodiments, the aqueous phase to oil phase ratio is between about 10:1 and about 75:1, and in certain other embodiments the aqueous phase to oil phase ratio is between about 13:1 and about 65:1. This is termed the "water-to-oil" or W:O ratio and can be used to determine the density of the resulting HIPE foam. As discussed, the oil phase may contain one or more of monomers, comonomers, photoinitiators, crosslinkers, and emulsifiers, as well as optional components. The water phase will contain water and in certain embodiments one or more components such as electrolyte, initiator, or optional components.

The HIPE can be formed from the combined aqueous 10 and oil 20 phases by subjecting these combined phases to shear agitation in a mixing chamber or mixing zone 30. The combined aqueous 10 and oil 20 phases are subjected to shear agitation produce a stable HIPE having aqueous droplets of the desired size. The emulsion making process produces a HIPE where the aqueous phase droplets are dispersed to such an extent that the resulting HIPE foam will have the desired structural characteristics. Emulsification of the aqueous 10 and oil 20 phase combination in the mixing zone 30 may involve the use of a mixing or agitation device such as an impeller, by passing the combined aqueous and oil phases through a series of static mixers at a rate necessary to impart the requisite shear, or combinations of both. Once formed, the HIPE can then be withdrawn or pumped from the mixing zone 30. One method for forming HIPEs using a continuous process is described in U.S. Pat. No. 5,149,720 (DesMarais et al), issued Sep. 22, 1992 and U.S. Pat. No. 5,827,909 (DesMarais) issued on Oct. 27, 1998.

In certain embodiments for a continuous process the HIPE can be withdrawn or pumped from the mixing zone and transported to a heating zone 50, such as a curing oven by being deposited on to a belt 40 travelling in a substantially horizontal direction. An initiator may be present in the aqueous phase, or as shown in FIG.1 an initiator 60 may be introduced during the HIPE making process, and in certain embodiments, after the HIPE has been formed but before the HIPE has been deposited on to the belt 40. The HIPE may be deposited on to the belt through one or more depositing devices 70 such as a die, sprayer, or caster. As shown in FIG.2, in the present invention two or more distinct HIPEs can be produced, which after polymerization will form two or more distinct layers in a HIPE foam, for example a first HIPE and a second HIPE, wherein each HIPE may have an individual composition (aqueous and oil phases) or individual combinations of properties, for example pore dimensions, mechanical properties, and the like, that differs from the other HIPEs. The individual HIPEs can be formed from one or more individual oil phases and one or more individual aqueous phases, and combinations thereof. For example, individual HIPEs can be formed from a single oil phase combined with 2 or more different aqueous phases, or as shown in FIG. 2 a single aqueous phase 11 combined with 2 or more individual oil phases 21, 22.

The individual aqueous 11 and oil phases 21, 22 enter separate mixing zones 31 and 32 and then are deposited the same way as individual HIPEs. For example, in a continuous process of the present invention a first die 71 can deposit one HIPE layer on to a belt 40 then the same die or a second die 72, as shown in FIG. 2, could deposit a second HIPE on top of the first HIPE. In certain embodiments, the top second HIPE may have a lower concentration of photoinitiator as compared to the bottom first HIPE such that a similar amount of radicals is formed in both HIPE layers. In another embodiment using the previously described continuous method a die could deposit HIPEs adjacently on to a belt where the individual HIPEs may or may not overlap each other, or any other means of moving one or more HIPEs from a mixing zone to produce a HIPE foam.

Examples of belts may include endless belts made of one or more metals, a resin, or combinations thereof; or sheet materials such as films that may be positioned on the belt and moving therewith. The average thickness of the HIPE, as measured from the surface of the HIPE that is in contact with the belt to the opposing HIPE surface, can be adjusted by the movement

speed of the belt, the flow of HIPE deposited on the belt, or the configuration of one or more depositing devices used to deposit the HIPE on a belt.

The belt can be any thickness or shape suitable for producing a HIPE foam. Further, the surface of the belt upon which the HIPE will be deposited, can be substantially smooth or may comprise depressions, protuberances, or combinations thereof. The protuberances or depressions may be arranged in any formation or order and can be used to provide patterns, designs, markings or the like to HIPE foam. The belt may comprise one or more materials suitable for the polymerization conditions (various properties such as heat resistance, weatherability, surface energy, abrasion resistance, recycling property, tensile strength and other mechanical strengths) and may comprise at least one material from the group including films, non-woven materials, woven materials, and combinations thereof. Examples of films include, fluorine resins such as polytetrafluoroethylene, tetrafluoroethylene-perfluoroalkylvinyl ether copolymers, tetrafluoroethylene-hexafluoropropylene copolymers, and tetrafluoroethylene-ethylene copolymers; silicone resins such as dimethyl polysiloxane and dimethylsiloxane-diphenyl siloxane copolymers; heat-resistant resins such as polyimides, polyphenylene sulfides, polysulfones, polyether sulfones, polyether imides, polyether ether ketones, and para type aramid resins; thermoplastic polyester resins such as polyethylene terephthalates, polybutylene terephthalates, polyethylene naphthalates, polybutylene naphthalates, and polycyclohexane terephthalates, thermoplastic polyester type elastomer resins such as block copolymers (polyether type) formed of PBT and polytetramethylene oxide glycol and block copolymers (polyester type) formed of PBT and polycaprolactone may be used. These materials may be used either singly or in mixed form of two or more materials. Further, the belt may be a laminate comprising two or more different materials or two or more materials of the same composition, but which differ in one or more physical characteristics, such as quality or thickness. In certain embodiments the belt or a film positioned on the belt and moving therewith may be transparent to UV light; allowing the UV light from a UV light source positioned below the belt, film or both to polymerize the monomers in a HIPE foam.

In certain embodiments, the belt 40 moves the HIPE into a heating zone 50 where the monomers present in the HIPE are polymerized. Without being bound by theory, it is believed that HIPE foam formation comprises two overlapping processes. These are the polymerization of the monomers and the formation of crosslinks between active sites on adjacent polymer backbones.

As used herein the term "polymerize" as in to polymerize monomers to form a HIPE foam, encompass both polymerization of monomers and formation of crosslinks between active sites on adjacent polymer backbones. Crosslinking provides HIPE foams with strength and integrity that is helpful to their further handling and use. The current invention involves increasing the overall level of polymerization and cross-linking, thereby reducing the amount of unpolymerized monomer in the HIPE foam. Polymerization can be initiated prior to reaching the heating zone by, for example, preparing the HIPE at a temperature sufficient to begin polymerization. However, the HIPE is polymerized beyond the point of shapability or moldability in the heating zone. Heat for the heating zone can be, for example, derived from an oven located above and below the HIPE or surrounding the HIPE. Heat can be from forced air ovens, IR heat lamps, microwave, steam or other suitable source. As an example of using steam the heat zone may be a steam tunnel wherein the HIPE is exposed to steam, thereby achieving highly efficient thermal transfer as water condenses onto the HIPE.

In certain embodiments, the temperature may be elevated in a step-wise manner so as to increase the rate of polymerization, initiate drying, or both as the HIPE becomes more completely polymerized. In addition, the curing of the HIPE may be accomplished by passing the web through a hot liquid bath composed of any hot liquid of sufficient temperature to initiate the curing of the monomers. Polymerization temperatures will vary depending on the type of emulsion being cured, the initiator being used, heat source used, and whether or not the heating zone is sealed, but will typically be above 25° C, often above 50° C. In certain embodiments, polymerization temperatures within the heating zone may reach between about 50° C. and 150° C. The HIPE is maintained in the heating zone for a time sufficient to polymerize at least 75%, preferably at least 90% of the monomers in the oil phase of the HIPE. Sufficient polymerization of the HIPE may be controlled by a combination of the initiator used, the temperature of the heat zone, the efficiency of the heat transfer in the heat zone, the rate at which the HIPE goes through the heat zone and the length of the heat zone.

Following the heat zone 50 the belt 40 moves the mostly polymerized HIPE foam to an Ultraviolet (UV) light zone 80 containing one or more sources of UV light. Exposure of the HIPE foam containing unpolymerized monomers, and in certain embodiments, one or more photoinitiators to the UV light zone 80 initiates polymerization of unpolymerized monomers in the oil phase of the HIPE foam following heat assisted polymerization. An examples of a source

of UV light is a UV lamp. There may be one or more sources of UV light used to polymerize the HIPE monomers. A UV light source may be positioned above or below the belt. The sources may be the same or differ. For example, the sources may differ in the wavelength of the UV light they produce or in the amount of time a HIPE is exposed to the UV light source. The UV light wavelength in the range from about 200 to about 800 nm, and in certain embodiments from about 250 nm to 450 nm, overlaps to at least some degree with the UV light absorption band of the photoinitiator and is of sufficient intensity and exposure duration to substantially complete the polymerization of the unpolymerized monomers. Without being limited to theory it is believed that due to the tendency of emulsions, such as HIPEs, to scatter light, in certain embodiments, long wavelengths in this range should be used because they are better able to penetrate the emulsions. Following the application of UV light the HIPE foam contains less than 400 ppm, in certain embodiments less than 100 ppm, and in certain other embodiments less than detection limits ppm residual or unpolymerized monomer, in less than about 10 minutes, less than about 30 seconds, less than about 10 seconds, or less than about 1 second. In certain embodiments, the entire emulsion making, polymerization, and monomer reduction processes will take less than 20 min, in certain other embodiments in further embodiments less than 15 minutes, and in still further embodiments less than 5 minutes.

Following polymerization, the resulting HIPE foam is saturated with aqueous phase that needs to be removed to obtain substantially dry HIPE foam. In certain embodiments, HIPE foams can be squeezed free of most of the aqueous phase by using compression, for example by running the HIPE foam through one or more pairs of nip rollers 90. The nip rollers 90 can be positioned such that they squeeze the aqueous phase out of the HIPE foam. The nip rollers 90 can be porous and have a vacuum applied from the inside such that they assist in drawing aqueous phase out of the HIPE foam. In certain embodiments, nip rollers 90 can be positioned in pairs, such that a first nip roller 90 is located above a liquid permeable belt 40, such as a belt 40 having pores or composed of a mesh-like material, and a second opposing nip roller 91 facing the first nip roller 90 and located below the liquid permeable belt 40. One of the pair, for example the first nip roller 90 can be pressurized while the other, for example the second nip roller 91, can be evacuated, so as to both blow and draw the aqueous phase out of the HIPE foam. The nip rollers may also be heated to assist in removing the aqueous phase. In certain embodiments, nip rollers are only applied to non-rigid HIPE foams, that is HIPE foams whose walls would not be destroyed by compressing the HIPE foam. In yet a further embodiment, the surface of the nip

rollers may contain irregularities in the form of protuberances, depressions, or both such that a HIPE foam can be embossed as it is moving through the nip rollers. When the HIPE has the desired dryness it may be cut or sliced into a form suitable for the intended application.

In certain embodiments, in place of or in combination with nip rollers, the aqueous phase may be removed by sending the HIPE foam through a drying zone 100 where it is heated, exposed to a vacuum, or a combination of heat and vacuum exposure. Heat can be applied, for example, by running the foam through a forced air oven, IR oven, microwave oven or radiowave oven. The extent to which a HIPE foam is dried depends on the application. In certain embodiments, greater than 50% of the aqueous phase is removed. In certain other embodiments greater than 90%, and in still other embodiments greater than 95% of the aqueous phase is removed during the drying process.

EXAMPLES

Preparation of High Internal Phase Emulsions (HIPE) and their subsequent polymerization into absorbent foams are illustrated in the following example. The HIPE samples comprised two layers –a bottom layer and a top layer, wherein the bottom layer had a smaller average pore size of 30 microns and the top layer had a larger average pore size of about 80 microns.

A. SMALL CELL LAYER HIPE FORMATION

Small Cell Layer Components:

To prepare the bottom small cell layer of the HIPE the aqueous phase, oil phase, and initiator contained the following components as shown below in Table 1.

TABLE 1

Oil Phase	% Amount Based on Total Weight of Oil Phase
2-ethylhexyl acrylate (EHA)	36.7%
2-ethylhexyl methacrylate (EHMA)	37.61%
ethyleneglycol dimethacrylate (EGDMA)	17.43%
Dimethyl ammonium methyl sulfate (DTDMAMS)	0.93%

Polyglycerol succinate (PGS)	6.48%
Photoinitiator – Darocur 1173*	0.99%
*BASF Corporation, Florham Park, NJ	
Aqueous Phase	% Amount Based on Total Weight of Aqueous Phase
CaCl ₂	3.85%
Water: oil ratio	26:1
Initiator in Aqueous Solution	% Amount Based on Total Weight of Aqueous Solution
Potassium Persulfate	3.50%
Water: oil ratio	1:1

Equipment:

The smaller celled HIPE is prepared in equipment comprising static mixers and a recirculation pump. The static mixers are manufactured by Sulzer (Sulzer Ltd. Zürcherstrasse 14, 8401 Winterthur, Switzerland). Forty-eight elements of SMX style mixers, sized to fit within a standard 1.5” diameter pipe were used as the primary mixing loop elements. Four sets of twelve elements welded so that each sequential segment is rotated 90° are fitted into independent sections of pipe fitted with 2” tri-clover quick disconnect piping flanges.

The aqueous phase is introduced into a recirculation loop via a modified 1 7/8” tubing 90° elbow with 2” tri-clover quick disconnect piping flanges, with a 1/2” pipe welded into the elbow to form an annulus such that the aqueous phase is entering the discharge end of the elbow, concurrent with the recirculation flow, both proceeding vertically downward. The end of the annular 1/2” pipe is internally threaded and a set screw with a 17/64” hole drilled in it to direct the aqueous incoming flow toward the static mixers.

Three sections of the SMX containing pipes, vertically oriented, follow the aqueous introduction elbow. Then the flow is directed by two elbows, both 1 7/8” tubing elbows with tri-clover fittings, first a 90° and then a 45°. The final section of SMX mixers is connected upward at a

convenient angle to have its discharge at about the same elevation as the inlet fittings to the recirculation pump.

The discharge from the final SMX mixer segment goes through a conical reducer to a 7/8" Tee. (Tee A). One side of the Tee is connected to a same diameter elbow fitted with a temperature probe, which then connects to another 7/8" Tee (Tee B). One side of Tee B connects to a Teflon lined hose 1 1/4" in diameter and 48" long. The hose connects to the stem side of a 7/8" Tee (Tee C). One side of Tee C's cross piece is connected upwardly to the inlet of the recirculation pump, a Waukesha Model 030 U2 lobe pump (Waukesha Cherry-Burrell Company, Delavan, Wisconsin). The other side of Tee C's cross piece is connected downwardly to a 7/8" to 5/8" conical reducer. The small end of the conical reducer uses a 3/4" tri-clover connection to a custom made section of 3/8" stainless steel tubing with a 3/4" tri-clover fitting welded onto the tube by first drilling a matching diameter hole in a 3/4" tri-clover end cap. This allows the tube to project into and past the intersection of the stem side of Tee C to the cross piece of Tee C. The end of the tube projecting inward toward the Waukesha pump is internally threaded and fitted with a set screw into which a 7/64" hole has been drilled. The other end of the tube is fitted with a 3/4" tri-clover fitting facing downward fabricated in the same way as mentioned above.

The discharge from the Waukesha pump transfers to a 1 3/8" diameter by 6" spool piece with a small port for a temperature probe and tri-clover sanitary fittings, followed by six elements of 1 1/4" Kenics helical static mixers (Chemineer Inc., Dayton, Ohio) in a section of pipe just long enough to contain them, with ends fitted with tri-clover fittings. Next is a 1 3/8" 90° tubing elbow with tri-clover fittings, a 1 3/8" diameter by 6" spool piece, a second 1 3/8" diameter by 6" spool piece fitted with a means to vent gasses from this, the high spot of the total first stage mixing assembly, and then a 1 3/8" to 1 7/8" conical spool piece connected to the aqueous injector elbow mentioned above. This completes the description of the mixing stage for the small celled HIPE.

It has been found that the supply pumps or the recirculation pump can lead to cyclic pulsations of flow. To mitigate that behavior, the free end of Tee A in the above description can be connected to a surge dampener assembly containing a pressure transducer to monitor pressures and a chamber which can be vented to allow for different volumes of air to be maintained in the chamber in order to dampen the pressure fluctuations.

The discharge from the mixing stage issues from Tee B through a Teflon lined 1 ¼" braided steel hose to a 1" piping elbow fitted with a similar injector tube arrangement to the aqueous injector elbow described above, but with 3/8" tubing instead of ½", and fitted with a set screw with a 3/32" drilled hole. The initiator solution is introduced through this arrangement. The discharge of the HIPE and the centrally introduced, collinear initiator stream flow are directed to a series of three segments of twelve elements of SMX mixers sized to fit in a 1" pipe section with tri-clover fittings. The flow then proceeds through a conical reducer into a custom coat hanger style die. The die then deposits the HIPE unto an endless belt moving at a speed of 10 meters per minute.

HIPE Formation:

To start this equipment, aqueous phase is heated to about 80 C and delivered to the aqueous injector point described above at a flow rate of about 2 liters/minute to conveniently fill the equipment and to pre heat the equipment to a temperature indicated by the temperature indicating devices with the loop of about 65C. The Waukesha pump is started at a theoretical rate of 2 liters per minute when aqueous phase is observed to be coming out of the die, which is higher than the pump, so that the pump is not run dry.

When the equipment temperature is reached, the oil phase is then delivered to the oil phase injector at a rate of 0.5 kilograms/minute. (Aqueous phases are metered in liters per minute and the oil phase is referred to in kilograms per minute in order to describe the theoretical density of the polymerized HIPE foam. This also means that one can change the salt concentration or salt type in the aqueous phase and still make the same density product without re-calculating flow rates in kilograms to accomplish the desired product). The water to oil ratio at this stage of startup is then 4:1. After a period of about 5 minutes from the first introduction of oil phase, low viscosity HIPE can be observed issuing from the die. At that point the aqueous temperature setpoint is adjusted to about 72C and the flow rate is uniformly increased from 2 liters per minute to 8.107 liters per minute over a period of 3 minutes. Only the aqueous phase temperature is controlled, since it is >92% of the total mass of HIPE. The recirculation pump, starting simultaneously with the start of the increase in aqueous phase flow, is uniformly increased in speed to yield a pumping rate of 28 liters per minute over a period of 2 minutes. The oil phase flow, also beginning at the same time as the increase in aqueous phase flow, is decreased uniformly to a flow rate of 0.313 kg/ minute over a period of 5 minutes. Sodium acrylate flow at

0.031 liters/minute is comingled with the aqueous flow prior to the introduction to the mixing loop and is generally started during the aqueous flow rate ramp. At equilibrium, the water to oil ratio at the discharge from the recirculation loop is 26:1. The HIPE issuing from the die at the end of the flow ramps is very thick and very white. About 2 minutes after the completion of all of the flow ramps, the initiator is introduced at a flow rate of 0.313 liters per minute, bringing the total water to oil ratio to 27:1. When deposited on the belt that transports the HIPE to the curing chamber with the belt running at 10 meters per minute the resulting layer of HIPE is approximately 2.5 mm thick.

B. LARGE CELL LAYER HIPE FORMATION

Large Cell Layer Components:

To prepare the top large cell layer of the HIPE the aqueous phase, oil phase, and initiator contained the following components as shown below in Table 2.

TABLE 2

Oil Phase	% Amount Based on Total Weight of Oil Phase
2-ethylhexyl acrylate (EHA)	72.02%
ethyleneglycol dimethacrylate (EGDMA)	21.51%
dimethyl ammonium methyl sulfate (DTDMAMS)	0.70%
Polyglycerol monoisostearate (PGMIS)	5.61%
Photoinitiator – Darocur 1173*	0.99%
*BASF Corporation, Florham Park, NJ	
Aqueous Phase	% Amount Based on Total Weight of Aqueous Phase
CaCl ₂	3.85%
Water: oil ratio	22:1
Initiator in Aqueous Solution	% Amount Based on Total Weight of Aqueous Solution
Potassium Persulfate	3.50%
Water: oil ratio	2:1

Equipment:

The larger celled HIPE is prepared in equipment comprising two sets of static mixers and two recirculation pumps in two loop arrangements. The static mixers are manufactured by Sulzer (Sulzer Ltd Zürcherstrasse 14 , 8401 Winterthur, Switzerland). Forty-eight elements of SMX style mixers, sized to fit within a standard 2" diameter pipe are used as the primary mixing loop elements. Four sets of twelve elements welded so that each sequential segment is rotated 90° are fitted into independent sections of pipe fitted with 2.5" tri-clover quick disconnect piping flanges.

The aqueous phase is introduced into the recirculation loop via a modified 2 3/8" tubing 90° elbow with 3" tri-clover quick disconnect piping flanges, with a 1/2" pipe welded into the elbow to form an annulus such that the aqueous phase is entering the discharge end of the elbow, concurrent with the recirculation flow, both proceeding vertically upward at an angle of about 10° to the horizontal.

The end of the annular 1/2" pipe is internally threaded and a set screw with a 3/8" hole drilled in it to direct the aqueous incoming flow toward the static mixers. A spool piece, 2 3/8" tubing, 6" long, with 3" tri-clover fittings connects the injector elbow to two sections of the SMX containing pipes, oriented upward at about 10° to the horizontal. Then the flow is turned to the reverse by two elbows, both 90° 2 3/8" tubing elbows with tri-clover fittings. The final two sections of SMX mixers are connected to a conical adaptor that starts at 2 3/8" and expands to 2 7/8". The conical adaptor connects to the stem end of a 2 7/8" tubing Tee (Tee A) fitted with a pressure transducer in the middle of the intersection between the stem and cross piece of the Tee. One side of Tee A connects to a 2 7/8" to 1 3/8" conical adaptor, and then to a 1 3/8", 90° elbow, then two 1 3/8" 45° elbows. The use of multiple elbows facilitates the fitting together of the large number of piping segments. From the 45° elbows, the flow continues to a 1 3/8" diameter, 2" long spool piece, followed by a 1 5/16" diameter, 26 1/4" spool piece into the stem side of a 1 3/8" tubing Tee (Tee B). The upper cross opening of Tee B connects to the oil injector assembly, comprising a 1 3/8" to 5/8" conical spool piece connected to an injector similar to the one mentioned above for the smaller celled HIPE oil injector. The lower cross opening of Tee B is attached to a Waukeshaw Model 30 U2 lobe pump. The discharge from the Waukeshaw pump connects to a 1 3/8", 90° elbow and then to six elements of Kenics helical static mixers in a 1 1/4" pipe. A 1 3/8", 90° elbow and then a 1 3/8", 45° elbow are next, and then another six element

section of Kenics helical static mixers in a 1 1/4" pipe. After that, a 1 3/8" spool piece with a temperature probe fitting and a 1 3/8", 90° elbow and finally a 1 3/8" to 2 3/8" spool piece connect to the aqueous injector equipped 2 3/8" tubing 90° elbow.

The other cross exit of Tee A connects to a cross piece of the secondary aqueous injector Tee, Tee C (2 7/8"). The aqueous injector tube, 5/8", enters the top of the Tee directed to be annular to the stem side of the Tee, and is fitted with a set screw drilled with a 5/16" hole. The stem side of Tee C connects to two 2 1/2" standard pipe sections of twelve elements of SMX static mixers, and then to two 2 7/8" 90° tubing elbows directing the flow back toward Tee C, but above it due to the approximately 10° upward slant both the outward bound and inward bound piping section have relative to horizontal. This arrangement was chosen to minimize entrained air in the mixers, and avoids the need for venting as is used in the smaller celled HIPE setup. The last two section of 2 1/2" SMX mixers discharge their flow into another 2 7/8" tubing Tee equipped with a pressure transducer, again at the intersection of the cross and stem pieces of the Tee, Tee D. One side of the Tee D cross piece connects to a 2 7/8" 90° tubing elbow and then into a Waukeshaw Model 130 U2 lobe pump. The lower discharge of the pump connects to a 2 7/8" 90° tubing elbow with a temperature probe fitting and connects to the cross piece end of a 2 7/8" tubing Tee, Tee E. The other cross piece end of Tee E connects to a cross piece end of Tee C, completing the second mixing stage loop.

The stem side of Tee E connects to 2 7/8" to 1 3/8" conical reducer and then to a 1 3/8" 90° tubing elbow, and then to a surge dampener assembly similar to the one described in the aforementioned small celled HIPE setup. The remaining end of Tee D similarly goes to a 2 7/8" 90° tubing elbow and then to a 2 7/8" to 1 3/8" conical reducer and then to the cross piece side of a 1 3/8" tubing Tee, Tee G. The other cross piece end of Tee G goes to another surge dampener, while the stem side of Tee G goes to a 1 3/8" x 33" Teflon lined flex hose.

The flex hose connects to the initiator mixer assembly through a 1 3/8" 90° tubing elbow equipped with a 3/8" injector tube equipped with a 1/4" set screw with a 1/8" hole. The initiator and HIPE are then mixed in forty-eight elements of SMX static mixers sized to fit within a 1.75" diameter pipe. Again, twelve elements are welded together for each of four piping segments. The HIPE then passes through a conical reducer to a coat hanger style die, and the HIPE waterfalls onto the smaller cell sized HIPE passing underneath the die.

HIPE Formation:

To start up the system, aqueous phase is delivered to the first stage injector at a rate of 2 liters per minute at a temperature of about 80 C, and the second injector at a rate of 1 liter per minute at the same temperature. When aqueous phase is observed coming out of the die, which is higher than any of the pumps, the pumps are started. When the internal temperature indicated by the temperature probes all exceed 65 C, the oil phase is introduced to the oil injector at a rate of 0.50 kg/minute. After several minutes, when HIPE is observed issuing from the die, the first aqueous temperature target is shifted to 75 C and the flow rate changed to 2.828 liters per minute uniformly over a time of 3 minutes. At the same time the oil phase flow rate is lowered to 0.202 kg/minute over a period of 5 minutes, the first recirculation pump is increased uniformly to 8 liters per minute over 3 minutes and the sodium acrylate solution feed is started at a flow rate of 0.02 liters per minute, mixing with the aqueous phase prior to introduction into the mixing loop. After the flow rate changes are completed, the second aqueous flow is increased from 1 liter/minute to 1.596 liters per minute over a period of two minutes.

At the completion of the second aqueous flow ramp, the initiator solution is introduced to the initiator injector at a flow rate of 0.404 liters per minute. The HIPE provided to the 0.33 meter wide die is then at an internal phase ratio of 24:1, and the layer thickness when provided on top of the smaller celled HIPE passing by at 10 meters per minute is 1.5 mm.

The HIPE is then transferred by the belt to a curing oven for polymerization of the monomers. The internal temperature of the oven is maintained at about 100°C. The HIPE resides in the curing oven for about 8 minutes.

Following the curing oven the HIPE is passed under (at a speed of 10 meters per minute) a UV lamp (I300MB irradiator using P300MT power supply; Fusion UV Systems, Inc., Gaithersburg, Maryland) equip with a 4" long 300W/inch Fusion H+ bulb in conjunction with a LC-6B bench-top conveyor (Fusion UV Systems, Inc.).

Quantitative light measurements for a single pass under the UV lamp are shown in Table 3. The measurements were taken with a Power Puck (10 Watt, EIT, Sterling, Va.). To simulate multiple passes under a UV lamp; once the sample has passed under the UV lamp it was removed from

the belt and then placed back on the belt, such that the sample would pass under the UV lamp again. This process was then repeated as necessary.

TABLE 3

First UV Lamp		
Spectral Range	Joules/cm ²	Watts/cm ²
UVA	1.46	3.37
UVB	0.49	1.11
UVC	0.04	0.09
UVV	0.95	2.08

C. TEST METHODS

Four HIPE foam samples (including both the top and bottom layer) produced by the method described above were measured to determine the concentration of residual (unpolymerized) monomers, using a gas chromatograph (GC) with a capillary column and a flame ionization detector (FID). Excessive levels of unpolymerized monomers are indicative of problems in the method used to produce HIPE foam. Monomers measured in this method include ethylhexyl acrylate (EHA), ethylhexyl methacrylate (EHMA), and ethylene glycol dimethacrylate (EGDMA).

Equipment

Gas Chromatograph... Agilent G2630B – 6850 Series with flame ionization detector (Agilent Technologies, Wilmington, DE), or equivalent.

Autosampler Agilent G2880B – 6850 Series (Agilent Technologies), or equivalent.

GC Control Station Agilent G1875BA ChemStation PC Bundle (Agilent Technologies), or equivalent.

Capillary Column..... J&W Scientific DB-5, 30 m x 0.32 mm I.D. with 0.25 um film (Agilent Technologies - part no. 123-5032), or equivalent.

Injector..... 1 uL splitless injector.

Balance Analytical balance with resolution of 0.1 mg

- .Pipette, variable..... Capable of delivering 0.25, 0.50, and 1.0 mL aliquots (such as VWR cat. no. 83009-170 variable volume 100 – 1000 uL pipette).
- Vial, 40 mL CS200 clear glass vials (VWR cat. no. 80076-562), with Teflon-lined plastic caps (VWR cat. no. 16161-213), or equivalent.
- Vial, 2 mL..... Clear glass vials (VWR cat. no. 66030-002), with septum caps (VWR cat. no. 69400-043), or equivalent.
- Cyclohexane..... HPLC grade, 99.9+ % purity (Sigma-Aldrich cat. no. 270628).
- EHA Standard (Sigma-Aldrich cat. no. 290815).
- EHMA Standard (Sigma-Aldrich cat. no. 290807).
- EGDMA Standard (Sigma-Aldrich cat. no. 335681).
- Dispenser..... EMD Optifix Solvent-50 bottle-top dispenser for cyclohexane (EMD Chemicals, Inc., Gibbstown, NJ - part no. 10108148-1), or equivalent.
- Helium Gas..... GC grade (ultra-high purity).
- Hydrogen Gas GC grade (ultra-high purity).
- Nitrogen Gas GC grade (ultra-high purity).
- Air GC grade (ultra-high purity).
- Transfer Pipets Disposable plastic pipets, such as Samco cat. no. 232 (Samco Scientific Corp., San Fernando, CA), or equivalent.

Test Procedure

GC Operating Conditions

- Inlet Temp. 280° C
- Injection Volume 1 uL
- Purge Time 30 s
- Purge Flow 30 mL/min Helium
- Column Flow..... 1.5-3.0 mL/min Helium

Initial Temp. 90 °C

Initial Time 17-18 min

Detector Temp..... 300 °C

Detector Gas Flows.... 20 mL/min Nitrogen (makeup); 30 mL/min Hydrogen; 400 mL/min Air

EHA Ret. Time 9.5-11.5 minutes

EHMA Ret. Time..... 11.8-15.3 minutes

EGDMA Ret. Time ... 12.0-15.8 minutes

Calibration

1. Weigh 50 +/- 5 mg of EHA Standard (recording the actual weight to the nearest 0.1 mg) into a 50 mL volumetric flask, dilute to volume with cyclohexane, stopper, and mix well.
2. Weigh approximately 50 +/- 5 mg of EHMA Standard (recording the actual weight to the nearest 0.1 mg) into a separate 50 mL volumetric flask, and dilute to volume with cyclohexane, stopper, and mix well.
3. Weigh approximately 50 +/- 5 mg of EGDMA Standard (recording the actual weight to the nearest 0.1 mg) into a separate 50 mL volumetric flask, and dilute to volume with cyclohexane, stopper, and mix well.
4. Into a single 25 mL volumetric flask, pipette 1.0 mL from each of the three flasks prepared above, dilute to volume with cyclohexane, stopper, and mix well (resulting in a combined standard containing 40 +/- 4 ug/mL of EHA, EHMA, and EGDMA).
5. Pipette 0.25 mL from the solution prepared in Step 4 into a 50 mL volumetric flask, dilute to volume with cyclohexane, stopper, and mix well (resulting in a combined 0.2 ug/mL standard).
6. Pipette 0.25 mL from the solution prepared in Step 4 into a 25 mL volumetric flask, dilute to volume with cyclohexane, stopper, and mix well (resulting in a combined 0.4 ug/mL standard).

7. Pipette 0.25 mL from the solution prepared in Step 4 into a 10 mL volumetric flask, dilute to volume with cyclohexane, stopper, and mix well (resulting in a combined 1.0 ug/mL standard).
8. Pipette 0.50 mL from the solution prepared in Step 4 into a 10 mL volumetric flask, dilute to volume with cyclohexane, stopper, and mix well (resulting in a combined 2.0 ug/mL standard).
9. Pipette 1.0 mL from the solution prepared in Step 4 into a 10 mL volumetric flask, dilute to volume with cyclohexane, stopper, and mix well (resulting in a combined 4.0 ug/mL standard).
10. Fill six separate 2 mL vials with the following: (1) = cyclohexane only (blank); (2) = 0.2 ug/mL standard; (3) = 0.4 ug/mL standard; (4) = 1.0 ug/mL standard; (5) = 2.0 ug/mL standard; (6) = 2.0 ug/mL standard.
11. Tightly cap each vial with a septum cap and load the vials in the autosampler (ensuring to maintain the (1) through (6) order).
12. Initiate the GC analysis program.
13. Based on the actual weights of EHA, EHMA, and EGDMA recorded in steps 1-3 above, combined with the results from analysis of the 6 standard vials from step 12, utilize the GC's linear regression calibration program to generate standard curves of Peak Area vs. Concentration for each monomer.

Sample Testing

1. Use a razor knife to obtain a HIPE foam specimen strip weighing 0.20 – 0.40 g.
2. Weigh the strip on the analytical balance and record the weight (in grams) to the nearest 0.1 mg.
3. Use a scissors to cut the strip into small pieces (approximately 1 cm x 1 cm) and transfer the pieces into a 40 mL vial.
4. Use the bottle-top dispenser to add 30 mL of cyclohexane to the vial.

5. Tightly cap the vial and invert 3 times, ensuring all the specimen pieces are thoroughly wetted, to initiate extraction of residual monomers into cyclohexane.
6. Store the vial undisturbed for at least 16 hours to allow extraction to continue.
7. Invert the vial 3 more times to complete the extraction phase.
8. Use a fresh (unused) disposable pipet to fill a 2 mL vial with cyclohexane extract from the 40 mL vial into a 2 mL vial.
9. Tightly cap the 2 mL vial and load the vial into the GC sampler.
10. Initiate the GC analysis program.

Reporting

Program the GC so the output is in units of $\mu\text{g/mL}$. Multiply this output by 30 mL, then divide the product by the sample weight (g) from step 2 above, giving a result in units of $\mu\text{g/g}$. Report the EHA, EHMA, and EGDMA concentration to the nearest whole $\mu\text{g/g}$.

The four HIPE samples prepared and tested as described above were tested for levels of unpolymerized ethylhexyl acrylate (EHA) monomer, the results of which are shown in the graph of FIG. 3. The levels of unpolymerized EHA monomer were measured and averaged between the four samples and depicted in the graph of FIG. 3. The graph shows following polymerization in the curing oven the samples had an average level of unpolymerized EHA monomer of about 1400 ppm. Following exposure of the HIPE samples to UV light the amount of unpolymerized EHA monomer decreased to almost undetectable amounts following continued exposure to UV light; demonstrating that the methods of the present invention reduce the amount of unpolymerized monomer following polymerization of a HIPE to a HIPE foam.

The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is

intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as “40 mm” is intended to mean “about 40 mm.”

Every document cited herein, including any cross referenced or related patent or application, is hereby incorporated herein by reference in its entirety unless expressly excluded or otherwise limited. The citation of any document is not an admission that it is prior art with respect to any invention disclosed or claimed herein or that it alone, or in any combination with any other reference or references, teaches, suggests or discloses any such invention. Further, to the extent that any meaning or definition of a term in this document conflicts with any meaning or definition of the same term in a document incorporated by reference, the meaning or definition assigned to that term in this document shall govern.

While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.

CLAIMS

What is claimed is:

1. A High Internal Phase Emulsion foam formed by polymerizing a High Internal Phase Emulsion comprising:
 - a) an oil phase comprising
 - i) monomer;
 - ii) cross-linking agent;
 - iii) emulsifier;
 - b) aqueous phase;
 - c) photoinitiator;wherein the High Internal Phase Emulsion foam comprises less than 400 ppm unpolymerized monomer.
2. The High Internal Phase Emulsion foam of claim 1 comprising less than 100 ppm unpolymerized monomer.
3. The High Internal Phase Emulsion of claim 1 or 2, wherein the photoinitiator is present in an amount between about 0.05% and 10% photoinitiator by weight of the oil phase.
4. The High Internal Phase Emulsion of any of the preceding claims, wherein the photoinitiator absorbs UV light at wavelengths of about 200 nm to about 800nm.
5. The High Internal Phase Emulsion of any of the preceding claims, wherein the photoinitiator is at least one of benzyl ketals, α -hydroxyalkyl phenones, α -amino alkyl phenones, or acylphospine oxides.
6. The High Internal Phase Emulsion of any of the preceding claims, wherein the aqueous phase comprises an initiator, preferably wherein the initiator is at least one of ammonium persulfate, sodium persulfate, potassium persulfate, or 2,2'-azobis(N,N'-dimethyleneisobutyramidine)dihydrochloride.

7. The High Internal Phase Emulsion of any of the preceding claims, wherein monomer is at least one of alkyl acrylate or alkyl methacrylate, preferably wherein the monomer is at least one of ethylhexyl acrylate, butyl acrylate, hexyl acrylate, octyl acrylate, nonyl acrylate, decyl acrylate, isodecyl acrylate, tetradecyl acrylate, benzyl acrylate, nonyl phenyl acrylate, hexyl methacrylate, 2-ethylhexyl methacrylate, octyl methacrylate, nonyl methacrylate, decyl methacrylate, isodecyl methacrylate, dodecyl methacrylate, tetradecyl methacrylate, or octadecyl methacrylate.
8. The High Internal Phase Emulsion of any of the preceding claims, wherein emulsifier is at least one of sorbitan monoesters of branched C₁₆-C₂₄ fatty acids; linear unsaturated C₁₆-C₂₂ fatty acids; linear saturated C₁₂-C₁₄ fatty acids, polyglycerol monoesters of -branched C₁₆-C₂₄ fatty acids, linear unsaturated C₁₆-C₂₂ fatty acids, linear saturated C₁₂-C₁₄ fatty acids, diglycerol monoaliphatic ethers of -branched C₁₆-C₂₄ alcohols, linear unsaturated C₁₆-C₂₂ alcohols, or linear saturated C₁₂-C₁₄ alcohols.

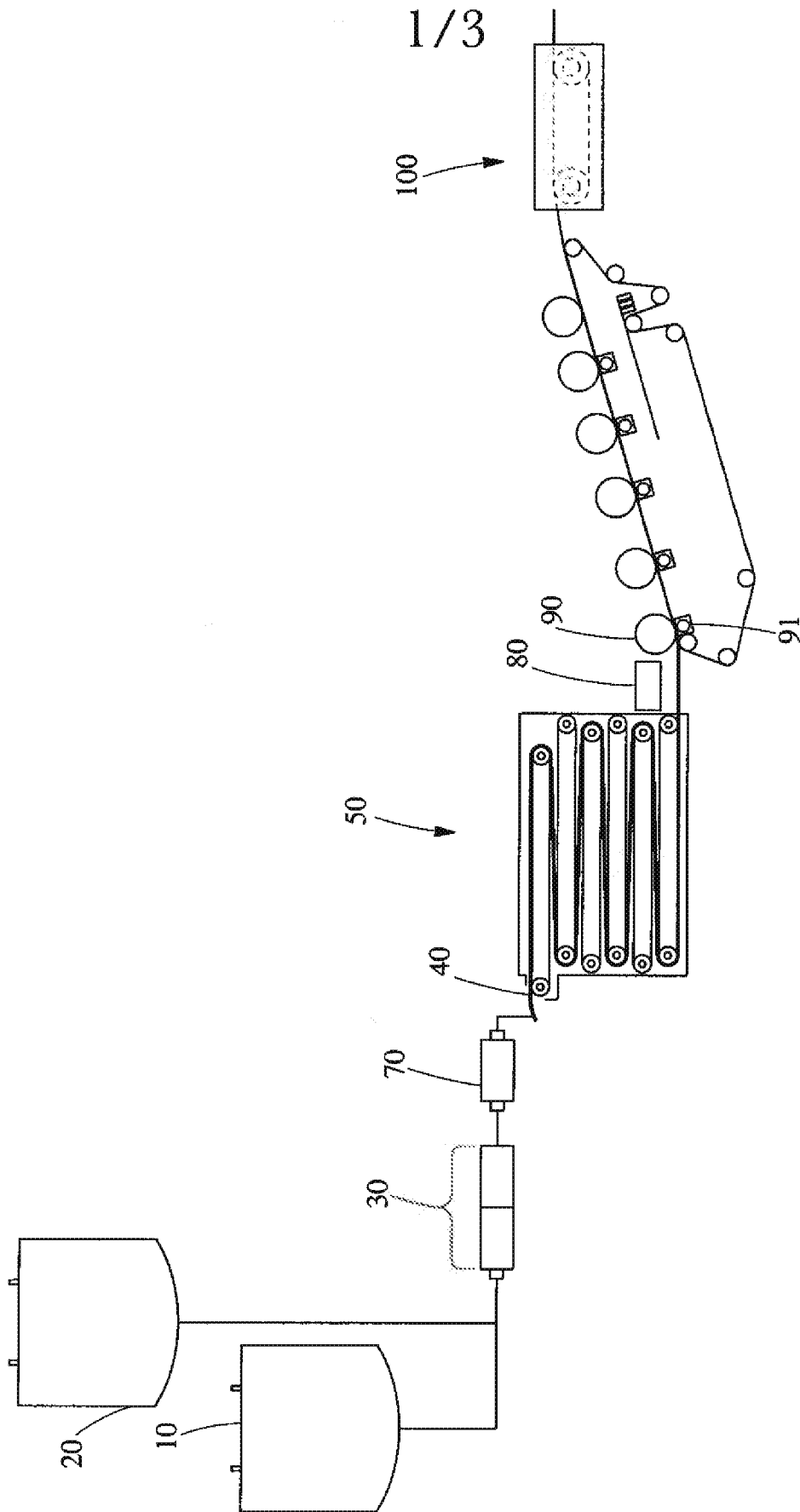


Fig. 1

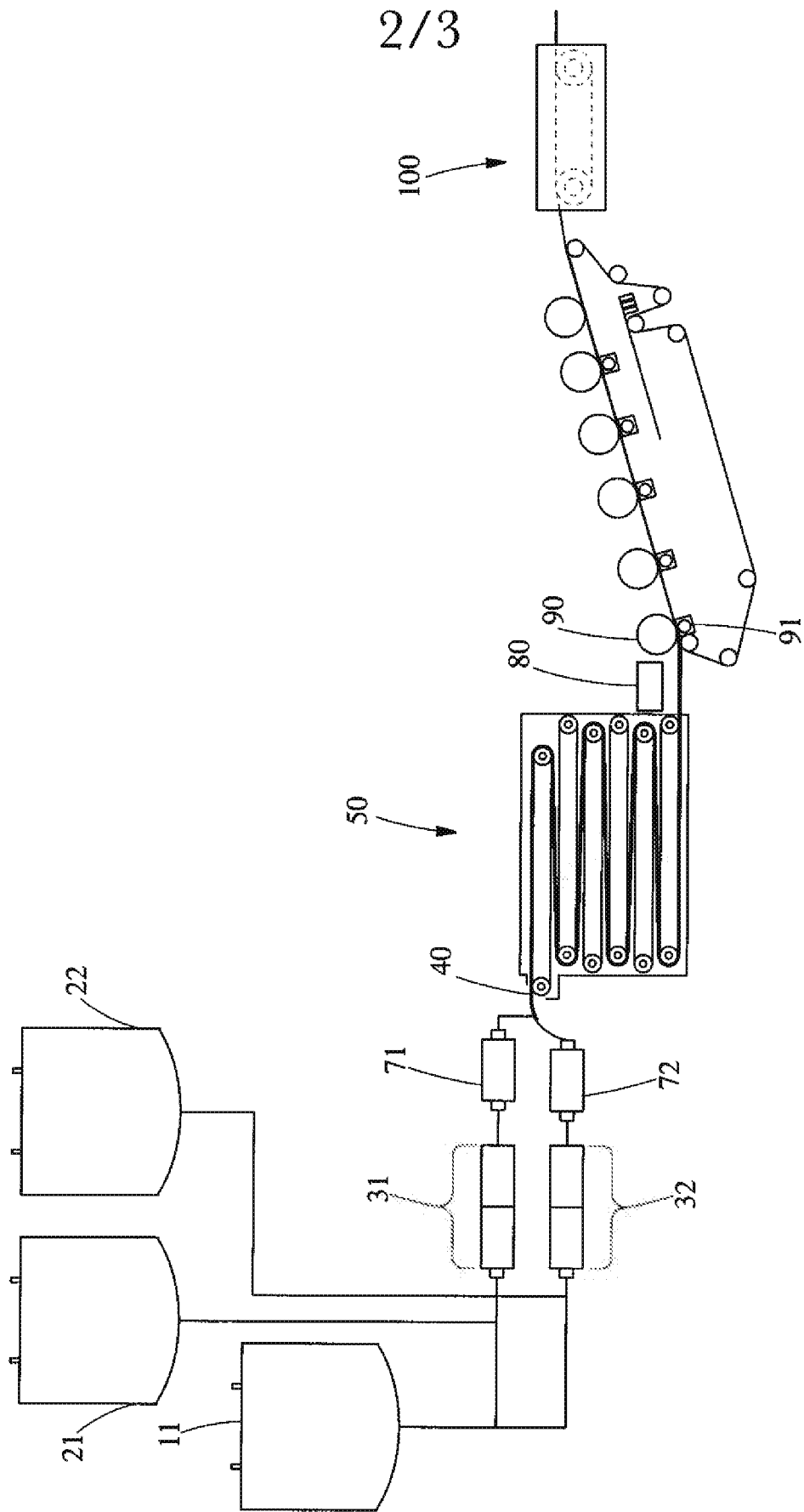


Fig. 2

3/3

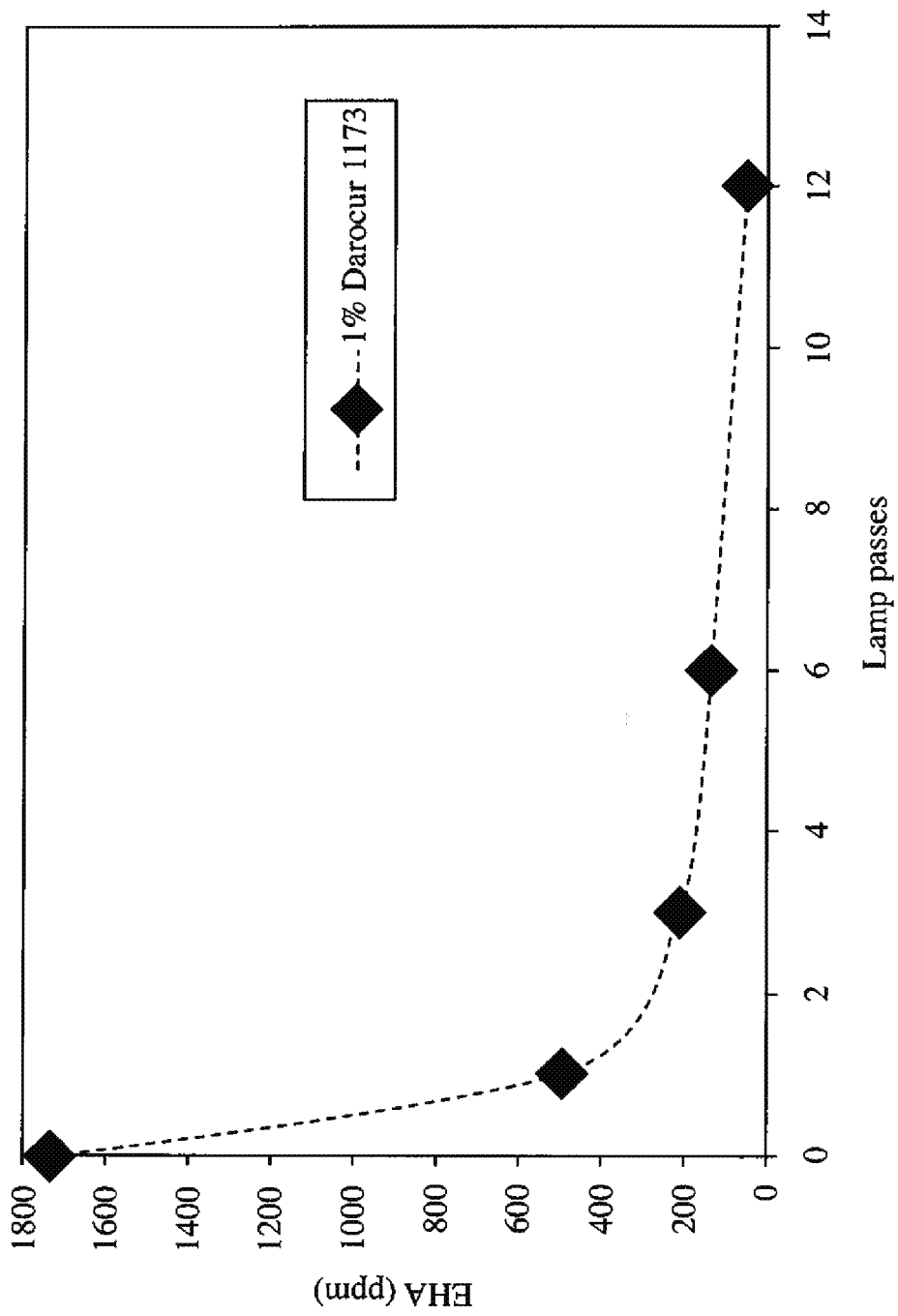


Fig. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/060996

A. CLASSIFICATION OF SUBJECT MATTER INV. C08J9/28 C08F2/24 C08F2/48 C08F2/32 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) C08J C08F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 750 261 B1 (CLEAR SUSANNAH C [US] ET AL) 15 June 2004 (2004-06-15) column 5, line 39 - line 63; claims 1-16; examples 1-15 -----	1-8
X	WO 01/21693 A1 (3M INNOVATIVE PROPERTIES CO [US]) 29 March 2001 (2001-03-29) page 21, line 6 - line 28; claims 1-16; examples 1-29 -----	1-8
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed		"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family
Date of the actual completion of the international search 23 March 2011		Date of mailing of the international search report 04/04/2011
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Gold, Josef

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2010/060996

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