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(54) Title: PROCESS FOR PREPARING LOW DENSITY POROUS CROSSLINKED POLYMERIC MATERIALS

(57) Abstract

In a process for the preparation of a low density porous crosslinked polymeric material by polymerizing a water-in-oil high internal phase emulsion, curing time of the monomers in the emulsion can be reduced without adversely affecting polymer properties by first advancing one or more of the monomers. All or a portion of the monomers are advanced in the presence of an advancement initiator or a free-radical-producing radiation source for about 5 % to about 95 % of the time effective to form a solid. Then, a water-in-oil high internal phase emulsion is formed with the advanced monomers and optionally additional monomers or the advanced monomers are added to a water-in-oil high internal phase emulsion containing other monomers. The emulsions containing the advanced monomers are cured. The process provides an improved method to incorporate volatile monomers in the porous polymeric material. The curing time is further reduced by carrying out the polymerization and crosslinking in the presence of an alkylperoxycarbonate or an alkylperoxycarboxylate polymerization initiator that is branched at the 1-position and/or the α-position.

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DESCRIPTION

PROCESS FOR PREPARING LOW DENSITY POROUS CROSSLINKED POLYMERIC MATERIALS

Technical Field

This invention relates to the preparation of low density, porous, crosslinked, polymeric materials. In one aspect, the invention relates to reducing curing time in a high internal phase emulsion polymerization process to manufacture low density porous crosslinked polymeric materials.

Background Art

Open-cell polymeric foams can be used as a matrix to contain various liquids and gases and they are capable of commercial applications such as diapers and ion exchange resins. High absorption capacity, low density, porous polymer blocks can be prepared by polymerizing a specific type of water-in-oil emulsion known as a high internal phase emulsion (HIPE) having relatively small amounts of a continuous oil phase and relatively greater amounts of an internal water phase.

Such high absorption capacity, low density foams are prepared in U.S. 4,522,953 by polymerizing the monomers in the oil phase of a high internal phase water-in-oil emulsion with a water-soluble polymerization initiator such as potassium persulfate. It has been found that, in order to obtain foams by this method with high absorption properties and low unreacted monomer content, curing must be conducted for 16 hours or longer at a temperature of 60°C. It would be desirable to reduce the curing time without significantly affecting the resulting foam properties.

Further, it is desirable to incorporate volatile monomers such as butadiene and isoprene as mentioned in U.S. Patent No. 5,149,720. However, such monomers are difficult to incorporate and tend to volatilize during the preparation and cure of the water-in-oil emulsion.

It is therefore an object of the invention to provide a high internal phase water-in-oil emulsion polymerization process with short curing times. It is another object of the invention to provide an improved method to incorporate volatile monomers in a low density crosslinked polymeric material produced by the high internal phase water-in-oil emulsion process.

Disclosure of the Invention

According to the invention, a process for the production of a porous crosslinked polymeric material is provided, comprising the steps of:

(a) providing an aqueous mixture comprising water and an electrolyte;

(b) advancing one or more vinyl monomers in the presence of an effective amount of an advancement initiator or by a free-radical-producing radiation source to produce an advanced monomer component;

(c) adding one or more multifunctional unsaturated crosslinking monomers (i) to the one or more vinyl monomers prior to advancing in step (b), (ii) to the advanced monomer component prior to emulsion forming step (e), or to both (i) and (ii) to form an advanced monomer mixture;

(d) providing a surfactant to the aqueous mixture, the vinyl monomer, the advanced monomer component, the advanced monomer mixture, or any combinations of the aqueous mixture, vinyl monomer, advanced monomer component and advanced monomer mixture;

(e) combining and mixing said aqueous mixture and said advanced monomer mixture in a mixing vessel under conditions effective to produce a water-in-oil emulsion having at least 90 weight percent, based on the emulsion, of water as the internal phase; and

(f) heating the emulsion at a temperature of at least about 25°C to polymerize and crosslink the advanced monomers. A process in which an advanced monomer component is added to a water-in-oil high internal phase emulsion is also provided.

Further, a process in which a branched peroxide is used as the polymerization initiator or an advancement initiator is provided to produce a porous crosslinked polymeric material.

The time necessary for curing the emulsion is reduced without significantly affecting the resulting foam properties by advancing the monomers prior to forming a water-in-oil high internal phase emulsion.

Best Mode for Carrying Out the Invention

It has been found that a low density porous crosslinked polymeric material (hereinafter "foam") with high absorption capacity and low monomer content can be prepared in a shorter curing time (less than about 8 hours) by first advancing (partially polymerizing) the monomers prior to formation of a water-in-oil high internal phase emulsion. Further, it has been now found that desirable open-cell isoprene or butadiene incorporated foams can be produced by the process of the invention.

Many monomers which are gaseous at room temperature (e.g., allene, methyl allene, 1,3-butadiene, vinyl chloride, vinyl fluoride) or low boiling liquids (e.g., isoprene, piperylene, chloroallenes, polyfluoro-olefins) may be useful in foam material prepared by a high internal phase water-in-oil emulsion method. However, their volatility introduces processing problems which are addressed by advancing the monomers according to the inventive process.

In one embodiment of the inventive process, a foam is produced by advancing at least a portion of a monomer mixture containing at least one vinyl monomer and a multifunctional unsaturated crosslinking monomer in the presence of an advancement initiator or by a free-radical-producing radiation source, thereby producing an advanced monomer mixture, then forming a water-in-oil high internal phase emulsion containing such advanced monomer mixture, water as the internal phase and a surfactant and curing the advanced monomers and monomers in such water-in-oil high internal phase emulsion.

In another embodiment, one or more vinyl monomers are advanced in the presence of an effective amount of an advancement initiator or by a free-radical-producing radiation source to produce an advanced monomer component and the multifunctional unsaturated crosslinking monomer is added to the vinyl monomer prior to advancing, to the advanced monomer component prior to emulsion forming, or to both the vinyl monomer and advanced monomer component to form an advanced monomer mixture. Then, a curable high internal phase water-in-oil emulsion is formed containing the advanced monomer mixture, optionally additional vinyl monomers, surfactant, and aqueous solution as the internal phase. Then the advanced monomers and any monomers in the curable emulsion are cured.

In another embodiment, one or more vinyl monomers are advanced in the presence of an effective amount of an advancement initiator or by a free-radical-producing radiation source to produce an advanced monomer component. The advanced monomer component is then added and mixed to a water-in-oil high internal phase emulsion containing, in the continuous phase of the emulsion, a monomer component containing one or more vinyl monomers, one or more multifunctional unsaturated crosslinking monomers, or a combination of these monomers to form an advanced monomer emulsion. The water-in-oil high internal phase emulsion can be formed in a conventional manner such as those prepared in United States Patent Nos. 4,522,953, 5,149,720 and 5,189,070. Optionally additional vinyl monomers and additional multifunctional unsaturated crosslinking monomers can be added to the advanced monomer component, to the emulsion, to the advanced monomer emulsion, or to any combination of these. Multifunctional unsaturated crosslinking monomers can be added to one or more vinyl monomers to be advanced and advanced along with the vinyl monomers to form the advanced monomer component. If only vinyl monomers are present in the emulsion, one or more multifunctional unsaturated crosslinking monomers can be added to one or more monomers to be advanced, advanced monomer component, to the emulsion, to the advanced monomer emulsion, or to any combination of these in an effective amount to crosslink the monomers to form a foam. Then the advanced monomers and any monomers in the advanced monomer emulsion are cured.

The term "advancement" or "advanced" includes any oligomerization or partial polymerization of some of all of the monomers. The advanced monomers thus generally contain a mixture of monomers, and various oligomers/polymers.

The advancement may be carried out, for example, by mixing the entire monomer mixture together with an advancement initiator, warming to an effective temperature for polymerization and oligomerizing the mixture, or a single component or selected components may be advanced and then blended with the rest of the monomers desired in the continuous phase of the emulsion or blended into a water-in-oil high internal phase emulsion containing the rest of the monomers. Which approach is followed will be determined by the objectives desired, since the final molecular structure of the foam will be affected by which route is chosen, and the molecular structure achieved will affect resulting foam properties.

Various monomers may be used in the preparation of the foams, provided the monomers can be dispersed in or form an oil phase of a water-in-oil high internal phase emulsion and have a polymerizable vinyl group. Suitable vinyl monomers include, for example, monoalkenyl arene monomers such as styrene, α-methylstyrene, chloromethylstyrene, vinylethylbenzene and vinyl toluene; acrylate or methacrylate esters such as 2-ethylhexyl acrylate, n-butyl acrylate, isobutyl acrylate, t-butyl acrylate, hexyl acrylate, n-butyl methacrylate, lauryl methacrylate, and isodecyl methacrylate; conjugated diolefins such as butadiene, isoprene and piperylene; allenes such as allene, methyl allene and chloroallene; olefin halides such as vinyl chloride, vinyl fluoride and polyfluoro-olefins; and mixtures thereof.

Suitable crosslinking agents can be any multifunctional unsaturated monomers capable of reacting with the vinyl monomers. Multifunctional unsaturated crosslinking monomers include, for example, difunctional unsaturated crosslinking monomers such as divinyl benzene, diethylene glycol dimethacrylate, 1,3-butanediol dimethacrylate, and allyl methacrylate; tri-, tetra- and penta-functional unsaturated crosslinking monomers such as trimethylolpropane trimethacrylate, pentaerythritol tetramethacrylate, trimethylolpropane triacrylate, pentaerythritol tetraacrylate, glucose pentaacrylate, glucose diethylmercaptal pentaacrylate, and sorbitan triacrylate; and poly-functional unsaturated crosslinking monomers such as polyacrylates (eg. surcrose per(meth)acrylate and cellulose (meth)acrylate). Crosslinking monomers are typically present in an amount of from about 2 weight percent to about 70 weight percent, preferably from about 5 weight percent to about 40 weight percent based on the total monomer mixture. Some of these crosslinking monomers can be incorporated as a non-crosslinked monomer as long as at least about 2 weight percent of the crosslinking monomers are crosslinked.

Suitable advancement initiators are monomer-soluble free radical polymerization initiators. Monomer-soluble (oil soluble) free radical polymerization initiators include, for example, azo compounds such as azobisisobutyronitrile (AIBN) and peroxides such as benzoyl peroxide, methyl ethyl ketone peroxides, di-2-ethylhexyl peroxydicarbonate and other alkylperoxycarbonates and alkylperoxycarboxylates including branched peroxides listed below. The advancement initiator should be present in at least an amount effective to partially polymerize or oligomerise the monomers, but can also be in an amount effective to completely polymerize and crosslink the monomers. Typically the advancement initiator can be present from about 0.005 to about 20 weight percent, preferably from about 0.1 to about 4 weight percent based on the monomers. The advancement initiator is added to the monomer mixture containing one or more vinyl monomers with or without the crosslinking monomer and optionally a surfactant.

Preferably the monomer mixture is advanced provide a ratio of viscosity of monomer mixture to water within the range of from about 1000:1 to about 1:2, more preferably from about 50:1 to about 1.5:2. Generally, the ratio of viscosity for a non-advanced monomer to water is about 1:2. The viscosity of the advanced monomer mixture will vary depending on the monomer used.

The viscosity of the advanced monomer will be higher than the viscosity of the unadvanced monomer mixture. The viscosity is also dependent on temperature, and is quite low at ambient temperature, typically about 0.4 cp for the unadvanced monomer mixture, and up to about 100 cp for the advanced monomer mixture. The viscosity will be expressed as a ratio between the viscosity of the monomer mixture and that of the advanced monomer mixture, or the viscosity of the advanced monomer mixture plus surfactant and the unadvanced mixture plus surfactant, because the absolute viscosity values are a function of temperature and whether or not the surfactant has been added to the mixture (normally addition of the surfactant raises the viscosity several-fold). If the advanced mixture is in the numerator, and the non-advanced (fresh) in the denominator, then the ratio should be greater than 1.00 to show advancement. Preferably, the ratio is within the range from about 1.03 to about 50, more preferably from about 1.07 to about 30, most preferably from about 1.15 to about 15.

Since the viscosities are generally low, it is convenient to measure them at -78°C. Thus, the viscosity of a 1:1:3 weight percent mixture of styrene: divinyl benzene: 2-ethylhexyl acrylate is about 300 cp at -78°C. When 12 parts per 100 parts of weight of monomer mixture of a sorbitan monolaurate surfactant is added to the monomer mixture, the viscosity at -78°C increases to about 2900 cp. On advancing the monomer/surfactant mixture the viscosity increases with time of advancement as described in the illustrative embodiment described below. The level of advancement preferred will depend on the particular mixture of monomers and the relative importance of rapid cure, volatility and properties.

To obtain the advanced monomer mixture, the monomer mixture is heated in the presence of the advancement initiator at a temperature above about 25°C, preferably at a temperature within the range of about 25°C to about 150°C, more preferably within the range of about 50°C to about 100°C for a time effective to form the advanced monomer mixture with a desired viscosity, or irradiated by a free-radical-producing radiation source for a time effective to form the advanced monomer mixture with a desired viscosity. Such time is preferably within the range of about 5% to about 95% of the time necessary to form a solid mixture. The mixture is solid when the mixture no longer visibly deforms. The time necessary to form a solid mixture can be conveniently measured by a Solidity Test described below. More preferably, the advancement is done for a time within the range of about 10% to about 90%, most preferably from about 35% to about 88% of the time necessary to form a solid mixture. The advanced monomer mixture which is preferred is one which forms a stable emulsion, cures rapidly, and yields a good porous polymeric product relative to the unadvanced monomer mixture.

Advancement of the monomer mixture has various advantages besides the acceleration of cure time of the emulsion described above; among these is the ability to use comonomers which are not effective when used directly in the conventional emulsion system such as isoprene and butadiene, the reduction of volatiles from the emulsion curing line, the reduction of soluble organics in recycle water, the elimination of odors, and the use of low boiling monomer mixtures at atmospheric pressure.

To aid in the determination of level of advancement, the level of unsaturation in a mixture of monomers containing double bonds may be assessed by various means, such as infrared determination of the C=C stretching frequency, NMR examination of the vinylic carbons or protons, ultraviolet absorption measurements, dielectric constant, average molecular weight by HPLC, or other means of measuring molecular weight or unsaturation. One of the simplest and most direct measures is the reaction of halogen with olefinic bonds. Such tests result in determination of Bromine or Iodine number corresponding to the number of grams of halogen reacted with a certain amount (normally 100g) of the sample.

In one embodiment, if it is desirable to incorporate vinyl chloride for example, into a HIPE foam material, but toxicity concerns limit the amount of gas phase monomer tolerable in the process, the monomer can be mixed with comonomers, such as styrene, divinylbenzene, acrylates, and/or the like, in the presence of an advancement initiator in a sealed reaction vessel, and the reaction vessel warmed to a temperature effective to begin an oligomerization and/or polymerization reaction. After the desired level of reaction has occurred, the vessel may be vented and depressured or evacuated, to remove unreacted vinyl chloride monomer, and leave a polymerizable liquid "advanced monomer" mixture containing vinyl chloride molecules incorporated into larger molecular structures. This advanced monomer then can be polymerized with less potential health hazard of handling vinyl chloride in the mixture, but with the property benefits of the final vinyl chloride containing polymer structure.

In another embodiment, low boiling monomers such as butadiene or isoprene can be readily incorporated in the HIPE foam material either by a monomer mix approach in which a mixture of one or more low boiling monomers, optionally other vinyl monomers, and a crosslinker is advanced preferably until up to about 1/3 of the monomer is used, or the low boiling component itself can be advanced and then blended with the higher boiling components.

For example, to incorporate butadiene in the porous polymeric product, an autoclave or a pressure reactor ("reaction vessel") can be charged with liquid butadiene, and purged of air by venting some of the butadiene, or alternatively, by chilling the butadiene in liquid nitrogen or in dry ice, and evacuating the gas cap of permanent gases. Optionally other vinyl monomers and crosslinkers can be added. Before charging the butadiene, an effective amount of a suitable advancement initiator such as t-butyl peroxyisobutyrate to advance the butadiene is charged to the reaction vessel. The reaction vessel is then warmed to about 80°C-85°C to allow butadiene to react for a time sufficient to lower the butadiene partial pressure. The advancement reaction for low boiling monomers is preferably carried out until the absolute pressure in the reaction vessel at room temperature is less than about 14.7 psia (or below boiling) at atmospheric pressure. For example, if pressure of less than 14.7 psia is required at around 27°C (80°F) to be able to handle the monomers at 27°C (80°F) without having it boil, the absolute pressure in the reaction vessel should be reduced to a pressure at most of about 60 psia at 82°C to indicate a level of reaction just sufficient to prevent boiling at 27°C (80°F). Once the desired pressure range is reached at the reaction temperature, the advanced monomer mixture can be optionally blended with other monomer components to further lower the vapor pressure of the monomer mixture and make the emulsification and curing process simpler. A wide range of temperature may be used to perform the advancement depending on the initiator and the monomer used. For example, for 1,3-butadiene, higher or lower temperatures than about 80°C-85°C may be used, but the temperature should be below about

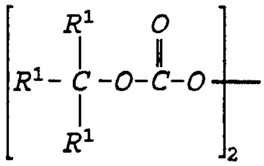
152°C, the critical temperature of butadiene, so that the monomer may remain in the liquid instead of the supercritical gas state. In addition, the temperature should be below the ceiling temperature of the oligomers formed to allow polymerization to occur. On the low temperature side, the temperature should be high enough to give a satisfactory rate with whatever initiator system is used. As a practical matter, that means that for many low boiling volatile monomers, the temperature preferred for the advancement reaction will be within the range from about room temperature to about 150°C, more preferably from about 50°C to about 100°C.

For the inventive process, it is also desirable to use a fast curing initiator to reduce the cure time. It has been found that the known oil-soluble initiators reported in the literature such as benzoyl peroxide and AIBN are generally slower than the water-soluble potassium persulfate initiator and provide incomplete curing of the resulting foams without addition of additional polymerization initiators after the formation of the emulsion or in the aqueous mixture. Therefore, it was desirable to develop a faster curing monomer-soluble polymerization initiator.

It has been found that branched alkyl carbonate peroxides branched at the 1-carbon position or branched alkyl carboxylate peroxides branched at the α-carbon position and/or 1-carbon position (hereinafter "branched peroxides") cure faster than the conventional oil-soluble initiator such as benzoyl peroxide. This branching at the 1-carbon position and/or α-carbon position can be secondary or tertiary.

The preferred branched alkyl carbonate peroxide can be represented by the formula:

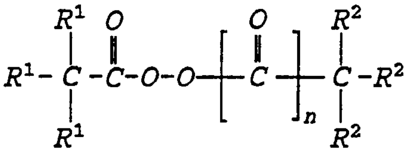
where R^1 is independently C_1 to C_{16} hydrocarbon groups or hydrogen in which at least two of the R^1 are hydrocarbon groups. Hydrocarbon groups can be alkyl, alkenyl or aryl



$$\left[R^1-\overset{R^1}{\underset{R^1}{C}}-O-\overset{O}{\overset{\|}{C}}-O\right]_2-$$

groups.

The preferred branched alkyl carboxylate peroxide can be represented by the formula:



$$R^1-\overset{R^1}{\underset{R^1}{C}}-\overset{O}{\overset{\|}{C}}-O-O-\left[\overset{O}{\overset{\|}{C}}\right]_n-\overset{R^2}{\underset{R^2}{C}}-R^2$$

$n=0,1$

where R^1 and R^2 are independently C_1 to C_{16} hydrocarbon groups or hydrogen in which at least two of the R^1 or R^2 are hydrocarbon groups. Preferably at least two of both R^1 and R^2 are hydrocarbon groups. Hydrocarbon groups can be alkyl, alkenyl or aryl groups.

Examples of the branched peroxides include t-butyl peroxyisobutyrate, t-butyl peroxycrotonate, t-butyl peroxypivalate, di-isobutyryl peroxide, di-t-butyl diperoxyphthalate, t-butyl perbenzoate, cumylperoxy neodecanoate, 2,5-dimethyl-2,5-bis(benzoylperoxy)hexane, 2,5-dimethyl-2,5-bis(2-ethylhexanoylperoxy)hexane, t-butyl peroctoate, 1,1,3,3-tetramethylbutylperoxy-2-ethyl hexanoate, dicyclohexyl peroxydicarbonate, di(sec-butyl) peroxydicarbonate, diisopropyl peroxydicarbonate, and t-butyl peroxyisopropylcarbonate. Commercial examples of the branched peroxide include Lupersol™ 11, Lupersol™ 80, Lupersol™ 118M75, Lupersol™ 225, Lupersol™ 227, Lupersol™ 229, Lupersol™ 256, Lupersol™ 259, Lupersol™ KBD, Lupersol™ TBIC, Luperox™ 118, Luperox™ 229, and Luperox™ IPP (from Atochem North America). The most preferred advancement and/or polymerization initiator is t-butyl peroxyisobutyrate.

These branched peroxide initiators also improve the conventional water-in-oil high internal phase polymerization processes such as those described in U.S. Patent No. 4,522,953 where no advancement takes place prior to the formation of an emulsion. Further these branched peroxide initiators are also useful when the initiator is added after the formation of the emulsion as described in U.S. Patent No. 5,210,104, issued May 11, 1993.

When advancement initiators such as benzoyl peroxide, AIBN and methyl ethyl ketone peroxide are used, additional polymerization initiator should be added in the aqueous mixture or in the emulsion. When such polymerization initiator is added to the emulsion, the polymerization initiators can be, for example, oil-soluble (monomer-soluble) initiators such as branched peroxides listed above or water-soluble initiators such as potassium or sodium persulfate and various redox systems such as ammonium persulfate together with sodium metabisulfite. When such a polymerization initiator is added to the aqueous mixture, the polymerization initiators can be any of the water-soluble initiators mentioned above.

When the additional polymerization initiator is added to the emulsion, it can optionally be blended into the emulsion by any blending technique such as, for example, a static mixer or a pin mixer at a low shear rate, to form a curable water-in-oil high internal phase emulsion. The rate of shear must be high enough to blend the initiator but low enough not to allow the emulsion to coalesce or liquify.

The surfactant used in making the high internal phase emulsion can be added to the aqueous phase or monomer phase (monomer mixture) depending on the solubility of the surfactant used. Suitable surfactants include, for example, nonionic surfactants such as sorbitan esters (eg., sorbitan monooleate and sorbitan monolaurate), glycerol esters (eg. glycerol monooleate and glycerol monoricinoleate), PEG 200 dioleate, partial fatty acid esters of polyglycerol, and castor oil 5-10 EO; cationic surfactants such as ammonium salts (eg., distearyl dimethyl ammonium chloride and dioleyl dimethyl ammonium chloride); and anionic surfactants such as bis-tridecyl sulfosuccinic acid salt. Commercially available surfactants include, for example, SPAN® emulsifying agents 20, 40, 60, 65, 80 and 85 (from Fluka Chemical Corp. or Aldrich Chemical Co.), EMSORB 2502 (from Henkel) and ALKAMULS® sorbitan esters SML, SMO, SMS, STO and ALKAMULS® sorbitan ester ethoxylates PMSL-20 and PSMO-20 (from Alkaril Chemicals Ltd.) among others. The surfactant is present in an amount effective to form a water-in-oil high internal phase emulsion (HIPE). Preferably, the surfactant is present from about 2 to about 40% by weight, more preferably about 5 to about 25% by weight based on the monomers.

To form a polymeric foam product with suitable density and high absorption capacity, the water-in-oil high internal phase emulsion (HIPE) typically contains, as the internal phase, at least about 90 weight percent, based on the emulsion, of water, corresponding to a water to oil weight ratio of at least about 9:1, more preferably at least about 95 weight percent of water, most preferably at least about 97 weight percent of water, corresponding to a water to oil weight ratio of at least about 33:1.

The internal aqueous phase can preferably contain a water-soluble electrolyte to stabilize the HIPE and to make the foam more water wettable. Suitable electrolytes include inorganic salts (monovalent, divalent, trivalent or mixtures thereof), for example, alkali metal salts, alkaline earth metal salts and heavy metal salts such as halides, sulfates, carbonates, phosphates and mixtures thereof. Such electrolyte includes, for example, sodium chloride, sodium sulfate, potassium chloride, potassium sulfate, lithium chloride, magnesium chloride, calcium chloride, magnesium sulfate, aluminum chloride and mixtures thereof. Mono- or di-valent salts with monovalent anions such as halides are preferred.

The curable water-in-oil high internal phase emulsions (curable HIPE) can be cured in a batch process or in a continuous process. In a batch process, the curable HIPE is collected in a suitable container with the desired shape and cured at a temperature of at least about 25°C for a time effective to polymerize and to cure the monomers. The HIPE is preferably polymerized and crosslinked (cured) at a temperature within the range of about 25°C to about 90°C, as long as the emulsion is stable at the curing temperature.

Alternatively, a multiple-step process as described in a United States Patent No. 5,189,070 can also be used, the disclosure of which is herein incorporated by reference. In the multi-step process the emulsion is pre-cured at a temperature of less than about 65°C until the emulsion has a Rheometrics dynamic shear modulus of greater than about 500 pascal, (lightly gelled, having a consistency like a jelly or a gelatin referred to as "gel"), then cured at a temperature of above about 70°C for a time effective to cure the gel. The cure temperature can be as high as about 175°C under suitable pressure to prevent water from boiling.

The emulsions can be heated, for example, by hot water, hot air, steam, IR, RF, microwave or ohmic heating. The HIPE should be cured until the desired properties are obtained. Typically, to obtain a cured foam, the emulsions should be cured for at least about 4 hours at 60°C or at least about 1/2 hour at 60°C then 3 hours at a temperature of above about 70°C. Generally, the extent of reaction after curing is at least about 85% of the monomers, preferably at least about 90%, more preferably at least about 95% (i.e., less than about 5% of free monomers), most preferably at least about 99% (i.e., less than about 1% of free monomers) in order to obtain good properties.

These foams can be post-cured to improve the foam properties. Better properties such as, for example, increased free swell (i.e., amount of liquid a foam can initially absorb), and/or good resistance to compression deflection (i.e., retention of liquid under load) can be obtained depending on the monomer formulation by post-curing the foam at a temperature of above about 75°C, preferably greater than 90°C, by steam, hot air or other heating source. Such heating may be performed initially in a heat exchanger, oven, over heated rollers or by other means.

When the temperature is near or above the boiling point of water, pressure is preferably applied to keep the water in the liquid phase and to obtain better properties. If desired, the pressure may be lowered to boil some of the water, but in normal practice the water will be maintained in the liquid state to stabilize the monomer. The use of pressure to maintain the aqueous phase and oil phase in the liquid state allows very rapid curing of emulsions at very high temperatures, provided the emulsions are stable at the high temperatures used. Pressure can be applied to the emulsion, if desired, at a pressure generally from above atmospheric pressure, typically within the range of about atmospheric pressure to about 1.03 MPa (150 psig). When the temperature is about 100°C, a pressure from about 7 to 70 kPa gauge (about 1 to 10 psig) is sufficient; when the temperature is about 130°C, a pressure from about 210 to 480 kPa gauge (about 30 psig to 70 psig) is preferred.

Once the curing and/or post-curing process is completed, the water incorporated in the foam may be squeezed out, dried by heat or flashed by lowering the pressure to a suitable level to evaporate the remaining liquid to give the desired degree of dryness in the product foam. These drying techniques will preferably be used after the desired state of cure is developed in the foam material.

These foams prepared by the inventive process may be washed prior to, after or between drying stages to yield an absorbent block which is especially useful for the absorption of liquids. Typically, these foams are washed to reduce the electrolyte content of the foam with a solvent such as, for example, an alcohol, a low concentration electrolyte solution (lower concentration than the water phase) such as 1% calcium chloride solution or deionized water. The washed foams can be conveniently dried by squeezing the water and/or solvent out of the foams and air or heat drying.

The foams produced by the inventive process possess high absorption capacities and good uniform properties especially suitable for use as liquid absorbent articles.

Illustrative Embodiment

The following illustrative embodiments describe the process of the invention and are provided for illustrative purposes and are not meant as limiting the invention.

Washing and Drying Method

The following washing and drying method was used for all of the examples below: After the foam blocks were cured, the blocks were sliced to 0.35 inches (0.89 cm) thickness. Then, each individual slice was placed on a 0.04 inch (0.1 cm) mesh screen between a 9" X 6.75" (22.9 cm X 17.1 cm) stainless steel plate that allowed the slice to be squeezed to a 0.045 inch (1.14 mm) thickness. The squeezed slices were placed in an Arbor-press made by DAKE and the calcium chloride solution was squeezed out. The slices were then washed and squeezed twice by soaking the slices in 7.6 liters (2 US gallons) of 1% calcium chloride solution and placing in the Arbor-press. Then, after the slices were squeezed, a paper towel was placed on both sides of the washed slices which were squeezed again to remove excess water from the slices. The slices were then placed in an oven at a temperature of 60°C for 4 hours to dry. The washed and dried foam slices were analyzed for physical properties as discussed below.

TESTING METHODS

Solidity Test:

A flat-tipped probe of about 6 mm diameter is placed on top of an advanced monomer mixture to create a pressure at the flat-tip of about 2.1 kPa (0.3 psi). The ease and penetration of the object into the gel was measured. The monomer mixture is considered solid when the object no longer penetrates or penetrates less than about 1 mm.

Viscosity:

At selected times, aliquots of approx. 5 ml are removed and placed in 8 dram vials. If the aliquots are above ambient temperature, the aliquots are then quickly cooled in wet ice to ambient temperature (approx. 24 °C). The aliquots are chilled in acetone/dry ice slush bath for approx. 10 minutes to a temperature of approx. -78°C. The warm aliquots may be chilled immediately to approx. -78°C. While the aliquots are kept cold, the viscosity is run using Brookfield Viscometer, Model RVTD equipped with a #6 Spindle (manufactured by Brookfield Engineering Lab, Stoughton, Massachusetts).

Bromine Test:

Determination of bromine numbers is done potentiometrically using a "bromine number solvent" consisting of acetic acid, trichloroethylene, methanol with 1% sulfuric acid and 1/5% water from Ricca Company. Alternatively, a suitable solvent is 1400 ml of acetic acid, 268 ml of methylene chloride, 268 ml of methanol, and 36 ml of a 1:5 mixture of sulfuric acid and water. 100 Milligrams of sample is dissolved in 100 ml of the solvent and then titrated with 0.5N bromine/bromate titrant in a Kyoto AT310 potentiometric titrator. The titration is done in a sealed cell kept between 0°C to 5°C, using a platinum double ring electrode. The level of saturation of the solution with bromine is followed potentiometrically, and the bromine number values are reported as grams of bromine reacted per 100 grams of sample.

Free Swell ("FS")/Dry Thickness ("DT")/Foam Density ("FD")/Percent Strain/Resistance to Compression Deflection ("RTCD"):

A 2"x 2" (5.08 x 5.08 cm) square is cut from a foam slice. The thickness of the foam sample is measured while it is dry ("dry thickness") using a dead weight thickness gage (a digital linear gage model EG-225 made by Ono Sokki) exerting 50 grams force applied to a 1.60" diameter disk. This thickness is called the "caliper." The foam square is soaked in warm 88°F (31°C) Syn-Urine from Jayco for 17 minutes. From the 2" x 2" (5.08 x 5.08 cm) square, a circle of 1.129" (2.868 cm) diameter is cut. This disk is re-equilibrated in the Syn-Urine for 5 minutes. The wet disk is then weighed ("initial wet weight").

The thickness of the wet sample is measured using the same load gage ("initial wet caliper"). The disk is then placed under a 5.1 kPa (0.74 psi) stress where stress is the total dead weight applied to the gage divided by the cross-sectional area. The thickness of the disk is measured under this stress after 15 minutes ("wet caliper"). After 15 minutes, the specimen disk is weighed to measure the retained fluid.

The excess urine is squeezed from the disk and the remainder of the square from which it was cut. The foam is placed in boiling deionized water for 15 minutes. The foam is washed this way several times to remove inorganics. The foam is then removed, blotted dry, then placed in a vacuum oven at 60-70 °C and dried until the foam has fully expanded. The weight of the dry disk sample is then determined in grams ("final dry weight").

The following values were calculated from the above measurements.

Free swell= initial wet weight/final dry weight

Resistance to Compression Deflection (RTCD)=

wet weight after load at 15 minutes/final dry weight

Foam Volume (cm^3)=

$$\%Strain = \frac{initial\ wet\ caliper - wet\ caliper}{initial\ wet\ caliper} X\,100$$

$$(\text{diameter}/2)^2 \text{ x } 3.142 \text{ x initial wet caliper}$$

based on a 1.129" diameter circle cut (in cm)

Foam Density (mg/cm^3)= final dry weight x 1000/Foam Volume

Vertical Wicking Time ("VWT"):

From a foam slice, cut at 0.35 inches (0.89 cm) thickness, a 1 to 2 cm wide strip is cut, greater than 5 cm in length. The strip of foam is clamped or taped to a metal ruler, with the bottom of the foam strip flush with the 0 mark on the ruler. The ruler and foam are placed in a container of approximately 100 ml Syn-Urine from Jayco, in an incubator at 99°F (37°C) so the bottom of the strip (0 mark) is barely touching the surface of the Syn-Urine (less than 1mm). The Syn-Urine is dyed with food coloring to more easily monitor its absorption and rise in the foam. A stopwatch is used to measure the time required for the liquid level to reach 5 cm vertical height in the foam sample.

Percent Free Liquid:

The amount of unabsorbed water was measured by decanting fluid from the foam in the container after pre-curing or curing stage and weighing the decanted fluid.

EXAMPLE 1

This example demonstrates the change in viscosity as measured at -78°C as the monomer mixture is advanced according to the invention.

A 1:1:3 weight ratio of styrene: divinyl benzene: 2-ethylhexyl acrylate was mixed to produce a monomer mixture and viscosity was measured at -78°C. (Commercial divinyl benzene containing 55% divinyl benzene from Aldrich Chemical Co. was used.) To this monomer mixture, 12 parts by weight for 100 parts by weight of the monomer mixture of a sorbitan monolaurate surfactant (SPAN® 20 emulsifying agent from Fluka Chemical Corp. or Aldrich Chemical Co.) was added and viscosity was measured at -78°C. To this mixture 1 part by weight for 100 parts by weight of the monomer mixture of

Lupersol™ 80 initiator (t-butyl peroxyisobutyrate from Atochem North America) was added. The resulting mixture was advanced at 75°C and viscosity was measured at -78°C periodically as listed in Table 1 below. The viscosities were measured as described above.

TABLE 1

mixture	Time of Advancement (min)	Viscosity (cp)
Monomer	--	300
Monomer/surfactant	0	2900
Monomer/surfactant	16	3060
Monomer/surfactant	41	3260
Monomer/surfactant	72	3930
Monomer/surfactant	84	5600
Monomer/surfactant	120	infinite

Example 2

This example demonstrates the change in bromine numbers as the monomer mixture is advanced according to the invention.

A 1:1:3 weight ratio of styrene: divinyl benzene: 2-ethylhexyl acrylate was mixed to produce a monomer mixture. (Commercial divinyl benzene containing 55% divinyl benzene from Aldrich Chemical Co. was used.) To this monomer mixture, 12 parts by weight for 100 parts by weight of the monomer mixture of a sorbitan monolaurate surfactant (SPAN® 20 emulsifying agent from Fluka Chemical Corp. or Aldrich Chemical Co.) was added and bromine number was measured as described above. To this mixture 1 part by weight for 100 parts by weight of the monomer mixture of Lupersol™ 80 initiator (t-butyl peroxyisobutyrate from Atochem North America) was added. The resulting mixture was advanced at 72°C and bromine number was measured at 20 minute intervals as described above. The bromine numbers are shown in Table 2 below.

TABLE 2

Time of Advancement (min)	Bromine Number
--	49[a]
20	50
40	48
80	46
100	45
120	43

[a] Numbers are +/- 2.

As seen from the above table, the available double bonds have decreased 14% over the advancement time. The particular test used did not give a reliable indication for acrylate double bonds, which reacted more slowly than the styrenic double bonds. Thus, the bromine numbers are low relative to the theoretical numbers for the monomer mixture. However, the data show a clear drop in number of reactive double bonds with time of advancement which can be used to monitor the degree of advancement.

Example 3

This example demonstrates the change in bromine numbers as the monomer mixture containing a volatile monomer is advanced according to the invention.

3:2 weight ratio of isoprene:divinyl benzene were mixed to produce monomer mixtures. (Commercial divinyl benzene containing 55% divinyl benzene from Aldrich Chemical Co. was used.) To these monomer mixtures, 12 parts by weight for 100 parts by weight of the monomer mixtures of a sorbitan monolaurate surfactant (SPAN® 20 emulsifying agent from Fluka Chemical Corp. or Aldrich Chemical Co.) was added. Bromine number of the non-advanced mixture was measured as described above. To these mixtures 1 weight percent for 100 weight percent of the monomer mixtures of Lupersol™ 225 initiator (di(sec-butyl) peroxydicarbonate), Lupersol™ 80 initiator (t-butyl peroxyisobutyrate), Lupersol™ 223 initiator as comparative example (di(2-ethylhexyl) peroxydicarbonate), and Lupersol™ 188M75 initiator (alpha-cumyl peroxyneodecanoate) all from Atochem

North America, were added as listed below. The resulting mixture was advanced at the temperatures listed below and bromine numbers were measured as described above. The high temperature advancement runs were performed in an autoclave blanketed with nitrogen under pressures up to 400 psig. The bromine numbers are shown in Table 3 below.

TABLE 3

Initiator	Temperature (°C)	Time (min)	Bromine Number
--			176[a]
Lupersol™ 225	74 - 78	244	140
"	80 - 87	244	160
Lupersol™ 80	80 - 87	120	148
"	80 - 88	252	solid
Lupersol™ 223	80 - 86	180	176
Lupersol™ 188M75	80 - 86	240	172

[a] Numbers are +/- 5.

As seen from the above table, the available bromine double bonds have decreased about 21% over the advancement time. Since the isoprene polymers mostly retain a reactive double bond for each isoprene unit, the 21% observed decrease in double bonds represents from 21% to 42% of complete polymerization cure (depending on whether the monomer has both or only one bond reacted).

As can be seen from the table, Lupersol™ 80 initiator gives a greater degree of advancement at a shorter time when held at 80 to 87°C although the Self Accelerating Decomposition Temperature (SADT) of Lupersol™ 80 initiator is higher than for Lupersol™ 225, 223 or 188M75 initiators (80°C versus 0°C, 0°C and 15°C respectively). The amount of advancement is not just a function of the amount of peroxide decomposed but the matching of the rate of decomposition to the rate of polymerization. (The half life at 80°C of Lupersol™ 80 initiator (L80) is ca.7.5 hrs, while Lupersol™ 223 initiator (L223) is 10 min, Lupersol™ 225 initiator (L225) is 13 min, and Lupersol ™ 188M75 initiator (L188M75) is ca. 1 hr; at 60°C, the half lives are roughly

L80 =110 hrs, L223 = 0.83 hrs, L225 = 1.4 hrs, and L188M75 = ca 12.5 hrs, Lucidol Pennwalt, "Evaluation of Organic Peroxides from Half-Life Data", Lucidol Div. of Pennwalt, 1740 Military Road, Buffalo, New York 142140) However, even assuming roughly the same rates of decomposition, the 1-position or α-position branched peroxides such as di(sec-butyl) peroxydicarbonate, t-butyl peroxyisobutyrate and alpha-cumyl peroxyneodecanoate are clearly more effective at advancing the monomers than peroxides not branched at the 1-position or α-position such as di(2-ethylhexyl) peroxydicarbonate.

Example 4

This example demonstrates the reduction in cure time with increased advancement time according to the invention.

A 1:1:3 weight ratio of styrene: divinyl benzene: 2-ethylhexyl acrylate were mixed to produce a monomer mixture. (Commercial divinyl benzene containing 55% divinyl benzene from Aldrich Chemical Co. was used.) To this monomer mixture, 12 parts by weight for 100 parts by weight of the monomer mixture of a sorbitan monolaurate surfactant (SPAN® 20 emulsifying agent from Fluka Chemical Corp. or Aldrich Chemical Co.) was added and bromine number was measured as described above. To this mixture 1 part by weight for 100 parts by weight of the monomer mixture of Lupersol™ 80 initiator (t-butyl peroxyisobutyrate from Atochem North America) was added. The resulting mixture was advanced at 80°C for a specified time as listed below. A 30:1 water-in-oil emulsion was made by mixing a 70°C aqueous solution of 10% $CaCl_2$ and 0.14% potassium persulfate into the advanced monomer mixtures with an air motor and a paint mixer. Each emulsion was cured in a 60°C water bath in a 118 cm^3 (4 fluid oz.) bottle. Cure Time was determined by determining the time necessary for the emulsion to support a 2.1 kPa (0.3 psi) flat tipped probe at the surface of the emulsion and listed below in Table 4.

TABLE 4

Advancement Time (min)	Cure Time (min)
0	144
16	136
29	121
41	112
53	94
111	61
125	Solid during advancement

Example 5

This example demonstrates preparation of a low density crosslinked polymeric material by advancing the monomer mixture according to the invention.

In a container, 100.09 g of a monomer mixture (19.11 wt% styrene, 20.63 wt% divinyl benzene and 60.26 wt% of 2-ethyl hexyl acrylate) is mixed with 1.06 g of t-butyl peroxyisobutyrate (Lupersol™ 80 from Atochem North America). For divinyl benzene, commercial divinyl benzene containing 55% divinyl benzene from Aldrich Chemical Co. was used. To 80.03 g of the initiator-containing monomer mixture which has been heated for 12 minutes in a 80°C water bath, 10 g of Span® 20 emulsifying agent (sorbitan monolaurate from Fluka Chemical Corp. or Aldrich Chemical Co.) was added to give a 12.35% surfactant-containing mixture ("mixture-A" 12 minutes aging).

While stirring with a paint stirrer (model 06200 PM-70 made by SHUR-LINE® Inc.) attached to an air motor (#C-1712 1/2hp motor made by Arrow Engineering Co.), 600 cc of aqueous 10 wt% $CaCl_2$ and 0.15 wt% potassium persulfate solution was slowly added to 20.03 g of mixture-A which had been heated at 80°C for 16 minutes. A water-in-oil high internal phase emulsion formed with a desired 30:1 water-to-oil ratio. 60.87 g of the resulting emulsion was poured into a 118 cm^3 (4 fluid oz.) jar and labeled B1. The remaining emulsion (521.41 g) was poured into a 1.4 liter (3 US pint) tub and labeled B2. The emulsion was cured by placing this jar B1 in a 60°C water bath and periodically tested with a flat-tipped probe of about 6 mm diameter which creates a pressure at the flat-top of about 0.3 psi ("the probe") by placing the probe on top of the emulsion. After 136 minutes, the probe sat on top of the foam and did not sink. The emulsion in the tub was cured by heating the tub B2 in a 60°C incubator for 24 hours. 3.13 % of free water was poured off from the resulting foam.

While stirring in a similar manner to above, 600 cc of aqueous 10 wt% $CaCl_2$ and 0.15 wt% potassium persulfate solution was slowly added to 20.29 g of mixture-A which had been heated at 80°C for 29 minutes. 59.78 g of the resulting emulsion was poured into a 118 cm^3 (4 fluid oz.) jar and labeled C1. The remaining emulsion (558.0 g) was poured into a 1.4 liter (3 US pint) tub and labeled C2. The emulsion was cured by placing this jar C1 in a 60°C water bath and periodically tested by placing the probe described above on top of the emulsion. After 121 minutes, the probe sat on top of the foam and did not sink. The emulsion in the tub was cured by heating the tub C2 in a 60°C incubator for 24 hours. 1.74 % of free water was poured off from the resulting foam.

While stirring in a similar manner to above, 600 cc of aqueous 10 wt% $CaCl_2$ and 0.15 wt% potassium persulfate solution was slowly added to 20.32 g of mixture-A which had been heated at 80°C for 41 minutes. 62.18 g of the resulting emulsion was poured into a 118 cm^3 (4 fluid oz.) jar and labeled D1. The remaining emulsion (552.48 g) was poured into a 1.4 liter (3 US pint) tub and labeled D2. The emulsion was cured by placing this jar D1 in a 60°C water bath and periodically tested by placing the probe described above on top of the emulsion. After 112 minutes, the probe sat on top of the foam and did not sink. The emulsion in the tub was cured by heating the tub D2 in a 60°C incubator for 24 hours. 2.08 % of free water was poured off from the resulting foam.

While stirring in a similar manner to above, 600 cc of aqueous 10 wt% $CaCl_2$ and 0.15 wt% potassium persulfate solution was slowly added to 20.2 g of mixture-A which had been heated at 80°C for 53 minutes. 61.94 g of the resulting emulsion was poured into a 118 cm^3 (4 fluid oz.) jar and labeled E1. The remaining emulsion (543.82 g) was poured into a 1.4 liter (3 US pint) tub and labeled E2. The emulsion was cured by placing this jar E1 in a 60°C water bath and periodically tested by placing the probe described above on top of the emulsion. After 94 minutes, the probe sat on top of the foam and did not sink. The emulsion in the tub was cured by heating the tub E2 in a 60°C incubator for 23 hours. 1.77 % of free water was poured off from the resulting foam.

In a container, 99.77 g of a monomer mixture (19.11 wt% styrene, 20.63 wt% divinyl benzene and 60.26 wt% of 2-ethyl hexyl acrylate) was mixed with 1.19 g of t-butyl peroxyisobutyrate (Lupersol™ 80 from Atochem, North America) and 11.98g of Span® 20 emulsifying agent (sorbitan monolaurate from Fluka Chemical Corp. or Aldrich Chemical Co.) ("mixture-F"). For divinyl benzene, commercial divinyl benzene containing 55% divinyl benzene from Aldrich Chemical Co. was used.

While stirring in a similar manner to above, 600 cc of aqueous 10 wt% $CaCl_2$ and 0.15 wt% potassium persulfate solution was slowly added to 20.07 g of mixture-F which had been heated at 80°C for 60 minutes. 62.99 g of the resulting emulsion was poured into a 118 cm^3 (4 fluid oz.) jar and labeled H1. The remaining emulsion (538.63 g) was poured into a 1.4 liter (3 US pint) tub and labeled G2. The emulsion was cured by placing this jar G1 in a 60°C water bath and periodically tested by placing the probe described above on top of the emulsion. After 134 minutes, the probe sat on top of the foam and did not sink. The emulsion in the tub was cured by heating the tub G2 in a 60°C incubator for 22 hours. 4.94 % of free water was poured off from the resulting foam.

While stirring in a similar manner to above, 600 cc of aqueous 10 wt% $CaCl_2$ and 0.15 wt% potassium persulfate solution was slowly added to 20.27 g of mixture-F which had been heated at 80°C for 72 minutes. 61.08 g of the resulting emulsion was poured into a 118 cm^3 (4 fluid oz.) jar and labeled H1. The remaining emulsion (557.67 g) was poured into a 1.4 liter (3 US pint) tub and labeled H2. The emulsion was cured by placing this jar H1 in a 60°C water bath and periodically tested by placing the probe described above on top of the emulsion. After 132 minutes, the probe sat on top of the foam and did not sink. The emulsion in the tub was cured by heating the tub H2 in a 60°C incubator for 21 hours. 6.8 % of free water was poured off from the resulting foam.

While stirring in a similar manner to above, 600 cc of aqueous 10 wt% $CaCl_2$ and 0.15 wt% potassium persulfate solution was slowly added to 20.21 g of mixture-F which had been heated at 80°C for 84 minutes. 59.22 g of the resulting emulsion was poured into a 118 cm^3 (4 fluid oz.) jar and labeled I1. The remaining emulsion (551.61 g) was poured into a 1.4 liter (3 US pint) tub and labeled I2. The emulsion was cured by placing this jar I1 in a 60°C water bath and periodically tested by placing the probe described above on top of the emulsion. After 119 minutes, the probe sat on top of the foam and did not sink. The emulsion in the tub was cured by heating the tub I2 in a 60°C incubator for 20.33 hours. 1.6 % of free water was poured off from the resulting foam.

While stirring in a similar manner to above, 600 cc of aqueous 10 wt% $CaCl_2$ and 0.15 wt% potassium persulfate solution was slowly added to 19.98 g of mixture-F which had been heated at 80°C for 97 minutes. 63.78 g of the resulting emulsion was poured into a 118 cm^3 (4 fluid oz.) jar and labeled J1. The remaining emulsion (524.59 g) was poured into a 1.4 liter (3 US pint) tub and labeled J2. The emulsion was cured by placing this jar J1 in a 60°C water bath and periodically tested by placing the probe described above on top of the emulsion. After 110 minutes, the probe sat on top of the foam and did not sink. The emulsion in the tub was cured by heating the tub J2 in a 60°C incubator for 19 hours. 2.21 % of free water was poured off from the resulting foam.

While stirring in a similar manner to above, 600 cc of aqueous 10 wt% $CaCl_2$ and 0.15 wt% potassium persulfate solution was slowly added to 20.06 g of mixture-F which had been heated at 80°C for 111 minutes. 69.02 g of the resulting emulsion was poured into a 118 cm^3 (4 fluid oz.) and labeled K1. The remaining emulsion (552.48 g) was poured into a 1.4 liter (3 US pint) tub and labeled K2. The emulsion was cured by placing this jar K1 in a 60°C water bath and periodically tested by placing the probe described above on top of the emulsion. After 61 minutes, the probe sat on top of the foam and did not sink. The emulsion in the tub was cured by heating the tub K2 in a 60°C incubator for 18.25 hours. 6.65 % of free water was poured off from the resulting foam.

After 125 minutes, the remaining mixture-F was solid as tested by the above solidity test.

The properties of #2, tub samples are listed in Table 5.

Example 6

This example demonstrates another preparation of a low density crosslinked polymeric material by advancing the monomer mixture according to the invention and comparison run N.

A mixture-M was prepared in a similar manner to Example 5, except 100.23 g of monomer mixture (20.26 wt% styrene, 19.91 wt% divinyl benzene and 60.06 wt% of 2-ethyl hexyl acrylate) was mixed with 1.14 g of t-butyl peroxyisobutyrate (Lupersol™ 80 from Atochem, North America) and 12.34g of Span® 20 emulsifying agent (sorbitan monolaurate from Fluka Chemical Corp. or Aldrich Chemical Co.).

To 20.03 g of mixture-M, 600 cc of aqueous 10 wt% $CaCl_2$ and 0.15 wt% potassium persulfate solution was slowly added as in Example 5. 60.03 g of the resulting emulsion was poured into a 118 cm^3 (4 fluid oz.) jar and labeled N1. The remaining emulsion (540.28 g) was poured into a 1.4 liter (3 US pint) tub and labeled N2. The emulsion was cured by placing this jar N1 in a 60°C water bath and periodically tested by placing the probe described in Example 5 on top of the emulsion. After 127 minutes, the probe sat on top of the foam and did not sink. The emulsion in the tub was cured by heating the tub N2 in a 60°C incubator for 23 hours. 2.81 % of free water was poured off from the resulting foam.

In a similar manner to above, 600 cc of aqueous 10 wt% $CaCl_2$ and 0.15 wt% potassium persulfate solution was slowly added to 19.91 g of mixture-M which had been heated at 80°C for 12 minutes. 59.03 g of the resulting emulsion was poured into a 118 cm^3 (4 fluid oz.) jar and labeled O1. The remaining emulsion (531.0 g) was poured into a 1.4 liter (3 US pint) tub and labeled O2. The emulsion was cured by placing this jar O1 in a 60°C water bath and periodically tested by placing the probe described above on top of the emulsion. After 114 minutes, the probe sat on top of the foam and did not sink. The emulsion in the tub was cured by heating the tub O2 in a 60°C incubator for 22.75 hours. 6.02 % of free water was poured off from the resulting foam.

In a similar manner to above, 600 cc of aqueous 10 wt% $CaCl_2$ and 0.15 wt% potassium persulfate solution was slowly added to 20.1 g of mixture-M which had been heated at 80°C for 26 minutes. 62.88 g of the resulting emulsion was poured into a 118 cm^3 (4 fluid oz.) and labeled P1. The remaining emulsion (519.21 g) was poured into a 1.4 liter (3 US pint) tub and labeled P2. The emulsion was cured by placing this jar P1 in a 60°C water bath and periodically tested by placing the probe described above on top of the emulsion. After 89 minutes, the probe sat on top of the foam and did not sink. The emulsion in the tub was cured by heating the tub P2 in a 60°C incubator for 22.5 hours. 0 % of free water was poured off from the resulting foam..

In a similar manner to above, 600 cc of aqueous 10 wt% $CaCl_2$ and 0.15 wt% potassium persulfate solution was slowly added to 20.12 g of mixture-N which had been heated at 80°C for 37 minutes. 65.75 g of the resulting emulsion was poured into a 118 cm^3 (4 fluid oz.) jar and labeled Q1. The remaining emulsion (531.74 g) was poured into a 1.4 liter (3 US pint) tub and labeled Q2. The emulsion was cured by placing this jar Q1 in a 60°C water bath and periodically tested by placing the probe described above on top of the emulsion. After 78 minutes, the probe sat on top of the foam and did not sink. The emulsion in the tub was cured by heating the tub Q2 in a 60°C incubator for 22.25 hours. 4.36 % of free water was poured off from the resulting foam.

In a similar manner to above, 600 cc of aqueous 10 wt% $CaCl_2$ and 0.15 wt% potassium persulfate solution was slowly added to 19.99 g of mixture-N which had been heated at 80°C for 48 minutes. 64.74 g of the resulting emulsion was poured into a 118 cm^3 (4 fluid oz.) jar and labeled R1. The remaining emulsion (620.61 g) was poured into a 1.4 liter (3 US pint) tub and labeled R2. The emulsion was cured by placing this jar R1 in a 60°C water bath and periodically tested by placing the probe described above on top of the emulsion. After 82 minutes, the probe sat on top of the foam and did not sink. The emulsion in the tub was cured by heating the tub R2 in a 60°C incubator for 22 hours. 17.03 % of free water was poured off from the resulting foam.

The properties of #2, tub samples, are listed in Table 5 below.

TABLE 5

Sample	% Strain	RTCD	FD	FS	DT	VWT
B2	17.4	17.3	34.4	19.9	.447	71S
C2	11.9	15.0	37.2	15.8	.386	145S
D2	19.8	21.1	34.4	24.3	.342	90S
E2	22.4	10.7	32.6	21.1	.396	67S
G2	56.4	17.5	27.2	34.9	.344	70S
H2	37.0	15.8	35.9	19.1	.366	58S
I2	21.4	15.8	35.9	19.1	.366	68S
J2	28.6	19.4	33.8	23.9	.380	76S
K2	17.9	18.9	39.7	20.9	.391	161S
N2	28.4	18.7	33.1	23.8	.110	92S
O2	14.2	15.7	34.9	17.3	.379	91S
P2	9.5	16.5	36.8	17.2	.411	148S
Q2	10.5	14.4	37.3	15.0	.388	128S
R2	12.3	15.9	46.8	16.8	.313	128S

As can be seen from Table 5, the foams produced according to the process of the invention (obtained from the advanced monomer mixture) have comparable or better foam properties compared with an unadvanced conventionally prepared material of N2.

Example 7

This example demonstrates the advantage of the process of the invention for volatile monomers.

A 3:2 weight ratio of isoprene: divinyl benzene were mixed to produce a monomer mixture. (Commercial divinyl benzene containing 55% divinyl benzene from Aldrich Chemical Co. was used.) To this monomer mixture, 12 parts by weight for 100 parts by weight of the monomer mixture of a sorbitan monolaurate surfactant (SPAN® 20 emulsifying agent from Fluka Chemical Corp. or Aldrich Chemical Co.) was added. To this mixture 1 part by weight for 100 parts by weight of the monomer mixture of Lupersol™ 225 initiator (di(sec-butyl) peroxydicarbonate) from Atochem North America was added. The resulting mixture was advanced at the temperatures listed below. The high temperature advancement runs were performed in an autoclave blanketed with nitrogen under pressures up to 400 psig.

The mixtures were advanced for the times indicated below. To each advanced mixture an aqueous phase containing 10% $CaCl_2$ was added slowly to the advanced monomer mixture while stirring as in Example 5 to form a water-in-oil emulsion. The emulsion was poured into a 118 cm^3 (4 fluid oz.) jar and cured for a time and temperature as indicated in Table 6 below. Cure Time was determined by determining the time necessary for the emulsion to support a 2.1 kPa (0.3 psi) flat tipped probe at the surface of the emulsion.

TABLE 6

Advancement		Bromine No.	Cure Time	Foam Properties
Time	Temp.			
0		175+	>400 min.	Poor, Closed Cell Many Voids
250 min	60-80°C	144	260 min.	Normal to Poor
260 min	74-78°C	140	200 min.	Normal to Good
244 min	80-87°C	160	183 min.	Normal

As seen from the Table above, the effect of curing the emulsion containing a high mole fraction of isoprene as shown above at 60°C without advancement produces formation of closed cell foams, and broken, cracked, and disintegrated foam chuncks. At the curing temperature without advancement, emulsions containing such high mole fractions of isoprene forms pockets of gas, giving a "Swiss Cheese" appearance with many large voids when sliced. However, with the inventive process using advancement steps an open celled foam with good properties can be produced.

Example 8

This example further demonstrates the process of the invention.

1:1:3 Weight ratio of styrene: divinyl benzene:2-ethylhexyl acrylate were mixed to produce monomer mixtures. (Commercial divinyl benzene containing 55% divinyl benzene from Aldrich Chemical Co. was used.) To these monomer mixtures, 12 parts by weight for 100 parts by weight of the monomer mixture of a sorbitan monolaurate surfactant (SPAN® 20 emulsifying agent from Fluka Chemical Corp. or Aldrich Chemical Co.) was added. To these mixtures 1 part by weight for 100 parts by weight of the monomer mixture of the advancement initiators listed below were added. The resulting mixtures were advanced at the temperatures listed below and for the time listed below in Table 7.

To these advanced mixtures an aqueous phase containing 10% $CaCl_2$ was added slowly to the advanced monomer mixtures while stirring as in Example 5 to form a water-in-oil emulsion. In some batches as indicated in the Table below, 1 part by weight for 100 parts by weight of the monomer mixture of peroxide polymerization initiators or 0.14 part by weight for 100 parts by weight of the monomer mixture of potassium persulfate ("KPS") were added to the emulsion and mixed. The emulsions were poured into a 118 cm^3 (4 fluid oz.) jar and cured at 60°C. Cure Time was determined by determining the time necessary for the emulsion to support a 2.1 kPa (0.3 psi) flat tipped probe at the surface of the emulsion and listed below in Table 7.

TABLE 7

Advancement			Cure	
Time	Temp.	Initiator	Initiator	Time(min.)
0 min		--	Benzoyl peroxide	Would not cure
0 min			Lupersol™ 80[a]	212
24 min	75°C	Lupersol 80	--	190
24 min	75°C	Lupersol 80	KPS	190
36 min	75°C	Lupersol 80	KPS	179
60 min	75°C	Lupersol 80	Solidified during advancement	
0 min		Benzoyl peroxide	Lupersol 80	95
12 min	75°C	Benzoyl peroxide	Lupersol 80	100
24 min	75°C	Benzoyl peroxide	Lupersol 80	95
0 min		Lupersol 80	Benzoyl peroxide	173
12 min	75°C	Lupersol 80	Benzoyl peroxide	177
24 min	75°C	Lupersol 80	Benzoyl peroxide	173
48 min	75°C	Lupersol 80	Benzoyl peroxide	154
60 min	60°C	Benzoyl peroxide	--	158
60 min	60°C	Benzoyl peroxide	KPS	98

[a] t-butyl peroxyisobutyrate from Atochem North America.

As seen from the Table above, the emulsion did not cure properly using benzoyl peroxide as the polymerization initiator without advancement. The emulsion cured to form a foam when benzoyl peroxide was used as an advancement initiator in the oil phase before formation of the emulsion.

Example 9

This example demonstrates another preparation of a low density crosslinked polymeric material by advancing the monomer mixture according to the invention.

A 1:1:3 weight ratio of styrene: divinyl benzene:2-ethylhexyl acrylate were mixed to produce a monomer mixture. (Commercial divinyl benzene containing 55% divinyl benzene from Aldrich Chemical Co. was used.) To this monomer mixture, 12 parts by weight for 100 parts by weight of the monomer mixture of a sorbitan monolaurate surfactant (SPAN® 20 emulsifying agent from Fluka Chemical Corp. or Aldrich Chemical Co.) was added. To this mixture 1 part by weight for 100 parts by weight of the monomer mixture of Lupersol™ 80 (t-butyl peroxyisobutyrate from Atochem North America) was added. The resulting mixture was advanced at 75°C for approximately 20 minutes.

To this advanced mixture an aqueous phase containing 10% $CaCl_2$ was added slowly to the advanced monomer mixture while stirring as in Example 5 to form a water-in-oil emulsion. No additional polymerization initiator was added. The emulsion was poured into a 1.5 liter (3 US pint) tub and cured at 60°C for 16 hours. The properties of the foam are shown in Table 8 below.

<u>Example 10</u>

This example demonstrates another preparation of a low density crosslinked polymeric material by advancing the monomer mixture according to the invention.

1:1:3 Weight ratio of styrene: divinyl benzene:2-ethylhexyl acrylate were mixed to produce monomer mixtures. (Commercial divinyl benzene containing 55% divinyl benzene from Aldrich Chemical Co. was used.) To these monomer mixtures, 12 parts by weight for 100 parts by weight of the monomer mixture of a sorbitan monolaurate surfactant (SPAN® 20 emulsifying agent from Fluka Chemical Corp. or Aldrich Chemical Co.) was added. To these mixtures 1 part by weight for 100 parts by weight of the monomer mixture of Lupersol™ 80 (t-butyl peroxyisobutyrate from Atochem North America) for Example 10A and benzoyl peroxide (from Aldrich Chemical Co.) for Example 10B were added. The resulting mixtures were advanced at 75°C for 12 minutes.

To these advanced mixture an aqueous phase containing 10% $CaCl_2$ was added slowly to the advanced monomer mixtures while stirring as in Example 5 to form water-in-oil emulsions. To these emulsions, 1 part by weight for 100 parts by weight of the monomers of benzoyl peroxide for Example 10A and Lupersol™ 80 for Example 10B were added and mixed. The emulsions were poured into a 1.5

liter (3 US pint) tub and cured at 60°C for 16 hours. The properties of the foams are shown in Table 8 below.

TABLE 8

Example	% Strain	RTCD	FD	FS	DT	VWT
9	26.7	19.3	34.1	24.4	.129	126
10A	35.6	28.1	32.5	26.4	.363	70
10B	46	16.8	32.6	28.5	0.129	168

As can be seen from Table 8, the foams produced by the advancement process of the invention have comparable to superior properties compared with the comparative example, Example 6, N2, particularly in foam absorption capacity such as Free Swell.

CLAIMS

1. A process for the production of a porous crosslinked polymeric material comprising:

(a) providing an aqueous mixture comprising water and an electrolyte;

(b) advancing one or more vinyl monomers in the presence of an effective amount of an advancement initiator or by a free-radical-producing radiation source to produce an advanced monomer component having a viscosity ratio of advanced monomer component to the non-advanced monomer of greater than 1.00;

(c) adding one or more multifunctional unsaturated crosslinking monomers (i) to the one or more vinyl monomers prior to advancing in step (b), (ii) to the advanced monomer component prior to emulsion forming step (e), or to both (i) and (ii) to form an advanced monomer mixture;

(d) providing a surfactant to the aqueous mixture, the vinyl monomer, the advanced monomer component, the advanced monomer mixture, or any combinations of the aqueous mixture, vinyl monomer, advanced monomer component and advanced monomer mixture;

(e) combining and mixing said aqueous mixture and said advanced monomer mixture in a mixing vessel under conditions effective to produce a water-in-oil emulsion having at least 90 weight percent, based on the emulsion, of water as the internal phase; and

(f) heating the emulsion at a temperature of at least about 25°C to polymerize and crosslink the advanced monomers.

2. The process of claim 1 in which the one or more vinyl monomers is advanced by a monomer-soluble free-radical polymerization initiator.

3. The process of claim 2 in which the advancement initiator is present in an amount of about 0.005 to about 20 weight percent based on the monomer component in step (b).

4. The process of claim 1 in which the one or more vinyl monomers is advanced by a free-radical-producing radiation source selected from the group consisting of gamma rays, electron beams, neutrons and ultra-violet light.

5. The process of claim 3 in which the advancement initiator is an azo compound or a peroxide.

6. The process of claim 5 in which the advancement initiator is selected from the group consisting of alkylperoxycarbonates branched at the 1-carbon position or alkylperoxycarboxylates branched at the α-carbon position and/or 1-carbon position.

7. The process of claim 1 in which at least one of the vinyl monomers is selected from the group consisting of monoalkenyl arenes, acrylate or methacrylate esters, conjugated diolefins, allenes, olefin halides and mixtures thereof.

8. The process of claim 9 in which at least one of the multifunctional unsaturated crosslinking monomers is selected from the group consisting of divinyl benzene, diethylene glycol dimethacrylate, 1,3-butanediol dimethacrylate, allyl methacrylate, trimethylolpropane trimethacrylate, trimethylolpropane triacrylate, pentaerythritol tetramethacrylate, pentaerythritol tetraacrylate, glucose pentaacryalate, sorbitan triacrylate, glucosediethylmercaptal pentaacrylate, surcrose per acrylate, surcrose permethacrylate, cellulose methacrylate and cellulose acrylate.

9. The process of claim 1 in which the advanced monomer component has a viscosity ratio of advanced monomer component to the non-advanced monomer within the range of from about 1.03 to about 50.

10. A process for the production of a porous crosslinked polymeric material comprising:

(a) providing an aqueous mixture comprising water and an electrolyte;

(b) advancing one or more vinyl monomers in the presence of an effective amount of an advancement initiator or by a free-radical-producing radiation source for about 5% to about 95% of the time effective to form a solid thereby producing an advanced monomer component;

(c) adding one or more multifunctional unsaturated crosslinking monomers (i) to the one or more vinyl monomers prior to advancing in step (b), (ii) to the advanced monomer component prior to emulsion forming step (e), or to both (i) and (ii) to form an advanced monomer mixture;

(d) providing a surfactant to the aqueous mixture, the vinyl monomer, the advanced monomer component, the advanced monomer mixture, or any combinations of the aqueous mixture, vinyl monomer, advanced monomer component and advanced monomer mixture;

(e) combining and mixing said aqueous mixture and said advanced monomer mixture in a mixing vessel under conditions effective to produce a water-in-oil emulsion having at least 90 weight percent, based on the emulsion, of water as the internal phase; and

(f) heating the emulsion at a temperature of at least about 25°C to polymerize and crosslink the advanced monomers.

11. The process of claim 13 in which the one or more vinyl monomers is advanced by a monomer-soluble free-radical polymerization initiator.

12. The process of claim 14 in which the advancement initiator is present in an amount of about 0.005 to about 20 weight percent based on the monomer component in step (b).

13. The process of claim 13 in which the one or more vinyl monomers is advanced by a free-radical-producing radiation source selected from the group consisting of gamma rays, electron beams, neutrons and ultra-violet light.

14. The process of claim 15 in which the advancement initiator is an azo compound or a peroxide.

15. The process of claim 17 in which the advancement initiator is selected from the group consisting of

alkylperoxycarbonates branched at the 1-carbon position or alkylperoxycarboxylates branched at the α-carbon position and/or 1-carbon position.

16. The process of claim 13 in which at least one of the vinyl monomers is selected from the group consisting of monoalkenyl arenes, acrylate or methacrylate esters, conjugated diolefins, allenes, olefin halides and mixtures thereof.

17. The process of claim 13 in which the one or more monomers in step (b) is advanced for about 10% to about 90% of the time effective to form a solid.

18. The process of claim 23 in which the one or more monomers in step (b) is advanced for about 35% to about 88% of the time effective to form a solid.

19. A process for the production of a porous crosslinked polymeric material comprising:

(a) providing an aqueous mixture comprising water and an electrolyte;

(b) providing a monomer component comprising at least one vinyl monomer and from about 2 to about 70 weight percent, based on the mixture, of at least one multifunctional unsaturated crosslinking monomer;

(c) advancing at least a portion of said monomer component in the presence of an effective amount of an advancement initiator or by a free-radical-producing radiation source to produce an advanced monomer component having a viscosity ratio of advanced monomer component to the non-advanced monomer component of greater than 1.00;

(d) combining said advanced monomer component and any remaining monomer component if any to provide an advanced monomer mixture;

(e) providing a surfactant to the aqueous mixture, the monomer component, the advanced monomer component, the advanced monomer mixture or any combinations of the aqueous mixture, monomer component, advanced monomer component and advanced monomer mixture;

(f) combining and mixing said aqueous mixture and said advanced monomer mixture in a mixing vessel under conditions effective to produce a water-in-oil emulsion having at least 90 weight percent, based on the emulsion, of water as the internal phase; and

(g) heating the emulsion at a temperature of at least about 25°C to polymerize and crosslink the advanced monomers.

20. The process of claim 25 in which the monomer mixture is advanced by a monomer-soluble free-radical polymerization initiator.

21. The process of claim 26 in which the advancement initiator is present in an amount of about 0.005 to about 20 weight percent based on the monomer component in step (c).

22. The process of claim 27 in which the advancement initiator is an azo compound or a peroxide.

23. The process of claim 25 in which the vinyl monomer is selected from the group consisting of monoalkenyl arenes, acrylate or methacrylate esters, conjugated diolefins, allenes, olefin halides and mixtures thereof.

24. A process for the production of a porous crosslinked polymeric material comprising:

(a) providing an aqueous mixture comprising water and an electrolyte;

(b) providing a monomer component comprising at least one vinyl monomer and from about 2 to about 70 weight percent, based on the mixture, of at least one multifunctional unsaturated crosslinking monomer;

(c) advancing at least a portion of said monomer component in the presence of an effective amount of an advancement initiator or by a free-radical-producing radiation source for about 5% to about 95% of the time effective to form a solid thereby producing an advanced monomer component;

(d) combining said advanced monomer component and any remaining monomer component if any to provide an advanced monomer mixture;

(e) providing a surfactant to the aqueous mixture, the monomer component, the advanced monomer component, the advanced monomer mixture or any combinations of the aqueous mixture, monomer component, advanced monomer component and advanced monomer mixture;

(f) combining and mixing said aqueous mixture and said advanced monomer mixture in a mixing vessel under conditions effective to produce a water-in-oil emulsion having at least 90 weight percent, based on the emulsion, of water as the internal phase; and

(g) heating the emulsion at a temperature of at least about 25°C to polymerize and crosslink the advanced monomers.

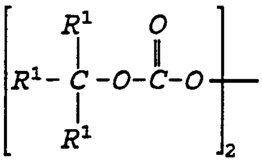
25. The process of claim 34 in which the advancement initiator is present in an amount of about 0.005 to about 20 weight percent based on the one or more vinyl monomers in step (e).

26. The process of claim 33 in which the advanced monomer component has a viscosity ratio of advanced monomer component to the non-advanced monomer within the range of from about 1.03 to about 50.

27. In a process for the production of a porous crosslinked polymeric material comprising polymerizing and crosslinking monomers in a water-in-oil high internal phase emulsion comprising a) a mixture of polymerizable monomers comprising at least one vinyl monomer and from 2 to 70 weight percent, based on the mixture, of at least one multifunctional unsaturated crosslinking monomer, b) at least 90 weight percent, based on the emulsion, of water as the internal phase, c) a surfactant, and d) a polymerization initiator, the improvement which comprises polymerizing the monomers in the presence of a polymerization initiator selected from the group consisting of alkylperoxycarbonates branched at the 1-carbon position and

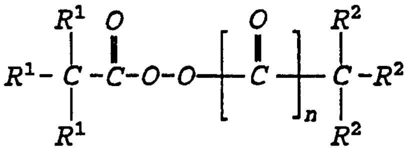
alkylperoxycarboxylates branched at least one of the α-carbon or 1-carbon position.

28. The process of claim 44 in which the polymerization initiator is an alkyl carbonate peroxide represented by the formula:



$$\left[R^1-\overset{R^1}{\underset{R^1}{C}}-O-\overset{O}{\overset{\|}{C}}-O \right]_2$$

wherein R^1 is independently C_1 to C_{16} hydrocarbon groups or hydrogen in which at least two of the R^1 are hydrocarbon groups, or an alkyl carboxylate peroxide represented by the formula:



$$R^1-\overset{R^1}{\underset{R^1}{C}}-\overset{O}{\overset{\|}{C}}-O-O-\left[\overset{O}{\overset{\|}{C}}\right]_n-\overset{R^2}{\underset{R^2}{C}}-R^2$$

$n=0,1$

wherein R^1 and R^2 are independently C_1 to C_{16} hydrocarbon groups or hydrogen in which at least two of the R^1 or R^2 are hydrocarbon groups.

29. The process of claim 45 in which the polymerization initiator is an alkyl carboxylate peroxide wherein at least two of both R^1 and R^2 are an alkyl group.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 94/00779

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08J9/28 C08F2/32

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)
IPC 6 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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,5 210 104 (BASS R.M. ET AL) 11 May 1993 see claims 1,2,8 ---	1,7
Y	DE,A,16 69 779 (WILL, G.) 7 October 1971 see claims 1,4 ---	1,7
A	EP,A,0 503 156 (SCHOCK & CO. GMBH) 16 September 1992 see claim 1 see examples ---	1
A	US,A,3 929 685 (JUNG B.) 30 December 1975 see claim 1 -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in 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

1

Date of the actual completion of the international search 10 October 1994	Date of mailing of the international search report 11. 11. 94
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Authorized officer Niaounakis, M

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/00779

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 8, 11-18, 20-23, 25-26, 28-29
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Said claims refer to either not-existing or misnumbered claims, or even to themselves, and therefore do not comply with the requirements set by Article 17(2) (a) (ii) and (b) of the PCT Regulations

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searches without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US 94/00779

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-5210104	11-05-93	AU-B-	4241393	09-05-94
		WO-A-	9409061	28-04-94
DE-A-1669779	07-10-71	NONE		
EP-A-0503156	16-09-92	DE-A-	4104295	27-08-92
		CA-A-	2061053	14-08-92
		JP-A-	4351512	07-12-92
		US-A-	5254599	19-10-93
US-A-3929685	30-12-75	NONE		