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(54) Title: METHOD FOR PREPARING ORGANIC PEROXIDES ON SITE

(57) Abstract: The present invention relates to a process for preparing an organic peroxide and the subsequent use thereof in a (co)polymerization reaction, wherein the process comprises the steps (a), b1 (or b2), (c), (d), and (e), said steps being: (a) the reaction of chlorine with carbon monoxide, (b1) the reaction of phosgene formed in step (a) with one or more alcohols in order to prepare chloroformate, (b2) the reaction of phosgene formed in step (a) with one or more organic acids to prepare acid chloride, optionally in the presence of a catalyst suitable to effect the reaction of phosgene with said one or more organic acids, (c) the reaction of chloroformate, acid chloride, or mixture thereof with (in)organic hydroperoxide and base in an aqueous environment, (d) the transfer of organic peroxide formed in step (c) to a polymerization vessel, and (e) the (co)polymerization of monomer in the polymerization vessel in the presence of one or more organic peroxides transferred in step (d), wherein all of steps (a)-(e) are conducted at one site.

METHOD FOR PREPARING ORGANIC PEROXIDES ON SITE

The present invention relates to processes for preparing organic peroxides (on site) by mixing chloroformate or acid chloride with (in)organic hydroperoxide and base in an aqueous environment. The present invention also relates to the use of said organic peroxides in (co)polymerization processes.

The importance of organic peroxides for (co)polymerization processes has long been recognized and, as a consequence, a plethora of documents report on the utility of organic peroxides, such as peroxydicarbonates, diacyl peroxides, and peroxy esters, as initiators for polymerization and co-polymerization processes of ethylenically unsaturated monomers. Due to the safety hazards associated with most organic peroxides in respect of handling, preparation, and transportation, specific safety measures are often required. Such can be accomplished, for example, by cooling the organic peroxides to relatively low temperatures and/or by preparing an organic peroxide composition wherein the organic peroxide is diluted and/or stabilized. All these safety measures facilitate the overall stability of the organic peroxide against thermal influence and impact shock. Alternatively, the organic peroxide that is to be used as initiator in a (co)polymerization process can be prepared immediately prior to use in the (co)polymerization process.

An example of a polymerization process using a peroxydicarbonate that is prepared immediately prior to use in such a process is disclosed in GB 1,484,675. The peroxydicarbonate is prepared by reacting at least one haloformate with at least one inorganic peroxide in the presence of water, a water-immiscible solvent, and a base. The thus obtained reaction mixture, comprising freshly prepared peroxydicarbonate, is then transferred to a polymerization vessel. A drawback to the process of GB 1,484,675 is that it requires transport of chloroformate to and storage thereof at the production plant where the peroxydicarbonate is to be prepared. For each desired peroxydicarbonate, a specific chloroformate derivative needs to be transported to and stored at the production plant. Since chloroformates are dangerous compounds to work with, the process of GB 1,484,675 requires adequate safety measures to be taken for transportation as well as storage.

WO 01/32613 discloses a process for producing peroxydicarbonates by first mixing haloformate, dispersant, and water and then gradually admixing to this reaction mixture another mixture comprising inorganic peroxide and alkali metal hydroxide. In addition, WO 01/32613 discloses a polymerization process of ethylenically unsaturated monomer wherein said ethylenically unsaturated monomer, water, dispersant, and freshly prepared peroxydicarbonate are mixed and allowed to react. The peroxydicarbonate is prepared outside the polymerization vessel (*ex situ*) and preferably the entire content of freshly prepared peroxydicarbonate is transferred to the polymerization vessel. Again, a drawback is that for each peroxydicarbonate to be prepared according to the process of WO 01/32613 a specific chloroformate derivative needs to be transported to and stored at the production plant, again requiring adequate safety measures to be taken into consideration.

A problem still unresolved in the prior art processes is to provide a method for convenient (on site) preparation of organic peroxides for immediate use, using inexpensive compounds that can be handled, transported, and stored easily and safely.

Hence, it is an objective of the present invention to provide a process to overcome this problem, said process being pre-eminently suited for convenient (on site) preparation of organic peroxides for immediate use, using inexpensive compounds that can be handled, transported, and stored easily and safely.

The term “immediate use” is used to indicate that the organic peroxides are not stored before their use in a subsequent step.

We have now found a process for preparing organic peroxides and the subsequent use thereof in a (co)polymerization reaction, wherein the process comprises the steps (a), b1 (or b2), (c), (d), and (e), said steps being:

(a) the reaction of chlorine with carbon monoxide,

(b1) the reaction of phosgene formed in step (a) with one or more alcohols in order to prepare chloroformate,

(b2) the reaction of phosgene formed in step (a) with one or more organic acids to prepare acid chloride, optionally in the presence of a catalyst suitable to effect the reaction of phosgene with said one or more organic acids,

(c) the reaction of chloroformate, acid chloride, or a mixture thereof with (in)organic hydroperoxide and base in an aqueous environment,

(d) the transfer of organic peroxide formed in step (c) to a polymerization vessel, and

(e) the (co)polymerization of monomer in the polymerization vessel in the presence of one or more organic peroxides transferred in step (d),

wherein all of steps (a)-(e) are conducted at one site.

It is noted that the term “one site” means a site area including the adjacent area that is not part of the public domain. Hence, the term “one site” includes two or more sites which are located at such a distance from each other so as to enable transport of any one of the products of steps (a)-(c) to another site within a short timespan so as to enable the process of the invention to be carried out within an acceptable timespan so as to have the advantages of the present invention (vide supra). For example, two or more sites are linked by one or more pipelines, via which products of steps (a)-(c) can be transported from one site to another.

Preferably, all of steps (a)-(e) of the process of the present invention are conducted within a timespan of 4 weeks, preferably 3 weeks, more preferably 2 weeks, even more preferably 7 days, even more preferably still 4 days, and most preferably 2 days.

In a preferred embodiment, the present invention relates to aqueous dispersion (co)polymerization processes wherein at least one organic peroxide according to the above-described process for preparing organic peroxides is used.

In another preferred embodiment, the present invention relates to the process for preparing organic peroxides and the subsequent use thereof in a (co)polymerization reaction according to the invention at the site of a vinyl chloride monomer producer. Producers of polyvinyl chloride (PVC) often have a chlorine-handling facility on site, for example, due to the on site production of vinyl chloride monomer (VCM). This chlorine-handling facility can also be used to provide chlorine for step (a) of the process of the present invention. Carbon monoxide is abundantly available, inexpensive, and easy to handle. Furthermore, it is convenient for a producer of polymer products to use alcohols and/or organic acids, since also alcohols and organic acids are generally widely available, easy to handle, and inexpensive. Furthermore, alcohols and organic acids generally do not require adequate safety measures and can therefore be stored in conventional storage vessels. An additional advantage is that this process allows producing only the amount of chloroformate or acid chloride required for the preparation of the corresponding organic peroxide. Consequently, practically no residue of chloroformate or acid chloride will remain, which otherwise would have required adequate safety measures for storage or, alternatively, would have been discarded as waste material. For example, it is preferred not to have storage of chloroformates, since chloroformates are not fully stable and may form alkyl chlorides and carbonates upon storage.

Step (a), i.e. the generation of phosgene by reaction of chlorine with carbon monoxide, is conducted according to a conventional procedure known in the art, for example, as disclosed in *Kirk & Othmer*, Vol. 17, page 419. The chlorine and carbon monoxide must be extremely dry to avoid corrosion of the reactor and other equipment used and to prevent decomposition of phosgene by water and by other impurities. In a preferred embodiment, the reactor used to generate the phosgene gas (reactor 1) is in close proximity to the reactor where the phosgene is consumed (*ex situ*) (reactor 2). The term "in close proximity" is used to indicate that the distance between reactor 1 and reactor 2 is such that the phosgene in reactor 2 is preferably consumed within 1 hour after generation of the phosgene gas in reactor 1. More preferably, the phosgene gas is consumed within 15 minutes after production, most preferably within 5 minutes after production. This eliminates the need for storage and transportation of this hazardous gas. The reactor to generate the phosgene gas may be a conventional "phosgene generator" commercially available from, for example, Aker Kvaerner.

The process for preparing chloroformate from phosgene and alcohol as in step (b1) is well-known in the art, for example, from US 4,778,913 and US 4,584,142. The process for preparing acid chloride from phosgene and organic acid as in step (b2) is also well-known in the art, for example, from T.A. Ryan, C. Ryan, E.A. Seddon, K.R. Seddon, *Phosgene and Related Carbonyl Halides* (Elsevier, 1996), p. 488".

Alcohols suitable for use in step (b1) are well-known compounds, most of them being commercially available. They are of the general formula R^1-OH, wherein R^1 represents an organic group, more particularly wherein R^1 represents a linear or branched, substituted or unsubstituted alkyl group, alkenyl group, alkynyl group, or cycloalkyl group. R^1 preferably has from 1 up to 40 carbon atoms, more preferably from 1 up to 30 carbon atoms, even more preferably from 1 up to 20 carbon atoms, and most preferably from 1 up to 12 carbon atoms. Preferred alcohols are selected from the group consisting of methanol, ethanol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, iso-butyl alcohol, tert-butyl alcohol, tert-amyl alcohol, 2-methyl-1-butanol, 3-methyl-2-butanol, n-pentyl alcohol, neopentyl alcohol, 2-pentanol, 3-pentanol, n-hexyl alcohol, 2-hexanol, 3-hexanol, 2-methyl-1-pentanol, n-heptyl alcohol, n-octyl alcohol, n-nonanol, n-decanol, n-undecanol, n-dodecanol, 2-(ethyl)hexyl alcohol, 2-phenyl-2-propanol, 1,1,3,3-(tetramethyl)butyl alcohol, 4-(tert-butyl)cyclohexyl alcohol, myristyl alcohol, cetyl alcohol, cyclohexyl alcohol, 3-methoxy butanol, 2-methoxy ethanol, 2-butoxy ethanol, diethylene glycol, triethylene glycol, 2-benzyloxy ethanol, 2-chloro ethanol, 3-bromo ethanol, and mixtures thereof. More preferred alcohols are selected from the group consisting of ethanol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, 2-methyl-1-butanol, 3-methyl-2-butanol, n-pentyl alcohol, neopentyl alcohol, 2-pentanol, 3-pentanol, n-hexyl alcohol, 2-hexanol, 3-hexanol, 2-methyl-1-pentanol, n-heptyl alcohol, n-octyl alcohol, n-nonanol, n-decanol, n-undecanol, n-dodecanol, 2-(ethyl)hexyl alcohol, 2-phenyl-2-propanol, 1,1,3,3-(tetramethyl)butyl alcohol, 4-(tert-butyl)cyclohexyl alcohol, 3-methoxy butanol, and mixtures thereof.

If present, the substituents on R^1 are preferably selected from the group consisting of hydroxide, carboxylic acid esters, and alkoxy groups. Hence, R^1-OH can also be a diol compound or triol compound.

Organic acids suitable for use in step (b2) are well-known compounds, most of them being commercially available. They are of the general formula R^2(O)-OH, wherein R^2 represents an organic group, more particularly wherein R^2 represents a linear or branched, substituted or unsubstituted alkyl group, alkenyl group, alkynyl group, or cycloalkyl group. R^2 preferably has from 1 up to 40 carbon atoms, more preferably from 1 up to 30 carbon atoms, even more preferably from 1 up to 20 carbon atoms, and most preferably from 1 up to 12 carbon atoms. Preferred organic acids are selected from the group consisting of acetic acid, chloroacetic acid, dichloroacetic acid, hydroxyacetic acid, propionic acid, acrylic acid, 3-benzoylacrylic acid, methacrylic acid, propenoic acid, 2-hydroxypropanoic acid, isobutyric acid, 2-chloro-2-methylpropionic acid, 2-hydroxyisobutyric acid, 3-phenylpropenoic acid, butyric acid, 2-methylbutanoic acid, 2-butenoic acid, 2-methyl-2-butenoic acid, 3-methyl-2-butenoic acid, 2,3-dimethyl-2-butenoic acid, 2-ethyl-2-butenoic acid, 2,2-dimethylbutanoic acid, 2-ethylbutanoic acid, 3-hydroxybutanoic acid, 3-hydroxybutyric acid, 4-hydroxybutanoic acid, pentanoic acid, 2,2-dimethylpentanoic acid, 2,2-dimethylvaleric acid, 2-hydroxypentanoic acid, 3-hydroxypentanoic acid, 4-hydroxypentanoic acid, 5-hydroxypentanoic acid, 2-pentenoic acid, 4-methyl-2-pentenoic acid, 2,3-dimethyl-2-pentenoic acid, 3,4-dimethyl-2-2-pentenoic acid, 4-hydroxy-2-pentenoic acid, 2,2-dimethylpropionic acid, hydroxypivalic acid, hexanoic acid, 2-hydroxyhexanoic acid, 6-hydroxyhexanoic acid, 2,2-dimethylhexanoic acid, 2-ethylhexanoic acid, 3,5,5-trimethylhexanoic acid, 2-hexenoic acid, 2,4-hexadienoic acid, benzoic acid, 2-methylbenzoic acid, 3-methylbenzoic acid, 4-methylbenzoic acid, 4-tert-butylbenzoic acid, 3-chlorobenzoic acid, 2,4-dichlorobenzoic acid, heptanoic acid, 2,2-dimethylheptanoic acid, cyclohexane carboxylic acid, octanoic acid, neodecanoic acid, 8-hydroxyoctanoic acid, 2-octenoic acid, phenylacetic acid, phenoxyacetic acid, nonanoic acid, 2-nonenoic acid, decanoic acid, lauric acid, oxalic acid, succinic acid, hydroxysuccinic acid, itaconic acid, methylsuccinic acid, diglycolic acid, maleic acid, fumaric acid, citraconic acid, pentanedioic acid, hexanedioic acid, 3,5,5-trimethyl hexanedioic acid, 2,4,4, trimethyl hexanedioic acid, p-phenylene diacrylic acid, 1,4-cyclohexane dicarboxylic acid, phthalic acid, terephthalic acid, isophthalic acid, decanedioic acid, cyclohexane-1,4-diacetic acid, undecanedioic acid, dodecanedioic acid, citric acid, 1,2,4-benzenetricarboxylic acid, 1,3,5-benzenetricarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid, methoxy acetic acid, ethoxy acetic acid, ethylenediamine tetraacetic acid, and mixtures thereof.

If present, the substituents on R^2 are preferably selected from the group consisting of carboxylic acid, carboxylic acid esters, and alkoxy groups. Hence, R^2(O)-OH can also be a dicarboxylic acid or tricarboxylic acid.

Optionally, in step (b2) use may be made of a catalyst suitable to effect the reaction of phosgene with the one or more organic acids used. Depending on the reaction conditions of step (b2), a conventional type of catalyst may be used in the usual amounts known in the art, as will be clear to a person of ordinary skill.

Many documents in the art disclose the preparation of peroxydicarbonate, peroxyesters and/or diacyl peroxides by mixing chloroformate and/or acid chloride with (in)organic hydroperoxide and base in an aqueous environment. As already mentioned above, GB 1,484,675 and WO 01/32613 both disclose the preparation of peroxydicarbonate by reacting at least one haloformate with at least one inorganic peroxide in an aqueous environment in the presence of a base.

In the process of the present invention the prepared chloroformate and/or acid chloride is preferably mixed with (in)organic hydroperoxide and base in an aqueous environment within 3 weeks after preparation of the chloroformate and/or acid chloride, more preferably within 1 week, most preferably within 48 hours.

A suitable base for use in the process of the present invention is preferably selected from the group consisting of alkali metal hydroxides, such as sodium hydroxide, potassium hydroxide, lithium hydroxide, calcium hydroxide, magnesium hydroxide, carbonates, such as sodium carbonate, potassium carbonate, lithium carbonate, calcium carbonate, bicarbonates, such as sodium bicarbonate, potassium bicarbonate, lithium bicarbonate, oxides, such as calcium oxide, magnesium oxide, and mixtures of any of the above-mentioned bases. More preferably, the base is selected from the group consisting of sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, calcium oxide, and mixtures thereof, and most preferably, the base is sodium hydroxide, sodium carbonate, sodium bicarbonate, or calcium oxide.

It is noted that the term "aqueous environment" is used to describe a solvent system that comprises water and optionally may comprise other (organic) solvents. Said other (organic) solvents may be water-miscible and/or water-immiscible solvents.

In a preferred embodiment of the invention, the base used is an aqueous solution of said base, preferably an aqueous solution of sodium hydroxide, potassium hydroxide, or a mixture thereof. The concentration of base in water is not critical, but the pH-value of the reaction mixture in the process for preparing organic peroxides by mixing chloroformate and/or acid chloride with (in)organic hydroperoxide and base in an aqueous environment preferably is more than 4, more preferably the pH-value is 5-14, and most preferably 9-14, during at least part of said process.

Preferred (in)organic hydroperoxides are selected from the group consisting of hydrogen peroxide and organic hydroperoxides of the general formula R^3-O-OH as specified below. Although it is preferred to use only one (in)organic hydroperoxide, it is also possible to use a mixture of two or more in(organic) hydroperoxides.

If the (in)organic hydroperoxide is an organic hydroperoxide of the general formula R^3-O-OH, wherein R^3 represents an organic group, more particularly wherein R^3 represents a linear or branched, substituted or unsubstituted alkyl group, alkenyl group, alkynyl group, or cycloalkyl group, R^3 preferably has from 1 up to 40 carbon atoms, more preferably from 1 up to 30 carbon atoms, even more preferably from 1 up to 20 carbon atoms, and most preferably from 1 up to 12 carbon atoms. Preferably, R^3 has at least 4 carbon atoms. Preferred organic hydroperoxides are selected from the group consisting of methyl hydroperoxide, ethyl hydroperoxide, n-propyl hydroperoxide, isopropyl hydroperoxide, sec-butyl hydroperoxide, isobutyl hydroperoxide, 1-phenyl-1-hydroperoxy ethane, hexylene glycol hydroperoxide, benzyl hydroperoxide, methylethyl ketone hydroperoxide, i.e. a mixture of 2,2'-dihydroperoxy-2-2'-di-n-butyl peroxide and 2,2-dihydroperoxy butane, cyclohexanone hydroperoxide, i.e. a mixture of 1,1'-dihydroperoxy-1,1'-dicyclohexyl peroxide and 1,1-dihydroperoxy cyclohexane, and cyclohexyl hydroperoxide. It is preferred to use tertiary organic hydroperoxides, i.e. hydroperoxides having one or more hydroperoxy groups linked to tertiary carbon atoms. Particularly preferred tertiary organic hydroperoxides are selected from the group consisting of tert-butyl hydroperoxide (TBHP), tert-amyl hydroperoxide (TAHP), 1,1,3,3-tetramethylbutyl hydroperoxide (TMBH), 2-hydroperoxy-2-methyl pentane, 2-hydroperoxy-2-methyl-3-butene, 2-hydroperoxy-2,4,4-trimethyl pentane, 2,5-dihydroperoxy-2,5-dimethyl hexane, 2,5-dihydroperoxy-2,5-dimethyl-3-hexyn, 2,6-dihydroperoxy-4-hydroxy-2,6-dimethyl heptane, 2-hydroperoxy-4-hydroxy-2-methyl butane, 2-hydroperoxy-4-hydroxy-2-methyl pentane, 2-hydroperoxy-4-hydroxy-2-methyl heptane, 3-ethyl-3-hydroperoxy-5-hydroxy hexane, cumyl hydroperoxide (2-phenyl-2-hydroperoxy propane), m- and p-isopropylcumyl hydroperoxide, m- and p-(tert-butylperoxy isopropyl)cumyl hydroperoxide, 1-hydroperoxy-1-methyl cyclohexane, 1-hydroperoxy-5-hydroxy-1,3,3-trimethyl cyclohexane, p-menthane hydroperoxide, pinane hydroperoxide, hexyleneglycol hydroperoxide, and mixtures thereof.

If the "(in)organic hydroperoxide" used in the process of the present invention is hydrogen peroxide, it is preferably used as an aqueous solution with a concentration of at least 1 percent by weight (%w/w), more preferably at least 10%w/w, even more preferably at least 30%w/w, and most preferably at least 50%w/w of hydrogen peroxide, and preferably at most 100%w/w and most preferably at most 70%w/w of hydrogen peroxide, based on the weight of the aqueous solution.

In a preferred embodiment wherein hydrogen peroxide is used, the hydrogen peroxide is reacted with base in an aqueous environment and a mixture of isobutyryl chloride and chloroformate as in step (c), to give a peroxide mixture that is very suitable for use in the production of PVC.

The most preferred (in)organic hydroperoxides for the present invention are selected from the group consisting of hydrogen peroxide, tert-butyl hydroperoxide, tert-amyl hydroperoxide, tert-tetramethylbutyl hydroperoxide, hexyleneglycol hydroperoxide, and mixtures thereof.

The one or more (in)organic hydroperoxides used in the present invention may be used as such (neat), as a solution in one more inert organic solvents, or as a solution or dispersion in water, optionally in combination with co-solvents. Here the term "inert" indicates that the solvent does not interfere with the organic one or more (in)organic hydroperoxides, which means that the amount of (in)organic hydroperoxide converted when solvent is present is at least 80% of the amount converted when no solvent is present.

The reaction of chloroformate or acid chloride with (in)organic hydroperoxide and base in an aqueous environment can be carried out using any conventional method known in the art. For example, (in)organic hydroperoxide can be mixed with base in water to form aqueous alkali metal peroxide. Subsequently, this aqueous alkali metal peroxide can be mixed with chloroformate (or acid chloride). Alternatively, (in)organic hydroperoxide, alkali metal hydroxide, and chloroformate (or acid chloride) can be intermixed at once. For both examples, the reaction can be conducted in a one-pot set up, or, alternatively, two or more vessels may be used. If desired, also various water-miscible or water-immiscible solvents may be used in the reaction. Optionally, one or more conventional dispersants may be added to the reaction. Preferred dispersants are selected from the group consisting of hydrolyzed polyvinyl acetate, methyl cellulose, hydroxy propyl cellulose, gelatin, polyvinylpyrrolidine, polyoxyethylene sorbitan monolaurate, polyacrylic acid, fatty alcohol ethoxylates, and mixtures thereof. It is more preferred to use hydrolyzed polyvinyl acetate and most preferred to use hydrolyzed polyvinyl acetate having a degree of hydrolysis of about 55% to 90%. If used, these dispersants are preferably used in an amount of at least 0.1%w/w, more preferably 0.3%w/w of dispersant, and preferably at most 10 %w/w, more preferably at most 6%w/w of dispersant, based on the amount of water. The dispersant may be added to the water as such (neat) or as a solution, for example in water.

Depending on the organic peroxide desired, i.e. peroxydicarbonate, peroxy ester, or diacyl peroxide, it will be obvious to a person of ordinary skill what exact method should be followed.

In a preferred embodiment, the invention relates to a process for preparing organic peroxide and the subsequent use thereof in a (co)polymerization reaction as described above, wherein the organic peroxide is a peroxydicarbonate, peroxy ester, diacyl peroxide and/or mixture thereof, each having a preferred half-life period of at least 0.0001 hour and at most 1.0 hour at the polymerization temperature. More preferably, the half-life of each of the organic peroxides is at most 0.8 hours, even more preferably the half-life of each of the peroxydicarbonate, peroxy ester, and/or diacyl peroxide is at most 0.5 hours and most preferably at most 0.3 hours at the polymerization temperature.

The (co)polymerization process can be conducted as a suspension process wherein the reaction mixture typically is a suspension of monomer in water or as an emulsion or micro-emulsion process wherein the monomer typically is emulsified in water. In both the suspension process and the emulsion process the usual additives will have to be used, such as surfactant(s), protective colloid(s), anti-fouling agent(s), pH-buffer(s), and the like.

The amount of organic peroxide of the present invention to be used as initiator in the (co)polymerization process of this invention is within the range used in conventional polymerization processes. Preferably at least 0.005%w/w and more preferably at least 0.01%w/w of initiator, and preferably at most 2%w/w, more preferably at most 1%w/w, and most preferably at most 0.5 %w/w of initiator, based on the weight of monomer(s) to be polymerized, is used. It is noted that the organic peroxide used as initiator may be used in combination with other (conventional) initiators which are known to the person skilled in the art.

The process of the present invention is pre-eminently suited for the (co)polymerization of one or more ethylenically unsaturated monomers, such as (meth)acrylic acid (esters), styrene, vinyl acetate, acrylonitrile, vinyl chloride monomer (VCM), and the like and mixtures thereof. As already indicated above, particularly for producers of polyvinyl chloride (PVC) an additional advantage of the present invention is that the chlorine-handling facility which is often already present on site for the preparation of VCM may also be used for the preparation of phosgene according to step (a).

In a preferred embodiment, the organic peroxide is added to the (co)polymerization mixture as a liquid, which can be a liquid organic peroxide (or mixture of two or more organic peroxides) as such (neat), a mixture of organic peroxide(s) in one or more conventional inert solvents, or an emulsion in water of one or more undiluted or diluted organic peroxides, optionally in the presence of one or more conventional adjuvants, such as dispersants and/or anti-freeze agents. Here the term “inert” indicates that the solvent does not interfere with the organic peroxide, which means that the amount of organic peroxide converted when solvent is present is at least 80% of the amount converted when no solvent is present.

A most preferred embodiment of the invention is a process wherein a polymer producer with a chlorine-handling facility on site is using chlorine gas from said facility to produce chloroformate or acid chloride on site, subsequently used within 1 hour for the production of organic peroxide for use in a process to make polymers.

The invention is further elucidated by the following example.

Example 1

A polyvinyl chloride was prepared in accordance with the process of the invention comprising the steps of:

- Vinyl chloride monomer (VCM) is produced from ethylene and chlorine in a process as described in ref. [1].
- CO is prepared by reduction of CO_2 in a process as described in ref. [2].
- Phosgene is prepared from chlorine and CO in a process as described in ref. [3]. The CO is obtained as described above, the chlorine is available from a chlorine-handling facility on site.
- The phosgene produced in the previous step and 2-ethylhexanol were immediately used to prepare 2-Ethylhexyl chloroformate according to the process described in ref. [4].
- 2-Ethylhexyl chloroformate of the previous step is used together with hydrogen peroxide and aqueous sodium hydroxide to prepare di(2-ethylhexyl) peroxydicarbonate in a process as described in ref. [5].
- Di(2-ethylhexyl) peroxydicarbonate of the previous step is used as initiator in a suspension polymerization process as described in ref. [6] to produce polyvinyl chloride (PVC) from VCM.

[1] *Kirk-Othmer Encyclopedia of Chemical Technology*, Online Electronic version, Copyright 2003, Article: "Vinyl Chloride", Chapter 4: "Manufacture". [DOI: 10.1002/0471238961.2209142503152306.a01]

[2] *Ullmann's Encyclopedia of Industrial Chemistry*, Online Electronic Version, Release 2003, 7th Edition., Article: "Carbon Monoxide", Chapter 4: "Production". [DOI: 10.1002/14356007.a05_203]

[3] *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 17, pp. 419-420.

[4] *Ullmann's Encyclopedia of Industrial Chemistry*, Online Electronic Version , Release 2003, 7th Edition., Article: "Chloroformic esters", Chapter 4: "Production". [DOI: 10.1002/14356007.a06_559]

[5] US patent 4,394,328.

[6] *Kirk-Othmer Encyclopedia of Chemical Technology*, Online Electronic version, Copyright 2003, Article: "Vinyl Chloride Polymers", Chapter 4: "PVC Resin Manufacturing Process".
[DOI (i.e. Digital Object Identifier) :
10.1002/0471238961.2209142519211313.a01]

With the process of Example 1 di(2-ethylhexyl) peroxydicarbonate is readily and conveniently prepared for immediate use, using inexpensive compounds. As the time between subsequent steps is short, the hazard risk of the intermediate products, such as phosgene and 2-ethylhexyl chloroformate, is minimized.

CLAIMS

1. Process for preparing an organic peroxide and the subsequent use thereof in a (co)polymerization reaction, wherein the process comprises the steps (a), b1 (or b2), (c), (d), and (e), said steps being:
   (a) the reaction of chlorine with carbon monoxide,
   (b1) the reaction of phosgene formed in step (a) with one or more alcohols in order to prepare chloroformate,
   (b2) the reaction of phosgene formed in step (a) with one or more organic acids to prepare acid chloride, optionally in the presence of a catalyst suitable to effect the reaction of phosgene with said one or more organic acids,
   (c) the reaction of chloroformate, acid chloride, or mixture thereof with (in)organic hydroperoxide and base in an aqueous environment,
   (d) the transfer of organic peroxide formed in step (c) to a polymerization vessel, and
   (e) the (co)polymerization of monomer in the polymerization vessel in the presence of one or more organic peroxides transferred in step (d),

   wherein all of steps (a)-(e) are conducted at one site.

2. A process according to claim 1 wherein all of steps (a)-(e) are conducted within a timespan of 4 weeks, preferably 3 weeks, more preferably 2 weeks, even more preferably 7 days, even more preferably still 4 days, and most preferably 2 days.

3. A process according to claim 1 or 2 wherein the one or more alcohols have the general formula R^1-OH, wherein R^1 represents a linear or branched, substituted or unsubstituted alkyl group, alkenyl group, alkynyl group, or cycloalkyl group, having from 1 up to 40 carbon atoms.

4. A process according to claim 3 wherein the one or more alcohols are selected from the group consisting of methanol, ethanol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, iso-butyl alcohol, tert-butyl alcohol, tert-amyl alcohol, 2-methyl-1-butanol, 3-methyl-2-butanol, n-pentyl alcohol, neopentyl alcohol, 2-pentanol, 3-pentanol, n-hexyl alcohol, 2-hexanol, 3-hexanol, 2-methyl-1-pentanol, n-heptyl alcohol, n-octyl alcohol, n-nonanol, n-decanol, n-undecanol, n-dodecanol, 2-(ethyl)hexyl alcohol, 2-phenyl-2-propanol, 1,1,3,3-(tetramethyl)butyl alcohol, 4-(tert-butyl)cyclohexyl alcohol, myristyl alcohol, cetyl alcohol, cyclohexyl alcohol, 3-methoxy butanol, 2-methoxy ethanol, 2-butoxy ethanol, diethylene glycol, triethylene glycol, 2-benzyloxy ethanol, 2-chloro ethanol, 3-bromo ethanol, and mixtures thereof.

5. A process according to claim 1 or 2 wherein the one or more organic acids have the general formula R^2-(O)OH, wherein R^2 represents a linear or branched, substituted or unsubstituted alkyl group, alkenyl group, alkynyl group, or cycloalkyl group, having from 1 up to 40 carbon atoms.

6. A process according to claim 5 wherein the one or more amino acids are selected from the group consisting of acetic acid, chloroacetic acid, dichloroacetic acid, hydroxyacetic acid, propionic acid, acrylic acid, 3-benzoylacrylic acid, methacrylic acid, propenoic acid, 2-hydroxy-propanoic acid, isobutyric acid, 2-chloro-2-methylpropionic acid, 2-hydroxyisobutyric acid, 3-phenylpropenoic acid, butyric acid, 2-methylbutanoic acid, 2-butenoic acid, 2-methyl-2-butenoic acid, 3-methyl-2-butenoic acid, 2,3-dimethyl-2-butenoic acid, 2-ethyl-2-butenoic acid, 2,2-dimethylbutanoic acid, 2-ethylbutanoic acid, 3-hydroxybutanoic acid, 3-hydroxybutyric acid, 4-hydroxybutanoic acid, pentanoic acid, 2,2-dimethylpentanoic acid, 2,2-dimethylvaleric acid, 2-hydroxypentanoic acid, 3-hydroxypentanoic acid, 4-hydroxypentanoic acid, 5-hydroxy-

pentanoic acid, 2-pentenoic acid, 4-methyl-2-pentenoic acid, 2,3-dimethyl-2-pentenoic acid, 3,4-dimethyl-2-2-pentenoic acid, 4-hydroxy-2-pentenoic acid, 2,2-dimethylpropionic acid, hydroxypivalic acid, hexanoic acid, 2-hydroxyhexanoic acid, 6-hydroxyhexanoic acid, 2,2-dimethylhexanoic acid, 2-ethylhexanoic acid, 3,5,5-trimethylhexanoic acid, 2-hexenoic acid, 2,4-hexadienoic acid, benzoic acid, 2-methylbenzoic acid, 3-methylbenzoic acid, 4-methylbenzoic acid, 4-tert-butylbenzoic acid, 3-chlorobenzoic acid, 2,4-dichlorobenzoic acid, heptanoic acid, 2,2-dimethylheptanoic acid, cyclohexane carboxylic acid, octanoic acid, neodecanoic acid, 8-hydroxyoctanoic acid, 2-octenoic acid, phenylacetic acid, phenoxyacetic acid, nonanoic acid, 2-nonenoic acid, decanoic acid, lauric acid, oxalic acid, succinic acid, hydroxysuccinic acid, itaconic acid, methylsuccinic acid, diglycolic acid, maleic acid, fumaric acid, citraconic acid, pentanedioic acid, hexanedioic acid, 3,5,5-trimethyl hexanedioic acid, 2,4,4, trimethyl hexanedioic acid, p-phenylene diacrylic acid, 1,4-cyclohexane dicarboxylic acid, phthalic acid, terephthalic acid, isophthalic acid, decanedioic acid, cyclohexane-1,4-diacetic acid, undecanedioic acid, dodecanedioic acid, citric acid, 1,2,4-benzenetricarboxylic acid, 1,3,5-benzenetricarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid, methoxy acetic acid, ethoxy acetic acid, ethylenediamine tetraacetic acid, and mixtures thereof.

7. A process according to any one of claims 1-6 wherein the base is selected from the group consisting of sodium hydroxide, potassium hydroxide, lithium hydroxide, calcium hydroxide, magnesium hydroxide, sodium carbonate, potassium carbonate, lithium carbonate, calcium carbonate, sodium bicarbonate, potassium bicarbonate, lithium bicarbonate, calcium oxide, magnesium oxide, and mixtures thereof.

8. A process according to any one of claims 1-7 wherein the (in)organic hydroperoxide is selected from the group consisting of hydrogen

peroxide, organic hydroperoxides of the general formula R^3-O-OH, R^3 representing a linear or branched, substituted or unsubstituted alkyl group, alkenyl group, alkynyl group or cycloalkyl group, and mixtures of hydrogen peroxide and/or one or more organic hydroperoxides of the general formula R^3-O-OH.

9. A process according to claim 8 wherein the organic hydroxyperoxide is a tertiary hydroperoxide selected from the group of consisting of tert-butyl hydroperoxide (TBHP), tert-amyl hydroperoxide (TAHP), 1,1,3,3-tetramethylbutyl hydroperoxide (TMBH), 2-hydroperoxy-2-methyl pentane, 2-hydroperoxy-2-methyl-3-butene, 2-hydroperoxy-2,4,4-trimethyl pentane, 2,5-dihydroperoxy-2,5-dimethyl hexane, 2,5-dihydroperoxy-2,5-dimethyl-3-hexyn, 2,6-dihydroperoxy-4-hydroxy-2,6-dimethyl heptane, 2-hydroperoxy-4-hydroxy-2-methyl butane, 2-hydroperoxy-4-hydroxy-2-methyl pentane, 2-hydroperoxy-4-hydroxy-2-methyl heptane, 3-ethyl-3-hydroperoxy-5-hydroxy hexane, cumyl hydroperoxide (2-phenyl-2-hydroperoxy propane), m- and p-isopropylcumyl hydroperoxide, m- and p-(tert-butylperoxy isopropyl)cumyl hydroperoxide, 1-hydroperoxy-1-methyl cyclohexane, 1-hydroperoxy-5-hydroxy-1,3,3-trimethyl cyclohexane, p-menthane hydroperoxide, pinane hydroperoxide, hexyleneglycol hydroperoxide, and mixtures thereof.

10. A process according to any one of claims 1-8 wherein the (in)organic hydroperoxide is hydrogen peroxide.

11. A process according to any one of claims 1-8 and 10 wherein the organic peroxide prepared is a peroxydicarbonate.

12. A process according to any one of claims 1-8 and 10 wherein the organic peroxide prepared is a diacyl peroxide.

13. A process according to any one of claims 1-9 wherein the organic peroxide prepared is a peroxyester.

14. Aqueous dispersion (co)polymerization process wherein at least one organic peroxide is used that is prepared in a process according to any one of claims 1-13.

15. A process according to claim 14 wherein one or more ethylenically unsaturated monomers selected from the group consisting of (meth)acrylic acid (esters), styrene, vinyl acetate, acrylonitrile, vinyl chloride monomer (VCM), and mixtures thereof are (co)polymerized.

16. A process according to claim 14 or 15 wherein the organic peroxide is prepared on site prior to use in the (co)polymerization process and the chloroformate or acid chloride, being a precursor for the organic peroxide, is prepared on site prior to the preparation of the organic peroxide.

17. A process according to claim 16 wherein phosgene used to make the chloroformate or acid chloride is made on site from chlorine available from a chlorine-handling facility that is on site in view of the production of vinyl chloride monomer, required for the polymerization process at hand.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/000434

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C409/34 C08F2/00

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 7 C07C 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, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	KIRK-OTHMER: "Encyclopedia of Chemical Technology" 1982, JOHN WILEY & SONS, NEW YORK, XP002279182 cited in the application page 419 - page 423	1-16
Y	GB 1 040 826 A (KUREHA CHEMICAL IND CO LTD) 1 September 1966 (1966-09-01) page 4, lines 6-58	1-16
Y	US 3 855 351 A (SANCHEZ J) 17 December 1974 (1974-12-17) examples I-VI	1-16
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

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"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 18 April 2005	Date of mailing of the international search report 26/04/2005
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 Cooper, S

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/000434

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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