



166166



G00002

Organic peroxide emulsions

- 5 The present invention relates to emulsions comprising at least one organic peroxide which are suitable for the suspension or emulsion (co)polymerization of an ethylenically unsaturated monomer, in particular vinyl chloride monomer.

10 The suspension or emulsion (co)polymerization of an ethylenically unsaturated monomer usually is practised using a protective colloid and/or a surface-active agent and, as polymerization initiator, a radical polymerization initiator, such as an organic peroxide, to obtain a polymer having a desired particle size distribution. Also, when producing a vinyl chloride based (co)polymer, the industry is looking for an improvement in productivity and a reduction of
15 environmental pollution, e.g., by reducing the amount of waste formed in the form of reactor fouling, and by reducing the loss of unreacted monomer. As a result, use is made of larger polymerization equipment which is becoming more and more automated and which is designed such that the whole polymerization process can be conducted without being open to the air (so-called closed
20 reactor technology).

The polymerization initiator compositions that are suitable for use in such processes are, to an increasing extent, water-emulsified organic peroxides rather than solvent-diluted organic peroxides. This development is mainly due to
25 the fact that aqueous peroxide emulsions can be easily handled and are very safe. Recently, various aqueous peroxide emulsions have been proposed for such use. In patent application JP Hei56-139509, for example, an aqueous emulsion of an organic peroxide containing an organic peroxide, a surface-active agent, a protective colloid, such as partially hydrolyzed polyvinyl acetate, and a water-soluble alcohol is disclosed. Similarly, in patent application JP
30 Hei61-130315, an aqueous emulsion of an organic peroxide containing an organic peroxide, a nonionic surface-active agent, polyvinyl acetate having an

average polymerization degree of not more than 600 and a degree of hydrolysis of at least 60 mol%, and a water-soluble alcohol is disclosed. The aqueous peroxide emulsions as described contain a protective colloid with a high solubility in water and are used in the suspension (co)polymerization of vinyl chloride. The terms (co)polymer and (co)polymerization as used throughout this document relate to homopolymers, all types of copolymers, such as block copolymers, tercopolymers, alternating copolymers, random copolymers, etc., as well as to the polymerization process to make such polymers.

It is furthermore noted that patent application JP Hei62-086005 discloses an emulsion comprising an organic peroxide, polyvinyl acetate having a degree of hydrolysis from 5 to 70%, and a water-soluble alcohol.

However, the conventional emulsions suffer from various drawbacks. More particularly, the emulsions as obtained in JP-A-56-139509 have a very high viscosity. Especially at the higher peroxide concentrations an emulsion with a remarkably high viscosity is formed which is inconvenient to handle during production, transport, and use. Also, if the amount of dispersing agent used as an emulsifying agent is reduced to lower the viscosity, the storage stability is greatly reduced.

The organic peroxide emulsions as produced by the methods described in JP-A-61-130315 and JP-A-62-086005 have an acceptable viscosity, but their storage stability is insufficient and they are inconvenient for practical use.

In addition, while some of the conventional emulsion compounds of organic peroxides show an acceptably low viscosity directly after production, they suffer from an unacceptable increase in viscosity over time during storage, for example when stored at a low temperature of about -20°C and/or when stored for a long period of time. This undesired phenomenon is specifically observed when the organic peroxide that is emulsified has a high water solubility and a low specific gravity.

Page 2b

It is noted that JP-A-58-134103 discloses a vinyl chloride suspension polymerization process wherein an emulsion of an organic peroxide is used to initiate the polymerization. In order to render PVC with a high electrical insulation, the surfactant used to make the organic peroxide emulsion is chosen from the group of non-ionic emulsifying agents, which do not have a polyoxyethylene radical.

Furthermore, US 5,278,262 discloses a polymerization apparatus and process to make PVC for pastes by means of a microsuspension or emulsion polymerization process. The organic peroxide initiators are added in the form of a solution in a solvent or in VCM.

One object of the present invention is to develop emulsions of one or more organic peroxides that suffer hardly if at all from these drawbacks. More

specifically, the invention relates to aqueous organic peroxide emulsions with a low viscosity that are stable for a long period of time.

After various experiments, the inventor found that by using chlorinated paraffin
5 as a further component in said aqueous organic peroxide emulsions, such emulsions are more easily produced and the resulting emulsions have a low viscosity and excellent storage stability for long periods of time.

Accordingly, the present invention relates to aqueous organic peroxide
10 emulsions comprising at least one organic peroxide, water, at least one antifreezing agent, at least one chlorinated paraffin, optionally at least one nonionic surface-active agent and/or optionally at least one or more protective colloids.

15 Preferably, the emulsions according to the invention comprise 0.5 to 15.0% by weight of the chlorinated paraffin, based on the weight of the total emulsion. Also, it is preferred to use a chlorinated paraffin that is liquid at about 20°C. In another preferred embodiment, the amount of chlorine in said chlorinated paraffin is from 40 to 72% by weight, based on the weight of the chlorinated
20 paraffin.

The invention furthermore relates to the use of said aqueous peroxide emulsions in a suspension or emulsion (co)polymerization of one or more ethylenically unsaturated monomers. Preferably, the emulsions according to the
25 invention are used for the (co)polymerization of vinyl chloride.

More preferably, the chlorinated paraffin that is used in the present invention contains 40 to 65% by weight of chlorine, based on the weight of the chlorinated paraffin. Such chlorinated paraffins are conventional products and are typically
30 obtained by chlorination of a paraffin wax or *n*-paraffin. The properties of the chlorinated paraffin change with the extent of chlorination. If the chlorine content exceeds 65% by weight, the chlorinated paraffin typically is a solid and handling

thereof is inconvenient. Accordingly, chlorinated paraffin with a chlorine content of 40 to 65% by weight generally is preferred.

Commercially available and suitable chlorinated paraffins include Empara® K-43, Empara K-45, and Empara K-50 (ex AJINOMOTO CO., LTD.); Toyoparax® A40 and Toyoparax ASO (ex TOSOH CORPORATION). They may be used alone or as a mixture of two or more chlorinated paraffins.

Preferably, the emulsions according to the invention comprise 0.5 to 15.0% by weight of the chlorinated paraffin. If the content of chlorinated paraffin in the aqueous organic peroxide emulsions of the present invention is below 0.5% by weight, the storage stability of the emulsion is insufficient. If the content of chlorinated paraffin in the aqueous organic peroxide emulsions of the present invention is above 15.0% by weight, the viscosity of the emulsion becomes too high. More preferably, the emulsions according to the invention comprise from 0.55 to 10.0% by weight of the chlorinated paraffin. Most preferred are aqueous peroxide emulsions comprising from 0.6 to 6.0% by weight of the chlorinated paraffin, since such emulsions have the best balanced properties.

It is preferred that the organic peroxide used in the preparation of the emulsions has a half-life of at least 10 hours at 75°C. In another preferred embodiment, the peroxides that are used have a freezing point of 0°C or lower. It is noted that if a mixture of organic peroxides is used, the freezing point of one of the peroxides may be above 0°C, provided that the freezing point of the mixture of organic peroxides is 0°C or lower. Alternatively, a peroxide with a freezing point above 0°C can be diluted with a solvent to lower its freezing point, as is explained below.

Examples of organic peroxides which can be used in the present invention include peroxydicarbonates, such as di(1-methylbutyl) peroxydicarbonate, di(n-decyl) peroxydicarbonate, di(sec-butyl) peroxydicarbonate, di(2-ethylhexyl) peroxydicarbonate, di(3-methoxybutyl) peroxydicarbonate, di(2-ethoxyethyl)

peroxydicarbonate, etc.; peroxyesters such as t-butyl peroxy pivalate, t-amyl peroxy pivalate, t-hexyl peroxy pivalate, t-octyl peroxy pivalate, t-butyl peroxyneodecanoate, t-amyl peroxyneodecanoate, t-hexyl peroxyneodecanoate, t-octyl peroxyneodecanoate, α -cumyl peroxyneodecanoate, t-butyl peroxyneodecanoate, and 1,1-dimethyl-3-hydroxybutyl peroxyneodecanoate, etc.; diacyl peroxides such as diisobutyryl peroxide, di(3,5,5 trimethylhexanoyl) peroxide, etc.; and mixtures of two or more of these peroxides. The term t-octyl is used to denominate the 1,1,3,3-tetramethylbutyl moiety.

The content of organic peroxide in the emulsions of the present invention usually is from 10 to 70% by weight, based on the weight of the emulsion. If the content is less than 10%, the transport costs become high, which is economically undesirable. A concentration of greater than 70% by weight typically is not possible due to safety constraints. Preferably, the concentration of peroxide in the emulsion is from 15 to 65% by weight, most preferably from 39 to 62% by weight.

In the present invention, the organic peroxide can be diluted with an organic solvent to improve its heat stability or to lower the freezing point. Preferred organic solvents to be used as a diluent are known plasticizers such as toluene, aliphatic hydrocarbons, dioctylphthalate (DOP), etc. When using such an organic solvent, it is preferred that the content of said organic solvent in the final emulsion is below 35% by weight, based on the weight of the emulsion.

The emulsions according to the invention comprise at least one antifreezing agent (antifreeze). All conventionally antifreezing agents can be used, but the use of lower alcohols or glycols is preferred. Practical examples of said preferred lower alcohols and glycols are methyl alcohol, ethyl alcohol, isopropyl alcohol, ethylene glycol, and mixtures thereof. It is preferred that these antifreezing agents are used in the range of from 5 to 25% by weight, preferably 13 to 20% by weight, of the emulsion, so that the freezing temperature of the

aqueous phase is -25°C or lower. By using such an amount, the emulsion will have an acceptably low viscosity at temperatures down to -25°C . An acceptable viscosity for the emulsions will typically range from about 50 mPa.s to about 500 mPa.s at -10°C , preferably from 100 to 500 mPa.s at -10°C .

5

Preferably, the water used to make the emulsion is deionized water. Preferably, the amount of water is in the range of from 20 to 35% by weight, based on the weight of the emulsion.

- 10 The nonionic surface-active agent or mixtures of nonionic surface-active agents which can, if necessary, be used in the present invention are of the conventional type. Examples include, but are not limited to, the sorbitan esters of higher fatty acids such as oleic acid, lauric acid, palmitic acid, stearic acid, etc., with an HLB value of not higher than 9 and the polyoxyethylene sorbitan
- 15 esters of oleic acid, lauric acid, palmitic acid, stearic acid, etc., with an HLB value of from 10 to 20. Examples of such nonionic surface-active agents are Rheodol® SP-L10, Rheodol SP-P10, Rheodol SP-O10, Rheodol TW-L120, Rheodol TW-P120, and Rheodol TW-O120 (ex Kao Corporation). It is preferred that a mixture of nonionic surface-active agents is used where at least one of
- 20 the nonionic surface-active agents has an HLB value of not higher than 9 and at least one other of the nonionic surface-active agents has an HLB value of from 10 to 20.

If used, the content of nonionic surface-active agent usually is from 0.1 to 1.0% by weight in the final emulsion. If the content is less than 0.1% by weight, the storage stability is reduced. If the content is more than 1.0% by weight, particularly of the nonionic surface-active agent having an HLB value of from 10 to 20, there is a possibility that the electrical insulation property of the polymer obtained using the emulsion becomes inferior.

30

The protective colloid which is used, if so desired, preferably is a polyvinyl acetate that is partially hydrolyzed (saponified) to a degree of from 5 to 85

mol%, and preferably from 5 to 70 mol%. Such partially hydrolyzed polyvinyl alcohols are also known as polyvinyl alcohols (PVA). The most preferred protective colloid is a polyvinyl acetate with a degree of hydrolysis from 50 to 70 mol%. Examples of such protective colloids include, but are not limited to, Unitika Resin UMR series (degree of hydrolysis from 5 to 70 mol%) ex Unitika Kasei K.K. If used in the emulsions of the present invention, the content of the protective colloid is from 0.1 to 10% by weight, based on the weight of the emulsion.

- 10 The emulsions of the present invention can be produced by any conventional method. The procedure used to make the present emulsions, which is just one of such conventional routes, is as follows.

First, the antifreeze and the optional PVA and/or a nonionic surface-active agent are dissolved and/or dispersed in the water to form an aqueous phase.

- 15 Separately, a mixture of one or more of the organic peroxides and one or more of the chlorinated paraffins is prepared, an oil phase. Then the oil phase is added to said aqueous phase and the resultant mixture is emulsified. Alternatively, the aqueous phase may be added to the oil phase, followed by emulsifying of the mixture. The emulsion thus obtained is an oil in water emulsion (water being the continuous phase) and shows excellent properties in terms of stability and safety.

- 25 The emulsifying step may be carried out by using any conventional dispersing equipment, for example by means of a paddle-type, propeller-type, or turbine-type mechanical rotary stirrer, a colloid mill, a homogenizer, such as an ultrasonic homogenizer, a high-speed shearing apparatus, and a line mixer. Preferably, the emulsion of organic peroxide has an average particle size (d_{50}) of not larger than 8 μm , in order to obtain a good storage stability.

- 30 The emulsions according to the present invention are useful to initiate the suspension or emulsion (co)polymerization of one or more ethylenically unsaturated monomers. Preferably, at least one monomer is selected from the

group of vinyl halides, such as vinyl chloride; vinylidene halide type monomers, such as vinylidene chloride; vinyl ethers; vinyl esters, such as vinyl acetate; (meth)acrylic acid and (meth)acrylic acid esters; aromatic vinyl monomers, such as styrene; α -olefins; maleic acid esters; fumaric acid esters; and ethylene. A more preferred monomer is vinyl chloride. As said, the vinyl chloride can be homopolymerized or copolymerized. In the latter case, the comonomers can be selected from other vinyl halides than vinyl chloride; vinylidene chloride; vinyl ethers; vinyl esters; (meth)acrylic acid and esters thereof; aromatic vinyl compounds, such as styrene; α -olefins; maleic acid esters; and fumaric acid esters. If the vinyl chloride is copolymerized, then it is preferred that the amount of the comonomer(s) is less than 30% by weight, based on the weight of all monomer.

The polymerization method as used by the inventors to evaluate the aqueous peroxide emulsions of the present invention is given hereinafter. However, the aqueous peroxide emulsions can be used in any conventional method of (co)polymerizing vinyl chloride monomer. Preferably, said conventional polymerization method is a suspension or emulsion (co)polymerization of vinyl chloride, since the use of emulsions according to the invention in such a process was found to lead to less fouling of the reactor. Because of the lower fouling level of the reactor, it needs to be opened less frequently, which reduces the amount of monomer escaping to the environment and reduces the exposure of the workers to the monomer. It is noted that in suspension (co)polymerizations a PVA typically is used as the protective colloid, while in emulsion (co)polymerizations a surface-active agent typically is used as the dispersion aid.

The aqueous peroxide emulsions according to the invention are pre-eminently suited to make compositions of organic peroxides with a specific gravity below 1 and a high water solubility. With a high water solubility it is meant to denote peroxides with a water solubility greater than 100 parts¹ per million by weight (ppm), preferably more than 500 ppm and even more preferably more than

1000 ppm. Such emulsions have a good stability without phase separation being observed, even when the emulsion is stored for a long period of time, such as more than 6 months. Also the emulsions were found to have a low viscosity, i.e. below about 500 mPa.s at -10°C, assuring ease of handling during
5 production, transportation, and use. Furthermore, the benefit of reduced scaling of the polymerization vessels was observed. Accordingly, the emulsions are particularly suited for use in automated closed reactor polymerizations of ethylenically unsaturated monomers, in particular of vinyl chloride.

10 The following examples and comparative examples elucidate the present invention.

Examples 1 to 7, Comparative Examples A to D

Emulsions with a composition as presented in Tables 1 and 2 were produced as
15 follows. A 1000 ml tall beaker equipped with an ordinary homogenizer, such as a Dissolver® or Ultra Turrax®, and a thermometer was charged with deionized water, antifreeze(s), protective colloid(s) and/or nonionic surface-active agent(s). This mixture was homogenized until a homogeneous liquid was formed. Then the homogeneous liquid was cooled to a temperature of from 0 to
20 5°C. Subsequently a solution of the desired organic peroxide(s) and chlorinated paraffin(s) was added and the resultant mixture was stirred for 10 to 30 minutes until an emulsion was obtained.

The resulting emulsions were evaluated by analyzing the storage stability, the average droplet size, and the viscosity. The results are shown in Table 3.

25

To evaluate the stability, each emulsion was placed in a glass vessel and stored at -10°C. Every month, the emulsion was checked for phase separation. When the sample was uniform and no layer had formed after 6 months, the stability was considered to be good, when a layer separation occurred after 2 months,
30 the stability was usual, and when the layer separation occurred within 2 months, the stability was poor.

The average droplet size of the emulsion was measured using a Microtrack® FRA particle analyzer (ex Nikkiso K.K.). The average particle size is d50 as calculated per the operating manual, being the cumulative mean diameter of the particles.

5

The viscosity of the emulsions was measured at a temperature of -10°C and 0°C by means of an E-Type (cone-plate) viscometer ex Tokyo Keiki K.K.. The rotor has a diameter of 48mm, while the angle between cone and plate is $1^{\circ}34'$. The rotating speed is 1 or 2.5 rpm.

10

Table 1		Examples						
		1	2	3	4	5	6	7
Deionized water		29	30	27.5	28.4	31.7	27	28
Antifreeze	Methanol	-	8	7	15	-	10	8
	EG	20	9	8	-	15	7	8
Protective colloid	KP-08	2	-	-	-	-	-	1
	UMR-20M	-	2	-	-	-	1	-
Nonionic surface-active agent	TW-P120	-	-	0.2	0.3	0.3	-	-
	SP-L10	-	-	0.3	0.5	-	-	-
Organic peroxide	KE P	40	40	40	-	-	-	-
	TO 23	-	-	-	50	-	-	-
	KD-58	-	-	-	-	50	-	-
	KC MC	-	-	-	-	-	25	-
	TO 36	-	-	-	-	-	-	50
Diluting agent	DOP	-	-	-	-	-	25	-
	IP-1620	-	10	14	-	-	-	-
Chlorinated paraffin	EM K-43	9	1	3	6	3	5	5

Table 2		Comparative Examples			
		A	B	C	D
Deionized water		29	30	28.4	31.7
Antifreeze	Methanol	-	8	15	10
	EG	20	9	-	7
Protective colloid	KP-08	2	-	-	-
	UMR-20M	-	2	-	1
Nonionic surface-active agent	RO-P120	-	-	0.1	-
	RO SP-L10	-	-	0.5	-
Organic peroxide	KE P	40	40	-	-
	TO 23	-	-	50	-
	KD-58	-	-	-	-
	KC MC	-	-	-	25
	TO 36	-	-	-	-
Diluting agent	DOP	-	-	-	25
	IP-1620	-	10	-	-
Chlorinated paraffin	EM K-43	-	-	-	-

(Note) EG = Ethylene glycol, GO = Gohsenol®,

UR = Unitika Resin®, RO = Rheodol®,

KE = Kayaester®, TO = Trigonox®,

5 HC = Kayacarbon®, EM = Empara®

KC = Kayacarbon®

Gohsenol® KP-08 ex Nippon Synthetic Chemical Industry Co., Ltd. is a PVA with a degree of hydrolysis from 71.0 to 75.0 mol%.

10 Unitika Resin® UMR-20M ex Unitika Kasei K.K. is a PVA with a degree of hydrolysis of 65 mol%.

Rheodol® TW-P 120 ex Kao Corporation is a nonionic with an HLB value of

15.6.

Rheodol SP-L 10 ex Kao Corporation is a nonionic with an HLB value of 8.6.

Kayaester® P ex Kayaku Akzo Corporation is t-butyl peroxy pivalate (used as 75% solution, amount of pure product is given in the tables).

- 5 Trigonox® 23 ex Kayaku Akzo Corporation is t-butyl peroxyneodecanoate (pure product was used).

KD-58 ex Kayaku Akzo Corporation is t-hexyl peroxyneodecanoate (pure product).

- 10 Kayacarbon® MC ex Kayaku Akzo Corporation is di(3-methoxybutylperoxy) dicarbonate (used as 50% solution).

Trigonox 36 ex Kayaku Akzo Corporation is di(3,5,5-trimethylhexanoyl) peroxide (pure product).

DOP is generic dioctyl phthalate.

- 15 IP-1620® Solvent is an iso-paraffin-series aliphatic hydrocarbon ex Idemitsu Petroleum Chemistry Co., Ltd.

Empara® K-43 is a chlorinated paraffin ex Ajinomoto Co., Ltd.

Table 3

Example	d ₅₀ (μm)	Performance test			
		Viscosity directly after preparation (mPa.s)		Storage stability	
		-10°C	0°C	Time till layer separation Months	Evaluation
1	1.53	350	210	>6	+
2	1.08	410	200	>6	+
3	1.88	220	160	>6	+
4	3.20	150	80	>6	+
5	3.18	190	110	>6	+
6	5.22	430	260	>6	+
7	2.38	380	190	>6	+
A	6.68	170	110	1	-
B	3.35	560	280	3	O
C	7.32	130	90	1.5	-
D	13.60	350	180	1.5	-

The above-described emulsions were used to initiate the suspension polymerization of vinyl chloride. To this end a one-litre glass autoclave was charged with an aqueous solution of 0.13 g of PVA (degree of hydrolysis 73 mol%) and 0.8 g of sodium hydrogen carbonate in 370 g of deionized water. The autoclave was flushed with nitrogen atmosphere. After addition of the indicated amount of the organic peroxide (see Table 4), 185 g of vinyl chloride were added to the mixture. With proper mixing of the resultant mixture, the polymerization was carried out for 7 hours at 55°C. The polymer obtained was filtered, washed with water, and dried overnight at 50°C.

Table 4

	Organic peroxide used	Type	Amount	Polymer yield
			(g)	(%)
Example 8	Emulsion of Example 1	Emulsion	0.32	83
Comp. Ex. E	Kayaester P-70*	Solvent	0.18	82

* The commercial product Kayaester P-70 ex Kayaku Akzo Corporation, which is a dilution in IP-1620 solvent (70% peroxide).

From the results it can be seen that the emulsion of the present invention can be used to improve the suspension polymerization of vinyl chloride. Furthermore, it was noted that the residue attached to the inside wall of the autoclave, also known as the amount of fouling or scaling of the reactor, was lower when the emulsion according to the invention was used.

CLAIMS

1. Aqueous organic peroxide emulsions comprising at least one organic peroxide, water, at least one antifreezing agent, at least one chlorinated paraffin, optionally one or more nonionic surface-active agents, and optionally one or more protective colloids.
2. Emulsions according to claim 1 wherein the content of chlorinated paraffin is from 0.5 to 15.0% by weight to the emulsion compound.
3. Emulsions according to claim 2 wherein the chlorinated paraffin is a liquid at a temperature of 20-25°C and the content of chlorine in said chlorinated paraffin is from 40 to 65% by weight.
4. Emulsions according to any one of the preceding claims wherein the organic peroxide is selected from the group consisting of t-butylperoxy pivalate, t-amylperoxy pivalate, 1,1-dimethyl-3-hydroxybutylperoxy pivalate, t-butylperoxy neodecanoate, t-amylperoxy neodecanoate, and 1,1-dimethyl-3-hydroxybutylperoxy neodecanoate.
5. Emulsions according to any one of the preceding claims comprising water, 40-50% by weight of t-butylperoxy pivalate or t-butylperoxy neodecanoate, 1-7.5% by weight of a chlorinated paraffin, 10-25% by weight of an organic solvent, at least one protective colloid or nonionic surfactant and 15-20% by weight of antifreeze agent, up to a total of 100% by weight.
6. Use of an emulsion according to any one of claims 1-5 in a suspension or emulsion (co)polymerization of an ethylenically unsaturated monomer.
7. Use according to claim 6 wherein the ethylenically unsaturated monomer is vinyl chloride.