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(54) **Szerves peroxid vizes emulziós készítménye**

Az európai szabadalom ellen, megadásának az Európai Szabadalmi Közlönyben való meghirdetésétől számított kilenc hónapon belül, felszólalást lehet benyújtani az Európai Szabadalmi Hivatalnál. (Európai Szabadalmi Egyezmény 99. cikk(1))

A fordítást a szabadalmas az 1995. évi XXXIII. törvény 84/H. §-a szerint nyújtotta be. A fordítás tartalmi helyességét a Szellemi Tulajdon Nemzeti Hivatala nem vizsgálta.

AQUEOUS EMULSION COMPOSITION COMPRISING AN ORGANIC PEROXIDE

Field of the invention

This invention relates to an aqueous organic peroxide composition liquid at storage temperature, suitable for use in the polymerisation or copolymerisation of ethylenically unsaturated monomers and in particular vinyl chloride. The invention relates more particularly to an aqueous composition comprising an emulsifier based on polyvinyl acetate having a high degree of hydrolysis and a low viscosity in solution in water.

Special precautions in terms of safety need to be taken for the maintenance and handling of organic peroxides. Organic peroxides are conditioned in the form of aqueous emulsion. The presence of water, as a heat transfer fluid, makes it possible to absorb and dissipate the energy generated in the case of any peroxide decompositions. Furthermore, these emulsions comprise an antifreeze, helping maintain the emulsion in liquid form, at temperatures below -10°C, generally below -20°. These negative temperatures help prevent the uncontrolled decomposition of the peroxides during storage and transport operations.

An organic peroxide emulsion consists of peroxide droplets stabilised with an emulsifier. Over time, the emulsion is destabilised and the mean peroxide droplet size increases. The increase in the droplet size may give rise to phase separation. According to the minimum technical criteria, a peroxide emulsion is considered to be satisfactory if the mean droplet size does not exceed 20 µm (micrometre). A mean droplet size less than 10 µm, more advantageously less than 5 µm, is generally required, as well as a maximum size not exceeding 20 µm.

In addition to the safety considerations due to this destabilisation phenomenon, the use of a non-homogeneous organic peroxide emulsion as a polymerisation primer in a vinyl monomer emulsion or suspension may produce a lack of homogeneity in the final product. This lack of homogeneity is generally characterised by poorly gelled polymer particles during processing in the molten state ("fish eyes", hard grains). However, the presence of hard grains opacifies the polymer material. These stability considerations are thus very important for applications where product transparency is essential, particularly for medical applications.

As such, the peroxide droplets (by agglomeration of the peroxide(s) present in the emulsion, in particular after a certain interval) of an organic peroxide emulsion should have a small mean size, a homogeneous and monomodal size distribution, and be stable over time. In particular, the maximum diameter of these droplets should not exceed 20 µm. Indeed, peroxide droplet agglomeration or enlargement phenomena may give rise to total or partial demixing of the emulsion.

Steps for unloading the emulsion into intermediate storage silos, pumping and introducing a peroxide emulsion into a polymerisation reactor are important steps for the quality of the polymer obtained and the reliability of the polymerisation process. These handling steps must be performed as quickly as possible. For this purpose, it is crucial that the peroxide emulsion has a low viscosity such that the flow of the emulsion is facilitated as much as possible. At a given temperature, the viscosity of this type of emulsion varies in particular according to the shear rate. It decreases when the shear rate increases and is stabilised for rate values generally greater than 100 s^{-1}. As such, an organic peroxide emulsion should have a maximum dynamic viscosity of 1000 mPa.s (milliPascal-second) at low temperatures, typically of the order of -10°C for a shear rate of 100 s^{-1}. The dynamic viscosity measurements are made using coaxial cylinders which create the shearing, for example as per the standard DIN 53019.

However, those skilled in the art know that, for this type of emulsion, seeking to decrease the droplet size helps increase the viscosity (See paragraph 1.4 of the article by JP Canselier and M. Poux "Procédés d'émulsification - Mécanisme de formation des emulsions" Techniques de l'Ingénieur J2 152, pp 1-12, publication dated 10 June 2004).

As such, achieving these two primary objectives simultaneously is a major problem for those skilled in the art due to the contradictory choices to be envisaged.

Prior art

The use of partially hydrolysed polyvinyl acetate (PVA) is described extensively in the literature as a colloid agent for the stabilisation of organic peroxide emulsions, such as in the documents EP0032757 and US3988261.

A non-hydrolysed PVA is insoluble in water. The document WO 99/05101 discloses the use of PVA having a degree of hydrolysis between 45% and 68% for aqueous peroxyester emulsions. This document specifies that PVAs having a degree of hydrolysis greater than 68%, produce excessively viscous, unstable emulsions, the droplet size whereof varies excessively after a certain storage time, incapable of preventing the risks incurred following peroxide decomposition, unsuitable for the applications mentioned above.

The document WO 03/095500 discloses the use of PVA as a protective colloid, for aqueous peroxydicarbonate or diacyl emulsions, having a degree of hydrolysis in the wide range between 45% and 80%, more specifically, as disclosed in the examples, around a value of the degree of hydrolysis of 65%.

As such, the prior art teaches that, on one hand, in an aqueous organic peroxide emulsion, the use of polyvinyl acetates, having a degree of hydrolysis less than a maximum of 70%, produces emulsions of peroxyesters, peroxydicarbonates and diacyl peroxide meeting the extreme viscosity and stability conditions essential for handling such emulsions and that, on the other, beyond this limit in respect of the degree of hydrolysis of the PVA, the use thereof is in no way suitable in such an emulsion.

Brief description of the invention

Surprising, the applicant discovered, in contradiction with the teachings of the prior art, that emulsifiers based on polyvinyl acetate, having a high degree of hydrolysis, stabilise peroxide emulsions and meet the required conditions in respect of peroxide droplet size and viscosity of the emulsion. These features are fulfilled in the case of the very particular combination of features specific to polyvinyl acetate, i.e. a high degree of hydrolysis with a very low intrinsic viscosity.

The present invention thus relates to an aqueous organic peroxide emulsion comprising:

- from 10% to 65% by weight of one or more organic peroxides,
- from 2% to 25% by weight of at least one antifreeze agent,
- from 0.0 1% to 10% by weight of at least one emulsifying agent,
- optionally at least one additive,
- water, the amount of which is determined so as to form the remainder of the total composition (100%),

characterised in that the emulsifying agent is a colloid agent consisting of a polyvinyl acetate having a degree of hydrolysis of greater than 80% and a viscosity, measured in solution in water at 4% by weight at 20°C, of less than or equal to 5 mPa.s, said viscosity being measured with a Brookfield RVT viscometer, spindle No. 3, 20 rpm, according to the standard ISO 2555.

Further features or embodiments of the invention are described hereinafter:

- preferably, the viscosity of the partially hydrolysed polyvinyl acetate, measured in solution in water at 4% by weight at 20°C, is less than or equal to 3 mPa.s (still under the same measurement conditions;

- according to one possibility offered by the invention, the partially hydrolyzed polyvinyl acetate is modified in the acetate groups thereof by metal salts, preferably chosen from sodium carboxylates and sulphonates;

- advantageously, the composition according to the invention comprises a second emulsifying agent consisting of a nonionic surfactant of ethoxylated fatty acid type such as ethoxylated fatty acid mono-, di- or triglycerides or ethoxylated vegetable oils; ethoxylated fatty alcohol; a block copolymer comprising at least one alkylene oxide block type;

- preferably, this second emulsifying agent consists of an ethoxylated castor oil;

- advantageously, the degree of hydrolysis of the polyvinyl acetate is greater than 85%, more preferably between 86% and 89%;

- preferably, the organic peroxide or peroxides are chosen from peroxyesters, peroxydicarbonates and/or diacyl peroxides;

- according to one specific aspect of the invention, the composition exhibits a viscosity defined by a flow time of less than 200 seconds, preferably of less than 100 seconds, said flow time being measured at the temperature of 5°C according to the standard DIN 53211. For more precision, the standard DIN 53211 is herein characterised by a viscosity cup diameter of 4 mm; the dynamic viscosity is less than 1000 mPa.s and measured at -10°C for a shear rate of 100 s^{-1}, using a Haake Viscotester VT550, according to the standard DIN 53019.

- similarly, according to a specific feature of the invention, the composition comprises a plurality of droplets formed of peroxide in that the mean size (d_{50}) of said droplets is less than 10 µm (micrometre), preferably less than 5 µm, and the maximum size (d_{100}) of the droplets is less than 20 µm;

- advantageously, the composition according to the invention comprises more than 30% by weight of one or more organic peroxides, preferably more than 45% by weight;

- advantageously, the polyvinyl acetate is present at between 1% and 5% by weight, or between 0.5% and 3%.

The invention offers the following advantages and thus makes it possible to obtain:

- an emulsion having a small mean droplet size with a homogeneous and monomodal size distribution,
- an emulsion comprising a mean droplet size (d_{50}) less than 10 µm after production or during storage at -20°C for at least 12 weeks. The maximum size (d_{100}) does not exceed 20 µm.
- an emulsion compatible with the polymerisation of ethylenically unsaturated derivatives and in particular vinyl monomers such as vinyl chloride monomer,
- a liquid emulsion, having a very low viscosity allowing a very short flow time.

The present invention also relates to a process for the preparation of the composition according to any one of the preceding claims, characterized in that it comprises the successive stages of:

- dispersion of the antifreeze agent, optionally at least said additive and also the colloid agent in water, in order to obtain a homogeneous aqueous phase, then
- the peroxide is added to the aqueous phase, and
- the mixture thus formed is emulsified during an emulsification stage at a temperature of less than 5°C, preferably of less than -5°C.

Finally, the invention relates to the use of the composition mentioned above in the polymerisation or copolymerisation of ethylenically unsaturated monomers. Preferably, these ethylenically unsaturated monomers comprise vinyl chloride.

The organic peroxide emulsion according to the present invention can be used in applications such as the polymerisation of acrylic monomers, polymer modification reactions, cross-linking reactions, mass polymerisation reactions and curing processes as used in unsaturated polyester resins.

Detailed description of the invention

The invention relates to concentrated organic peroxide compositions in emulsion, said organic peroxide being present at a concentration of 10% to 65%, preferably greater than 30% and more preferably greater than 45%, by weight of the emulsion and is chosen from peroxyesters, peroxydicarbonates and diacyl peroxides.

Of the peroxyesters, the preferred peroxides are α-cumyl peroxyneodecanoate, α-cumyl peroxyneoheptanoate, 2,4,4 trimethylpentyl-2-peroxyneodecanoate, 3-hydroxy-1,1 dimethylbutyl peroxyneodecanoate, 3-hydroxy-1,1 dimethylbutyl peroxyneoheptanoate, tert-amyl peroxypivalate, tert-butyl peroxypivalate, tert-butyl peroxyneoheptanoate, 2,5-dimethyl-2,5 di (2-ethylhexanoyl peroxy) hexane, tert-amyl peroxy 2-ethylhexanoate, tert-butyl peroxy 2-ethylhexanoate, -1,1,3,3 tetramethyl butyl-peroxy-2 ethylhexanoate, 3-hydroxy-1,1 dimethylbutylperoxy 2-ethylhexanoate, tert-butyl peroxy isobutyrate and mixtures thereof.

Of the peroxydicarbonates, the preferred peroxides are di-sec-butyl peroxydicarbonate, dibutyl peroxydicarbonate, diisopropyl peroxydicarbonate, di(2-ethylhexyl) peroxydicarbonate, bis(3-methoxybutyl) peroxydicarbonate, bis(isobutyl) peroxydicarbonate, dineopentyl peroxydicarbonate, bis(1-methylheptyl) peroxydicarbonate, bis[2-(2-methoxyethoxy)ethyl] peroxydicarbonate, bis(3-methoxy-3 -methylbutyl) peroxydicarbonate, bis(2-ethoxyethyl) peroxydicarbonate and mixtures thereof.

Of the diacyl peroxides, the preferred peroxides are diisobutyroyl peroxide, di(3,5,5-trimethylhexanoyl) peroxide, di(2-ethylhexanoyl) peroxide, di(2-ethylbutanoyl) peroxide, as well as asymmetric peroxides such as, isobutyroyl octanoyl peroxide, isobutyroyl decanoyl peroxide, isobutyroyl lauroyl peroxide, 2-ethylbutanoyl decanoyl peroxide, 2-ethylhexanoyl lauroyl peroxide, and mixtures thereof.

In order to be able to be stored at temperatures below -10°C, preferably below -20°C, the composition according to the invention comprises an antifreeze and more particularly an antifreeze mixture.

In the case of the antifreeze agent, mention may be made for example of monools, diols and triols such as methanol, ethanol, ethylene glycol, isopropanol, n-propanol, propane-1,2-diol, propane-1,3-diol, glycerol, butan-1-ol, butan-2-ol, le butan-1,3-diol and butan-1,4-diol and mixtures thereof, these mixtures comprising at least two of the antifreeze agents listed above, one light alcohol type and other heavy alcohol type, advantageously a mixture of methanol and propane-1,2-diol.

The emulsifier according to the invention is a polyvinyl acetate having a degree of hydrolysis greater than 80% and a viscosity in solution in water at 4% by weight at 20°C less than 10 mPa.s, preferably less than 5 mPa.s.

In the case of the partially hydrolysed polyvinyl acetate, it may consist of Alcotex® 8804, Mowiol® 3-85 or Gohseran® L3266, all well-known to those skilled in the art.

The scope of the invention is not left when a mixture of partially hydrolysed polyvinyl acetate according to the present invention is used as an emulsifier.

According to one embodiment, the emulsifier according to the invention, i.e. partially hydrolysed polyvinyl acetate, is modified in the acetate groups thereof by metal salts, preferably chosen from sodium carboxylates and sulphonates.

A mixture of non-modified polyvinyl acetate with a modified polyvinyl acetate according to the invention may be used as an emulsifier mixture for the stabilisation of organic peroxide emulsions.

The PVAs modified in the acetate groups thereof are preferably chosen from Gohseran® L3266, well-known to those skilled in the art.

A second nonionic emulsifier may be used in combination with optionally modified partially hydrolysed polyvinyl acetate according to the invention and consists of a nonionic surfactant of ethoxylated fatty acid type such as ethoxylated mono-, di- or triglycerides, ethoxylated vegetable oils, ethoxylated fatty alcohols, block copolymer comprising at least one alkylene oxide block type. The ethoxylated vegetable oils are in particular ethoxylated castor oil (optionally hydrogenated) comprising 20 to 40 moles of ethylene oxide per mole of ricinoleic acid, commercial examples are in particular Remcopal® 20, Remcopal® R4097 and Remcopal® RH4090, well-known to those skilled in the art.

According to the invention, the second emulsifier, a nonionic surfactant of ethoxylated castor oil type is present at a concentration in the emulsion between 0.01 and 3% by weight, preferably between 0.5 and 2% by weight.

The emulsion according to the invention may also comprise one or a plurality of additives intended to provide the final thermoplastic composition with special properties/features. These additives will ideally be present for the final polymerisation or copolymerisation.

As such, in the case of the additive, it may be chosen from antioxidants; UV protection agents; processing agents, having the function of enhancing the final appearance during the processing thereof, such as fatty amides, stearic acid and salts thereof, ethylene bis-stearamide or fluorinated polymers; anti-fogging agents; antiblocking agents such as silica or talc, fillers such as calcium carbonate and nanofillers such as clays for example; coupling agents such as silanes; cross-linking agents such as peroxides; antistatic agents; nucleating agents; pigments; colorants; plasticisers; liquefiers and flame retardant additives such as aluminium or magnesium hydroxides.

The liquid aqueous organic peroxide emulsion according to the present invention may optionally contain additives including pH-adjusting agents such as phosphate and citrate buffers, chelating agents, biocides for example fungicides, antiozonants, antioxidants, anti-degradants, swelling agents or release agents. The emulsion may also contain additives routinely used for stabilising organic peroxide or delaying the decomposition thereof such as phlegmatising agents (isododecane, mineral oil) and hydroperoxides.

These additives may be added in the quantities routinely used and known to those skilled in the art. These additives are generally used in contents between 10 ppm and 10,000 ppm by weight with respect to the weight of polymer or final copolymer. Plasticisers, liquefiers and flame retardant additives may reach quantities well above 10,000 ppm.

The invention also relates to a process for the preparation of the emulsion described above, characterised in that the antifreeze agent, optionally one or more additives as well as at least one emulsifier are dispersed in water to obtain a homogeneous aqueous phase and peroxide is then added to said aqueous phase, the whole being subsequently emulsified during an emulsion step at a temperature less than 5°C, so as to limit the premature degradation of the peroxide and preferably less than -5° Celsius.

Apart from the specific successive steps of the process for the preparation of the composition according to the invention, the preparation of the emulsions differs in no way from the techniques and devices well-known to those skilled in the art. The temperature at which the emulsion is prepared is not critical but it should be sufficiently low to prevent a high decomposition rate, the result whereof would be a loss of concentration. The temperature chosen is essentially dependent on the organic peroxide(s). Moreover, to prepare the aqueous emulsions, deionised or distilled water is conventionally used.

The preparation process comprises an emulsion step with a mixer having a high shear rate to optimally divide and/or homogenise the peroxide in the aqueous phase. By way of example, mention may be made of mechanically rotating blade and anchor agitators, propeller agitators, i.e. one or a plurality of agitators mounted on a common shaft, turbine agitators, i.e. those comprising fixed baffles on the mixing tank or in a position adjacent to the agitating members. Colloid mills and homogenisers may also be used. According to one embodiment feature, the process according to the invention is characterised in that an ultrasonic mixer or a rotor-stator mixer is used.

Following the preparation of the emulsion according to the invention, the steps for pumping and introducing the emulsions into a polymerisation reactor should be performed as quickly as possible. The peroxide emulsions should have a low viscosity.

As such, the organic peroxide emulsions according to the invention have a dynamic viscosity range at -10°C, 100 s^{-1}, less than 1000 mPa.s, preferably less than 700 mPa.s immediately after production. The viscosity measurements are measured for example according to the standard DIN 53019 with a Haake Viscotester VT550 type device, at -10°C and for a shear rate of 100 s^{-1}.

The fluidity or flow time thereof using a consistometric cup technique is less than 200 seconds, preferably less than 100 seconds (standard DIN 53211, performed with a cup diameter of 4 mm and a temperature of 5°C).

The subsequent polymerisation or copolymerisation steps are not, within the scope of the present invention, different to those of the prior art. The polymerisation of the vinyl chloride monomer is performed in suspension at an initiation temperature between 45 and 70°C.

The invention also relates to the use of the emulsion defined above in the polymerisation or copolymerisation of ethylenically unsaturated monomers. A homopolymer is obtained by polymerisation when a single ethylenically unsaturated monomer is polymerised. A copolymer is obtained by polymerisation when at least two ethylenically unsaturated monomers are polymerised. It is understood that the monomers are capable of polymerising with one another.

By way of ethylenically unsaturated monomer, mention may be made of acrylates, vinyl esters, vinyl halide monomer, vinyl ethers, aromatic vinyl compounds such as styrene, butadiene and preferably vinyl chloride.

<u>Obtaining formulations of the test compositions:</u>

The comparative PVAs, numbered 1, 2, 3, 5, 7 and 8, along with the PVAs according to the invention, numbered 4, 6 and 9, serve as emulsifiers for emulsions 1 to 16 (emulsions 11 to 16 use the PVAs numbered above 4, 6 and 9) and are prepared according to the same procedure.

The aqueous phase containing the PVA, antifreeze agent and water is stirred between 500 and 1000 rpm (revolutions per minute) and maintained at a temperature of -5°C (Celsius). The organic peroxide is added progressively into the reactor containing this water/PVA/antifreeze mixture. Stirring is maintained for three minutes at 2000 rpm. The whole is then stirred vigorously using an "Ultraturrax type S-25N 18G" rotor-stator device for two minutes at 9500 rpm, then placed under stirring using a blade at 1000 rpm for one minute. Each emulsion is made out of 200 grams in total.

<u>Tests conducted:</u>

The dynamic viscosity measurements are performed using a "Haake Viscotester VT550" type viscometer. The measurement device is "SV-DIN 53019", referring to the standard DIN 53019. The measurement is made using coaxial cylinders creating the shearing. Between 5 and 10 ml (millilitre) of emulsion is introduced into the measurement chamber maintained at -10°C. The values given in the examples hereinafter correspond to a shear rate of 100 s^{-1} and are expressed in mPa.s. The measurement precision is ± 10% of the value indicated.

The flow time measurements are made using DIN 53211 type consistometric cups (viscosity cup diameter: 4 mm). The measurement is made on 100 g of emulsion after conditioning at a temperature of +5°C. The flow time measurements are expressed in seconds and the precision is ±10% of the value indicated.

The droplet size (d_{100} and d_{50}) is determined by conventional means using the light diffraction technique. The term d_{100} corresponds to a diameter such that 100% of the volume of the sample of organic peroxide droplets in the aqueous emulsion has a diameter less than d_{100} and the term d_{50} corresponds to the median diameter such that 50% of the volume of the sample of organic peroxide droplets in the aqueous emulsion has a diameter less than d_{50}. The measurements are made using a Malvern Master Sizer 2000® device at ambient temperature, the droplet sizes d_{50} or d_{100} are given within ± 0.5 µm.

Raw materials of test compositions

Essentially two types/families of emulsions were prepared to conduct the tests for characterising the compositions, according to the prior art and according to the invention.

The first emulsion consists of di(2-ethyl hexyl peroxydicarbonate) at 60% by weight and comprises:

- an antifreeze system which is a mixture of alcohols having a 20:80 mass ratio of propylene glycol/methanol, having an overall concentration 14%;
- a water/antifreeze ratio of 64:36 by weight;
- a di(2-ethyl hexyl peroxydicarbonate) content of 60% by weight. The di(2-ethyl hexyl peroxydicarbonate) is Luperox® 223 from Arkema of 97% purity;
- a partially hydrolysed polyvinyl acetate (PVA) content of 1.2% by mass;
- the remainder is distilled water.

The second emulsion consists of tert-butyl peroxyneodecanoate at 50% by weight and comprises:

- an antifreeze system which is a mixture of alcohols having a 40:60 mass ratio of propylene glycol/methanol, having an overall concentration 16%;
- a water/antifreeze ratio of 67:33 by weight;
- a tert butyl peroxyneodecanoate of 50% by weight. The tert butyl peroxyneodecanoate is Luperox® 10 from Arkema of 97% purity;
- a partially hydrolysed polyvinyl acetate (PVA) content of 1.2% by mass;
- the remainder is distilled water.

PVA characterisations:

The characteristics of the comparative PVAs and according to the invention are given in table 1:

TABLE 1

	Degree of polymerisation	Viscosity (mPa.s)	Degree of hydrolysis (%)
PVA 1	800	5.6-6.6	72.73
PVA 2	1630	36-42	78.5-81.5
PVA 3	2560	44-52	78.5-81.5

	Degree of polymerisation	Viscosity (mPa.s)	Degree of hydrolysis (%)
PVA 4	**360**	**3.5-4.5**	**88**
PVA 5	2440	45-49	86.7-88.7
PVA 6	**300**	**3**	**85-90**
PVA 7	Not known	6-7	86-90
PVA 8	1700	20-26	85-90
PVA 9	**Not known**	**2.5**	**87**
PVA 10	1100	2.2	42.45

The viscosity is measured at 4% in water at 20°C (Brookfield RVT viscosity, spindle No. 3, 20 rpm).

PVA 9 is a PVA modified by sulphonate functions.

It is observed that only PVAs No. 4, No. 6 and No. 9 meet the criteria (low viscosity and high degree of hydrolysis) defined in the invention. For easier reading, in the table as in the subsequent tables, the PVAs of emulsions according to the invention are shown in bold type.

A second emulsifier of nonionic surfactant type of ethoxylated castor oil type such as Remcopal® 20 (R20), is added at 1% by weight in emulsions 10 (with PVA according to the invention, more specifically that of No. 4 of the table above), 11 (with PVA according to the invention, more specifically that of No. 6 of the table above), 15 (with PVA according to the invention, more specifically that of No. 6 of the table above).

Emulsions:

Emulsions 1 to 11 and 16 correspond to di(2-ethyl hexyl peroxydicarbonate) peroxide emulsions, emulsions 12 to 15 correspond to tert-butyl peroxyneodecanoate peroxide emulsions, and are characterised in tables 2 and 3:

TABLE 2

	Emulsions 1-11, 16	Emulsions 12-15
di(2-ethyl hexyl peroxydicarbonate), %	60.0	
tert butyl peroxyneodecanoate, %		50.0
methanol, %	11.2	9.6

	Emulsions 1-11, 16	Emulsions 12-15
propylene glycol, %	2.8	6.4
surfactant, %	1.2	1.2
water, %	24.8	32.8

TABLE 3

	d_{50} (μm)	d_{100} (μm)	Viscosity (mPa.s)	Flow time (s)
Emulsion 1 (PVA 1)	4	12	1100	145
Emulsion 2 (PVA 2)	7.1	112	2200	> 300
Emulsion 3 (PVA 3)	7.4	141	1650	> 300
Emulsion 4 (PVA 4)	**3.9**	**13.3**	**790**	**92**
Emulsion 5 (PVA 5)	8.6	100	3090	> 300
Emulsion 6 (PVA 6)	**3.4**	**12.6**	**670**	**72**
Emulsion 7 (PVA 7)	4.1	19.9	1020	133
Emulsion 8 (PVA 8)	5.2	30.2	3250	> 300
Emulsion 9 (PVA 9)	**2.7**	**7.6**	**580**	**66**
Emulsion 10 (PVA 4/R20)	**1.8**	**4.0**	**580**	**83**
Emulsion 11 (PVA 6/R20)	**1.8**	**4.0**	**530**	**83**
Emulsion 12 (PVA 1)	3.3	8.7	608	64
Emulsion 13 (PVA 6)	**3.3**	**8.7**	**190**	**26**
Emulsion 14 (PVA 6/R20)	**3.8**	**11.1**	**363**	**38**
Emulsion 15 (PVA 6/R20)	**2.2**	**5.0**	**297**	**37**
Emulsion 16 (PVA 10)	4.0	12.6	570	67

It should be noted that, herein, emulsions No. 10, 11, 13, 14 and 15 are according to the invention.

PVAs having very high viscosities are not suitable for obtaining fluid emulsions, with short flow times and sufficiently fine droplet sizes.

The more the viscosity of the PVA is low and less than 5 mPa.s, the more the emulsion meets the performance criteria in terms of fluidity.

The viscosities of the emulsions comprising a nonionic surfactant of ethoxylated castor oil type (Remcopal® 20 or referred to as R20 above), are lower than those containing merely a PVA. Indeed, the addition of a nonionic surfactant such as an ethoxylated castor oil of Remcopal® 20 type to a PVA emulsifier according to the invention helps lower the viscosity of the corresponding emulsion. As such, the viscosity of the emulsion obtained is then similar to that obtained with a modified PVA, for example with sulphonate functions. Furthermore, in addition to lowering the viscosity, the addition of a second emulsifier according to the invention helps reduce the mean size of the organic peroxide droplets.

As a general rule, an emulsion of concentrated peroxyester at 50% by mass is slightly more fluid than an emulsion of concentrated peroxydicarbonate at 60% by mass. On the other hand, the emulsions stabilised with the PVAs according to the invention, are more fluid than those comprising a comparative PVA (according to the prior art). In the case of peresters, the addition of a nonionic surfactant of ethoxylated castor oil type helps, once again, lower the viscosity of the emulsion while reducing the droplet size. It should be noted that the tests described herein do not include diacyl peroxides but the results obtained on peroxyesters and peroxydicarbonates make it possible to envisage similar results with diacyl peroxides. Indeed, diacyl peroxides were the subject of equally satisfactory preliminary tests to those obtained with peroxyesters and peroxydicarbonates.

The emulsions produced with various comparative PVAs and according to the invention are stored at a temperature of -20° for several months. The characteristics of the various emulsions are measured after different storage times. The results are given in table 4:

TABLE 4

	Emulsion 1 (PVA 1)	**Emulsion 6 (PVA 6)**	**Emulsion 11 (PVA 6/R20)**	**Emulsion 9 (PVA 9)**	Emulsion 16 (PVA 10)
d_{50} (µm)					
t = 0	3.3	3.4	1.8	2.7	4.0
t = 4 weeks	3.6	/	/	3.1	4.2
t = 8 weeks	3.7	3.8	2.2	3.2	4.2
t = 12 weeks	3.8	4	2.3	3.3	4.4
d_{100} (µm)					
t = 0	10.0	12.6	4.0	7.6	12.6

	Emulsion 1 (PVA 1)	**Emulsion 6 (PVA 6)**	**Emulsion 11 (PVA 6/R20)**	**Emulsion 9 (PVA 9)**	Emulsion 16 (PVA 10)
t = 4 weeks	10.0	/	/	8.7	13.2
t = 8 weeks	10.0	14.8	5.8	8.7	15.1
t = 12 weeks	13.2	15.1	5.8	8.7	15.1
Viscosity (mPa.s)					
t = 0	1100	670	530	580	570
t = 4 weeks	1180	/	/	/	560
t = 8 weeks	1170	730	430	500	630
t = 12 weeks	1170	750	400	/	670
Flow time (s)					
t = 0	145	72	63	66	67
t = 4 weeks	170	/	/	56	70
t = 8 weeks	171	90	59	52	77
t = 12 weeks	198	95	57	/	85

The emulsions comprising a PVA according to the invention make it possible to preserve the satisfactory properties of the emulsion after at least 12 weeks of storage. The viscosities of the emulsions remain very fluid and less than 1000 mPa.s (measured according to the standard DIN 53019 with a Haake Viscotester VT550, at -10°C and for a shear rate of 100 s^{-1}), the flow times remain less than 150 seconds and preferably 100 seconds and the maximum sizes d_{100} do not exceed 20 µm (micrometer).

As a general rule, only the aqueous peroxide emulsion compositions according to the invention make it possible to solve both major technical problems, i.e. the enlargement of the peroxide droplets over time or, in other words, the stability of the emulsion as well as the frequently high cold viscosity of the emulsions, particularly resulting in unsatisfactory flow times.

Szabadalmi igénypontok

1. Szerves peroxid vizes emulziós készítménye, amely magában foglal:
- 10% - 65 tömeg% egy vagy több szerves peroxidot,
- 2% - 25 tömeg% legalább egy fagyásgátló szert,
- 0,01% - 10 tömeg% legalább egy emulgeáló szert,
- adott esetben legalább egy adalék anyagot,
- vizet, olyan mennyiségben, amely összességében a készítmény (100 %) maradékát képezi,

azzal jellemezve, hogy az emulgeáló szer polivinil-acetátból álló kolloid szer, amelynek hidrolízis foka nagyobb, mint 80% és a vízben 4 tömeg%-nál 20°C-on mért viszkozitása kisebb vagy egyenlő 3 mPa.s, amely viszkozitást az ISO 2555 szabvány szerint határozták meg Brookfield RVT viszkoziméteren, mérőorsó No. 3, 20 rpm.

2. Az 1. igénypont szerinti készítmény, **azzal jellemezve, hogy** a részlegesen hidrolizált polivinil-acetát az acetát csoportjain fém-sókkal módosított, amelyeket előnyösen a nátrium-karboxilátok és szulfonátok közül választunk.

3. Az előző igénypontok bármelyike szerinti készítmény, **azzal jellemezve, hogy** egy második emulgeáló szert tartalmaz, amely nem-ionos felületaktív anyag az etoxilált zsírsav típusból, mint etoxilált zsírsav mono-, di- vagy trigliceridek vagy etoxilált növényi olajok; etoxilált zsíralkohol; blokk kopolimer, amely legalább egy alkilén-oxid blokkot tartalmaz.

4. A 3. igénypont szerinti készítmény, **azzal jellemezve, hogy** a második emulgeáló szer etoxilált ricinus olaj.

5. Az előző igénypontok bármelyike szerinti készítmény, **azzal jellemezve, hogy** a polivinil-acetát hidrolízis foka nagyobb, mint 85%, előnyösebben 86% és 89%. közötti

6. Az előző igénypontok bármelyike szerinti készítmény, **azzal jellemezve, hogy** a szerves peroxidot vagy peroxidokat a peroxi-észterek, peroxi-dikarbonátok és/vagy diacil--peroxidok közül választjuk.

7. Az előző igénypontok bármelyike szerinti készítmény, **azzal jellemezve, hogy** a DIN 53211 szabvány szerint 4 mm átmérőjű edénnyel 5°C-on mért kevesebb, mint 200 másodperc, előnyösen kevesebb, mint 100 másodperc folyási idővel meghatározott viszkozitással rendelkezik.

8. Az előző igénypontok bármelyike szerinti készítmény, **azzal jellemezve, hogy** peroxidból képződött cseppecskék sokaságával rendelkezik és azzal, hogy a nevezett cseppecskék átlagos mérete (d_{50}) kevesebb, mint 10 μm (mikrométer), előnyösen kevesebb, mint 5 μm, és a cseppecskék maximális mérete (d_{100}) kisebb, mint 20 μm.

9. Az előző igénypontok bármelyike szerinti készítmény, **azzal jellemezve, hogy** több, mint 30 tömeg%, előnyösen több, mint 45 tömeg% egy vagy több szerves peroxidot tartalmaz.

10. Az előző igénypontok bármelyike szerinti készítmény, **azzal jellemezve, hogy** a polivinil-acetát 1 tömeg% és 5 tömeg% között van jelen.

11. Az 1-9. igénypontok bármelyike szerinti készítmény, **azzal jellemezve, hogy** a polivinil-acetát 0,5 tömeg% és 3 tömeg% között van jelen.

12. Eljárás az az előző igénypontok bármelyike szerinti készítmény előállítására, **azzal jellemezve, hogy** az alábbi egymás utáni lépéseket tartalmazza:

- a fagyásgátló szer, adott esetben legalább az említett adalék anyag, valamint a kolloid szer diszpergálása vízben, egy homogén vizes fázis előállítására, majd
- a peroxid hozzáadása a vizes fázishoz, és
- az így kapott keverék emulgeálása egy emulgeálási lépés során kevesebb, mint 5°C, előnyösen, kevesebb, mint -5°C hőmérsékleten.

13. Az 1-11. igénypontok bármelyike szerinti készítmény alkalmazása etilénesen telítetlen monomerek polimerizációjában vagy kopolimerizációjában.

14. A készítmény 12. igénypont szerinti alkalmazása **azzal jellemezve, hogy** az etilénesen telítetlen monomerek vinil-kloridot jelentenek.

A meghatalmazott:

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