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(54) **Aqueous emulsions of organic peroxides**

(57) An aqueous emulsion of organic peroxide comprising at least one organic peroxide having a freezing point less than 0°C and a 10 hrs half life temperature less than 75°C, at least one emulsifier, water, and at least one water soluble alcohol having a molecular weight less than 100.

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## SPECIFICATION

## Aqueous emulsions of organic peroxides

- 5 This invention relates to aqueous emulsions of organic peroxides and more particularly to  
aqueous emulsions of organic peroxides which are excellent in stability and safety and which are  
capable of being stored and transported at a low temperature and by means of a pump. 5
- Homopolymerization of vinyl halides such as vinyl chloride, vinyl bromide and vinyl fluoride or  
copolymerization of the vinyl halides with vinylidene halides such as vinylidene chloride and  
10 vinylidene fluoride or with vinyl type monomers having a terminal  $\text{CH}_2 = \text{C} <$  group such as  
ethylene, propylene and vinyl acetate has been carried out in general by a suspension or  
emulsion polymerization process. 10
- In these polymerization processes, the monomer or a mixture of monomers to be polymerized  
is dispersed in water in the presence of a dispersing agent, prior to the addition of a free-radical  
15 polymerization initiator. 15
- Recently, it has been highly desired to shorten the polymerization time per batch in order to  
improve the producibility of the obtained polymers. For this purpose, free-radical polymerization  
initiators which are highly reactive at low temperatures have been used.
- Such free-radical polymerization initiators mainly include organic peroxides such as peroxydi-  
20 carbonates, peroxyesters and diacyl peroxides. These compounds are used in highly purified  
form as a solution in a hydrocarbon solvent such as mineral spirit, hexane, cyclohexane or  
toluene, because they are so reactive and unstable that they give rise to explosion hazards. 20
- The solution is stored and transported in a safe form at a temperature below room  
temperature.
- 25 However, phase separation may occur in such solutions, resulting in a highly dangerous  
portion enriched in the organic peroxide. In addition, such a solution entails a fire hazard, since  
the solvent is inflammable, and further it is expensive since the solvent is costly. 25
- Further, the solvent tends to take part in the polymerization reaction, and some of the solvent  
thus frequently remains in the final product polymer and can cause problems in the practical use  
30 of the polymer. For example there are problems with food hygiene and safety problems in the  
production or the processing of the polymer. 30
- Attempts have been made to avoid the use of an organic peroxide diluted with a hydrocarbon  
solvent, by emulsifying the peroxide in water. For example, a polymerization initiator prepared  
by emulsifying the organic peroxide in an aqueous solution containing 1 to 10% by weight of  
35 polyvinyl alcohol and 1 to 6% by weight of polyoxyethylene sorbitanmonolaurate has been used  
in a process for homopolymerizing vinyl chloride or copolymerizing vinyl chloride with a  
vinylidene halide, as disclosed in Japanese Patent Laid-Open Publication No. 130,885/1975. 35
- A frozen organic peroxide emulsion comprising 30–70% by weight of the organic peroxide,  
an effective amount of emulsifier such as of polyvinyl alcohol, and residual water is described in  
40 Japanese Patent Laid-Open Publication No. 14,714/1977. 40
- However, these frozen organic peroxide emulsions are economically disadvantageous, since  
they need to be melted before use.
- Such an organic peroxide emulsion, once defrosted, decreases in stability and even possibly  
shows phase separation.
- 45 It is not practical for the purpose of lowering the freezing point, to use an increased amount of  
the emulsifier such as polyvinylalcohol, as described in the above mentioned patent publication,  
since this substance has a low solubility in water and gives only a small depression in freezing  
point. 45
- On the other hand, water-soluble alcohols of low molecular weight have been hitherto seen as  
50 unfavourable solvents as they greatly reduce the storage stability of organic peroxide. 50
- For example, the half-life of di-(isopropyl) peroxydicarbonate in various solvents in a  
concentration ranging from 5 to 50% is given in Industrial and Engineering Chemistry, 56 (12),  
33 (1964) authored by W.A. Strong. It is shown that though the values of the half-life are in  
the range of from 0.78 to 15 days at 25°C in almost all solvents, the compound exceptionally  
55 becomes very unstable in isopropyl alcohol (a water-soluble low molecular-weight alcohol), and  
vigorous decomposition takes place 25 minutes after dissolution. 55
- As seen above, it is a generally recognised phenomenon that water-soluble alcohols promote  
the decomposition of organic peroxides.
- A very small amount of polymerization initiator can produce a large amount of polymer and  
60 therefore, a small decrease in the concentration due to the decomposition of the organic  
peroxide may cause a large reduction in the polymer yield. Furthermore, the presence of  
decomposition products of organic peroxides during the polymerization process is undesirable in  
most cases and such decomposition products may considerably affect the polymerization rate  
and the resulting polymers. It is therefore very important that the organic peroxide does not  
65 decompose during storage. 65

This invention provides safe and stable aqueous emulsions of organic peroxides which are capable of being transported and stored at low temperatures and are capable of being transported by pumping.

It also provides such emulsions which do not require a defrosting step prior to use, and which are stable towards rapid changes in the atmospheric temperature or vibration.

A further object of this invention is to provide aqueous emulsions of organic peroxides which can be used as polymerization initiators in polymerization of ethylenically unsaturated monomers to produce a polymer excellent in quality.

This invention is based on the finding that, although a water soluble alcohol of low molecular weight has previously been considered to be an unfavourable solvent which remarkably reduces the storage stability of organic peroxides, the storage stability of the organic peroxide is improved when the water soluble alcohol of low molecular weight is present in an emulsion of an organic peroxide in water, and that the resulting aqueous emulsion hardly freezes.

The aqueous emulsion of organic peroxide (hereinafter referred to as PO emulsion) of the present invention is prepared by incorporating at least one water soluble alcohol having molecular weight of less than 100 as an antifreezing agent into a system comprising at least one organic peroxide having a freezing point of less than 0°C and having a 10 hrs half life temperature of less than 75°C, an emulsifier and water.

The preparation of the PO emulsion of this invention can be carried out by a process in that a solution obtained by dissolving an emulsifier and water-soluble alcohol having molecular weight of less than 100 in water, is added to the organic peroxide with stirring, or in that the organic peroxide is added into the above mentioned solution. In the preparation, the emulsifier can also be used in such way by dissolving it in the organic peroxide. The thus-prepared PO emulsion contains water as the continuous phase.

Organic peroxides used in this invention are one or a mixture of more than one organic peroxide whose 10 hr half life temperature is not more than 75°C and whose freezing point is not higher than 0°C. This invention includes the use of a mixture of one or more organic peroxides having a freezing point not higher than 0°C with one or more having a freezing point not lower than 0°C, which mixture shows, as a result, a freezing point not higher than 0°C. The "10 hours half-life temperature" means the temperature at which the organic peroxide must be maintained in order to decompose to one half of the original amount (as active oxygen content) after 10 hours, when the organic peroxide is diluted mainly with a solvent which is relatively inactive towards the peroxide, such as benzene or toluene, to give a solution having a concentration ranging from about 0.1 to 0.2 mole/l.

Examples of the above mentioned organic peroxides are peroxydicarbonates such as di-(n-propyl) peroxydicarbonate, di-(isopropyl) peroxydicarbonate, di-(sec-butyl) peroxydicarbonate, di-(capryl) peroxydicarbonate, di-(2-ethylhexyl) peroxydicarbonate, di-(2-ethoxyethyl) peroxydicarbonate and di-(methoxyisopropyl) peroxydicarbonate; peroxyester such as t-butyl peroxy-pivalate, t-butyl peroxyisobutyrate, t-butyl peroxy-3,5,5-trimethylhexanoate, and t-butyl peroxy-2-ethylhexanoate; and di-acyl peroxides such as di-propionyl peroxide, di-isobutyryl peroxide and di-(3,3,3-trimethylhexanoyl) peroxide.

An example of a suitable mixture of organic peroxides is a mixture of di(2-ethylhexyl) peroxydicarbonate and acetylcyclohexyl sulfonyl peroxide.

It is preferable to use among the above mentioned organic peroxides, one having a particularly hydrophobic substituent so as to obtain more stable PO emulsion.

A solvent can be incorporated into the emulsion in order to stabilize the above-mentioned organic peroxide or for the purpose of lowering the freezing point.

The amount of the organic peroxide in the PO emulsion of this invention is usually 5-80% by weight and preferably 10-65% by weight and preferably 10-65% by weight, since a smaller proportion results in unnecessarily high transportation costs and a higher proportion tends to reduce stability.

The other components are water, an emulsifier and a water-soluble alcohol having a molecular weight of not more than 100.

The water soluble alcohol having molecular weight of less than 100 which is used in this invention, is a low molecular weight alcohol which is completely miscible with water, for example, methanol, ethanol, n-propanol, isopropanol, or ethyleneglycol.

The use of the alcohol in a much smaller amount hardly causes a sufficient freezing point depression and in a much greater amount results in increasing decomposition of the organic peroxide.

Accordingly, it is preferable to use the alcohol in an amount ranging from 0.02 to 7 parts by weight per part by weight of the water.

Two or more of the above-mentioned water soluble alcohols may be used in combination.

As the emulsifier, substances which are known to exert surface activity, such as anionic surfactants, cationic surfactants, nonionic surfactants, amphoteric surfactants, and high molecular surfactants and protective colloid agents can be exemplified.

Examples of surface active agents which are preferably incorporated into the PO emulsion are sorbitan mono-, di- and triesters of lauric acid, palmitic acid, stearic acid or oleic acid and saccharose mono-, di-, and triesters of lauric acid, palmitic acid, stearic acid or oleic acid.

5 Examples of suitable protective colloids are water soluble synthetic or naturally occurring high molecular weight compounds such as polyvinyl alcohol, partly acetylated polyvinyl alcohols and cellulose derivatives. 5

Emulsification of the organic peroxide can be carried out by using one or more emulsifiers selected from the above.

10 For reasons of economy and to avoid possible undesirable affects, it is preferred to use as little emulsifier as possible while still obtaining a stable PO emulsion, and the amount used is usually in the range of 0.001 to 0.5 part by weight based on one part by weight of water used. 10

When the emulsifier is dissolved in water or the organic peroxide, it may be difficult to carry out the dissolution, but the use of the water soluble alcohol can improve the solubility.

15 A conventional apparatus can be used for producing the PO emulsion of this invention. Examples are ones provided with mechanically rotatable stirrers of the paddle-, propellor- or turbine- type. A colloid mill, a homogenizer, a high speed shear emulsifier, an ultrasonic homogenizer and the like can be used for this purpose. 15

The PO emulsion of this invention has the advantageous characteristics shown below.

20 First, conventional cooling processes can be applied to the PO emulsion without any affect on the emulsion when it is necessary to store it at a low temperature, and no defrosting step is necessary before it can be used as a polymerization catalyst. 20

25 Second, the emulsion is excellent in stability and thus it can be stored, handled and transported in a very safe way, because vigorous spontaneous decomposition and violent combustion on firing as seen in conventional radical polymerization initiators are prevented. As a water soluble alcohol of low molecular weight, which is usually of low density, is present in the emulsion, it is possible to prepare it in such manner that the aqueous phase forms an upper part if phase separation of the PO emulsion occurs. This contributes to the safety of the PO emulsion. In addition, the PO emulsion of this invention is stable when subjected to rapid changes in atmospheric temperature or fine vibrations. 25

30 Third, such PO emulsions are low-viscosity liquids and can be easily diluted with water. Therefore, they are suitable for transportation by pumping. Further, any leakages of the PO emulsion can be easily washed away. 30

35 One application of the PO emulsion of this invention is in the production of polymers from ethylenically unsaturated monomers and it is especially useful for the suspension polymerization of vinyl monomers such as vinyl halide monomers. 35

According to the process of the suspension polymerization of this invention, a vinyl polymer may be produced, by charging water, dispersing agent and the above mentioned monomer into the reaction vessel, then introducing the PO emulsion and stirring and heating to effect polymerization.

40 The charging of PO emulsion can be carried out in various ways, e.g. by pumping transportation after the PO emulsion has been diluted with water to the described viscosity and/or by charging after another radical polymerization initiator has been previously mixed with the PO emulsion. At the same time, separation of the emulsion can be prevented by selecting the type and amount of the emulsifier. 40

45 Polymers produced by using the PO emulsion of this invention are excellent in quality as compared with ones prepared by conventional processes since the additives such as the emulsifier and the alcohol are removed with the water. 45

This invention is further illustrated by way of the following Examples and Comparative Tests, which are for the purposes of illustration only.

50 In the description, all parts and % are by weight unless otherwise indicated. 50

#### EXAMPLE 1

55 Into a three neck flask of 500 ml capacity which was provided with a conventional stirring device and a thermometer, there were charged 40 parts of di-(2-ethylhexyl) peroxydicarbonate having a freezing point of not more than  $-50^{\circ}\text{C}$  and having a 10 hrs half life temperature of  $43.5^{\circ}\text{C}$ . 55

60 The content of the flask was heated to  $20^{\circ}\text{C}$ , wherein there was added dropwise under stirring an aqueous solution consisting of 43 parts of water, 12 parts of methanol, 2 parts of polyvinyl alcohol, 1.5 parts of sorbitan monolaurate (trade mark; Nonion LP-20R prepared by Nippon Oil and Fats Co., Ltd.) and 1.5 parts of sorbitan monooleate (Nonion OP-80R, Trade Mark, produced by Nippon Oil and Fats Co., Ltd.). After the addition, the stirring was continued for 20 minutes, whereby a homogeneous and stable milky PO emulsion having viscosity of 1.3 poises at  $21^{\circ}\text{C}$  was obtained. 60

65 Stability and safety tests were carried out as mentioned below using this PO emulsion. Results are listed in Table 1. 65

### Storage Stability Tests

Samples were placed into vessels maintained at  $-15^{\circ}\text{C}$  or  $30^{\circ}\text{C}$  respectively. After maintaining the samples for predetermined times at these temperatures, the organic peroxide content of the samples was determined. The storage stability of the samples was estimated from the decrease in the organic peroxide content and changes in the appearance of the samples.

The storage stability was estimated by classifying the results by the following symbols:

- ⊙ symbol shows that no change was observed over 1 to 30 days;
- symbol shows that not less than 50% of the organic peroxide had decomposed over 6 to 24 hours;
- △ symbol shows that not less than 50% of the organic peroxide had decomposed over 1 to 6 hours.
- × symbol shows that the sample had coagulated within 1 hour.

### Safety Test

#### 15 Combustion Test 15

Combustion tests were carried out using a Cleaveland open-type flash tester as shown in Japanese Industrial Standard – K 2274–62 to determine the flash points of the samples.

Combustion state was also observed. The result of the combustion test was classified by the following symbols;

- ⊙ symbol shows that the flash point was not less than  $70^{\circ}\text{C}$  and combustion proceeded gently;
- symbol shows that the flash point was within a range of  $66$ – $70^{\circ}\text{C}$  and that combustion was fairly intense;
- △ symbol shows that the flash point was within a range of  $62$ – $66^{\circ}\text{C}$  and that combustion was still more intense;
- × symbol shows that the flash point was not more than  $62^{\circ}\text{C}$  and that combustion was extremely intense;

### Rapid Heating Test

According to the Rapid Heating Test process prescribed by O.P.P.S.D. (Organic Peroxide Producer Safety Division), the heat stability of samples was estimated to measure temperatures at which decomposition takes place and the maximum temperatures attained. The results of heat stability by the rapid heating test was classified by the following symbols:

- ⊙ symbol shows that the maximum temperature was not higher than  $100^{\circ}\text{C}$ ;
- symbol shows that the maximum temperature was from more than  $100^{\circ}\text{C}$  to  $130^{\circ}\text{C}$ ;
- △ symbol shows that the maximum temperature was from more than  $130^{\circ}\text{C}$  to  $160^{\circ}\text{C}$ ;
- × symbol shows that the maximum reaching temperature was more than  $160^{\circ}\text{C}$ .

### COMPARATIVE TEST 1

Into a flask of 500 ml capacity which was provided with a conventional stirring device, there were charged 40 parts of di-(2-ethylhexyl) peroxydicarbonate and 60 parts of toluene and the contents were stirred to give a homogeneous solution.

### COMPARATIVE TEST 2

A homogeneous solution was prepared according to the same procedures as those in Comparative Test 1 except that instead of toluene methanol was used.

### COMPARATIVE TEST 3

According to the same procedures as shown in Example 1 except for using 40 parts of di-(2-ethylhexyl) peroxydicarbonate, 3 parts of polyvinyl alcohol, 4 parts of polyoxyethylene sorbitan monolaurate and 53 parts of water a PO emulsion which is one of the compositions described in Japanese Patent Laid-Open Publication No. 130885/1975, was prepared.

Then, the stability test and the safety test were carried out in the same manner as shown in Example 1 using the samples prepared in Comparative Tests 1 to 3. The results are shown in Table 1.

Table 1

5	Test	Sample	Example 1	Comparative Tests			5
				1	2	3	
10	Storage Stability Test	- 15°C	⊙	⊙	⊙	×	10
		30°C	○	○	△	○	
15	Safety Test	Combustion Test	⊙	×	×	⊙	15
		Rapid Heat Test	⊙	△	△	⊙	

From Table 1 it can be seen that the PO emulsion of Example 1 gave superior results to that of Comparative Test 1 (which was a toluene - dilution product) in the safety test and that the former PO emulsion was superior to the methanol-diluted product of Comparative Test 2 not only in the safety test but also in the storage stability test. Further, it was also recognised that the PO emulsion of Example 1 was superior in the storage test to the PO emulsion of Comparative Test 3, which was disclosed in Japanese Patent Laid-Open Publication No. 130885/1975.

#### EXAMPLE 2-4

PO emulsions containing di-(2-ethylhexyl) peroxydicarbonate in amounts of 20% (Example 2), 60% (Example 3) and 80% (Example 4) respectively were prepared according to the same procedures as those in Example 1 except for using the peroxydicarbonate in amounts of 15 parts in Example 2, 90 parts in Example 3 and 240 parts in Example 4. A homogeneous milky PO emulsion was obtained in every Example.

The viscosity values of these emulsions at 20°C were 1.0 poise in Example 2, 5.9 poises in Example 3 and 15 poises in Example 4, respectively.

#### COMPARATIVE TEST 4

A PO emulsion containing di-(2-ethylhexyl) peroxydicarbonate in an amount of 60% was produced in the same manner as in Comparative Test 3 except for using 90 parts of the peroxydicarbonate.

#### COMPARATIVE TEST 5

A homogeneous solution containing di(2-ethylhexyl) perixydicarbonate in the concentration of 60% was prepared in the same manner as in Comparative Test 1 except for using the peroxydicarbonate in an amount of 90 parts.

The storage stability test at - 15°C and the safety test for samples obtained in Examples 2-4 and Comparative Tests 4 and 5 were carried out in the same manner as shown in Example 1.

The results are shown in Table 2.

Table 2

50	Test	Sample	Examples			Comparative Test		50
			2	3	4	4	5	
55	Storage Stability Test (- 15°C)		⊙	⊙	⊙	×	⊙	55
		Combustion Test	⊙	○	△	○	×	
60	Safety Test	Rapid Heat Test	⊙	○	△	○	×	60
			⊙	○	△	○	×	

From Table 2, it can be seen that the PO emulsion of Example 3 was superior in the safety test to toluene-diluted product of Comparative Test 5 which contained the peroxydicarbonate in the same amount of 60% and that the PO emulsion was superior in the storage stability test to that of Comparative Test 4, which is disclosed in Japanese Patent Laid-Open Publication No. 130885/1975.

**EXAMPLE 5**

A PO emulsion was prepared in the same manner as shown in Example 1 except for using t-butylperoxyoctoate having freezing point of not more than  $-30^{\circ}\text{C}$  and 10 hrs life temperature of  $72.5^{\circ}\text{C}$  instead of di(2-ethylhexyl) peroxydicarbonate and also using 3% of sorbitan monopalmitate (Nonion PP-40 R, manufactured by Nippon Oil and Fats Co., Ltd.) instead of sorbitan monolaurate and sorbitan monooleate and further except for adding dropwise the above mentioned t-butylperoxyoctoate into the aqueous mixture solution. Then, a homogeneous milky PO emulsion having viscosity value of 1.1 poises at  $20^{\circ}\text{C}$  was obtained.

**EXAMPLE 6**

A PO emulsion was produced in the same manner as in Example 1 except for using ethylene glycol instead of methanol in Example 1. A homogeneous PO emulsion whose viscosity value was 1.2 poises at  $20^{\circ}\text{C}$  was obtained.

**EXAMPLE 7**

According to the same procedures as shown in Example 1, a PO emulsion was prepared, except for using 0.4 parts of saccharose monolaurate (trade mark: Ryoto Sugar Ester. S-1670 produced by Ryoto Sugar Manufacturing Co., Ltd) and 2.6 parts of sorbitan mono oleate instead of sorbitan monolaurate and sorbitan monooleate, whereby a white milky PO emulsion whose viscosity was 1.4 poises at  $20^{\circ}\text{C}$  was obtained.

**EXAMPLE 8**

According to the same procedures as shown in Example 1 a PO emulsion was prepared except for using di (3,5,5-trimethyl) hexanoyl peroxide whose freezing point is less than  $-70^{\circ}\text{C}$  and whose 10 hrs half life temperature is  $59.5^{\circ}\text{C}$ , instead of di(2-ethylhexyl) peroxydicarbonate and for using 6 parts of methyl alcohol and 6 parts of ethylenglycol instead of methyl alcohol and for dropping the said di (3,5,5-trimethyl) hexanoylperoxide into the mixed aqueous solution, thereby obtaining a white milky emulsion whose viscosity was 1.3 poises at  $20^{\circ}\text{C}$  and which was uniform, was obtained.

Respective samples were taken from PO emulsion which were obtained in Examples 5-8. Each sample was applied to the same stability test and safety test. It was found that the safety and stability of each sample was similar to Example 1.

**REFERENCE EXAMPLE 1 (Polymerization of vinyl chloride)**

There were charged 0.45 part of polyvinyl alcohol, 300 parts of water, 100 parts of vinyl chloride and 0.075 part of the PO emulsion which was obtained by Example 1, into an autoclave.

After the autoclave was evacuated, the content of the autoclave was heated up to  $58^{\circ}\text{C}$ , while stirring and the reaction was continued for 8 hours until the reaction was completed, thereby obtaining white powder of polyvinyl chloride with yield of 85%.

It was found that the thus obtained polymers had splendid heat stability and electrical stability without deriving any harmful properties from the methanol and the emulsifier which were contained in the PO emulsion. The polymer was easy to dry because it did not contain any oily solvents arising from the polymerization.

**CLAIMS**

1. An aqueous emulsion of organic peroxide comprising at least one organic peroxide having a freezing point less than  $0^{\circ}\text{C}$  and a 10 hrs half life temperature (as herein defined) less than  $75^{\circ}\text{C}$ , at least one emulsifier, water, and at least one water soluble alcohol having a molecular weight less than 100.

2. An aqueous emulsion of organic peroxide according to Claim 1, wherein the water soluble alcohol is one or more of methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol and ethylene glycol.

3. An aqueous emulsion of organic peroxide according to Claim 1, wherein the emulsifier is one or more of sorbitan mono-, di- and triester of lauric acid, palmitic acid stearic acid or oleic acid and saccharose mono-, di- and triesters of lauric acid, palmitic acid, stearic acid or oleic acid.

4. An aqueous emulsion according to Claim 1, wherein the organic peroxide constitutes 5 to 80 weight %, preferably 10 to 65 weight %, of the total weight of the emulsion and the emulsifier constitutes 0.001 to 0.5 part by weight and the water soluble alcohol 0.02 to 7 parts by weight per part by weight of the water, respectively.