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(54) Titre : TREILLIS POUR REVETEMENT EN PAPIER PREPARE AU MOYEN DE REGULATEURS DE MASSE
MOLECULAIRE EXEMPTS D'HALOGENE ET DE SOUFRE

(54) Title: LATICES FOR PAPER COATINGS BASED ON HALOGEN- AND SULFUR-FREE MOLECULAR WEIGHT
REGULATORS

(57) **Abrégé/Abstract:**

Disclosed is a polymer latex prepared with the aid of a peroxide as a halogen- and sulfur-free molecular weight regulator and a separate polymerization initiator. The polymer latex is to be used for paper coating applications, in particular in the area of odor-sensitive applications (e. g. food packaging). The peroxide has the formula: $R-O-O-H$, $R^1-O-O-R^2$, $R^1-CO-O-O-CO-R^2$, $R-CO-O-O-H$, $R^1-CO-O-O-R^2$ or $R^1-O-CO-O-O-CO-O-R^2$ in which R is H, alkyl, aryl or aryl-alkyl and R^2 is alkyl, aryl or aryl-alkyl. The polymer has a glass transition temperature of $-30^{\circ}C$ to $+70^{\circ}C$ and contains: (A) 10-80% of monovinyl aromatic monomer, (B) 0-70% of conjugated diene monomer, (C) 0-70% of acrylate monomer, and (D) 0-65% of another copolymerizable monomer, provided that the total of (B) and (C) is greater than 0.

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Abstract

Latices for paper coatings based on halogen- and sulfur-free molecular weight regulators

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5 of a peroxide as a halogen- and sulfur-free molecular weight
regulator and a separate polymerization initiator. The
polymer latex is to be used for paper coating applications,
in particular in the area of odor-sensitive applications
(e.g. food packaging). The peroxide has the formula:
10 $R-O-O-H$, $R^1-O-O-R^2$, $R^1-CO-O-O-CO-R^2$, $R-CO-O-O-H$, $R^1-CO-O-O-R^2$
or $R^1-O-CO-O-O-CO-O-R^2$ in which R is H, alkyl, aryl or aryl-
alkyl and R^2 is alkyl, aryl or aryl-alkyl. The polymer has a
glass transition temperature of $-30^{\circ}C$ to $+70^{\circ}C$ and contains:
(A) 10-80% of monovinyl aromatic monomer, (B) 0-70% of
15 conjugated diene monomer, (C) 0-70% of acrylate monomer, and
(D) 0-65% of another copolymerizable monomer, provided that
the total of (B) and (C) is greater than 0.

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Latices for paper coatings based on halogen- and sulfur-free molecular weight regulators

The present invention relates to polymer latices which are prepared with the aid of halogen- and sulfur-free molecular weight regulators and which can be used for paper coating applications, in particular in the area of odor-sensitive applications (e.g. food packaging).

Latices which can be used for coating paper and cardboard must have good properties with respect to binding power (i.e. pick resistance). For this purpose, it is necessary for the molecular weight of the polymer latices to be controlled by regulators during the polymerization. In the past, halogen-containing compounds (e.g. carbon tetrachloride) were used for this purpose. For ecological reasons, however, these regulators were "banned" from the polymer latices a few years ago and replaced by sulfur-containing regulators. The most well known group of these regulators are the mercaptans, whose most prominent member in turn is tert-dodecyl mercaptan (t-DDM).

Mercaptans meet the requirements very well with respect to the regulator effect in polymer latices, i.e. latices which have very good dry and wet pick resistances are obtained by the use of mercaptans. The major disadvantages of latices which have been prepared with the aid of mercaptans is, however, that they lead to undesired odor annoyances in certain applications in paper coating. This is a decisive disadvantage in particular in the area of packaging papers and packaging cardboards. Polymer latices which are used for these odor-sensitive applications therefore must not contain any sulfur-containing molecular weight regulators.

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U.S. Patent No. 5,837,762 describes the use of rosin-containing chain transfer agents for the preparation of polymer latices. The latices thus synthesized have a disadvantage that the regulator efficiency of rosin is very low in contrast to mercaptans. Thus, up to 9 pph of rosin have to be used in the polymerization of the latex in order to obtain acceptable values for the dry pick resistance in coated paper. In addition, rosin is a natural product which, depending on the source, is subject to certain quality variations. Finally, a third disadvantage which should be mentioned is that rosin has a strong natural color (yellow to brown) which may also lead to quality disadvantages in coated paper.

Outside the area of aqueous polymer dispersions (latices), patent literatures cite various peroxides which are said to have a regulating effect. Thus, for example, WO 9630415 A1 describes the use of alkoxyallyl (di)peroxides as molecular weight regulators in the free radical polymerization of styrene, methyl methacrylate and butyl acrylate. JP-63-179902 A2 reports on the use of cumyl hydroperoxide as a molecular weight regulator in the free radical polymerization of unsaturated monomers, such as, for example, styrene.

It was therefore desired to find alternative molecular weight regulator systems which are neither halogen-containing nor sulfur-containing and which are nevertheless suitable for the preparation of polymer latices having sufficient binding power (i.e. pick resistance) and which can be used in the area of odor-sensitive applications for the coating of paper and cardboard.

The invention relates to a polymer latex for use in coating paper and cardboard. The polymer latex has a glass

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transition temperature of from -30°C to 70°C , is prepared by using an initiator and a sulfur- and halogen-free chain transfer agent and comprises, in polymerized form:

- (A) from 10% by weight to 80% by weight of one or more
 5 monovinyl aromatic monomers;
- (B) from 0% by weight to 70% by weight of one or more conjugated diene monomers;
- (C) from 0% by weight to 70% by weight of one or more acrylate monomers; and
- 10 (D) the remainder, if present, of one or more other copolymerizable comonomers, provided that the sum of the percentages by weight of components (B) and (C) is greater than zero,

wherein the chain transfer agent is a peroxide
 15 selected from the group consisting of:

1. hydroperoxides of the general structural formula



in which R is H or one of the following radicals:

$\text{C}_1\text{-C}_{16}$ alkyl (linear or branched),

20 $\text{C}_1\text{-C}_{16}$ alkyl (linear or branched) in combination with $\text{C}_6\text{-C}_{18}$ aryl,

$\text{C}_6\text{-C}_{18}$ aryl;

2. peroxides of the general structural formula



25 in which R^1 and R^2 are identical or different and are one of the following radicals:

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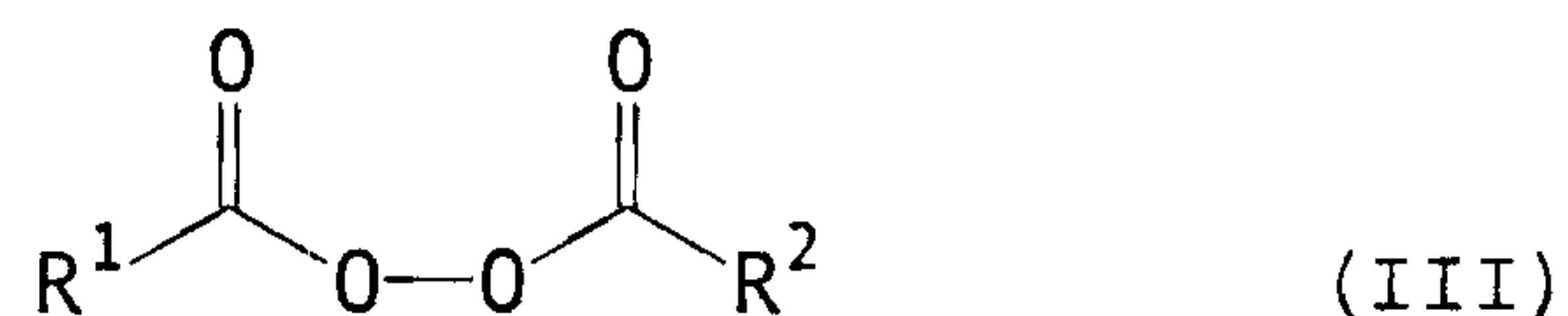
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C₁-C₁₆ alkyl (linear or branched),

C₁-C₁₆ alkyl (linear or branched) in combination
with C₆-C₁₈ aryl,

C₆-C₁₈ aryl;

5 3. peroxides of the general structural formula



in which R¹ and R² are identical or different and are one of
the following radicals:

10 C₁-C₁₆ alkyl (linear or branched),

C₁-C₁₆ alkyl (linear or branched) in combination
with C₆-C₁₈ aryl,

C₆-C₁₈ aryl;

4. peroxocarboxylic acids of the general structural formula

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in which R is H or one of the following radicals:

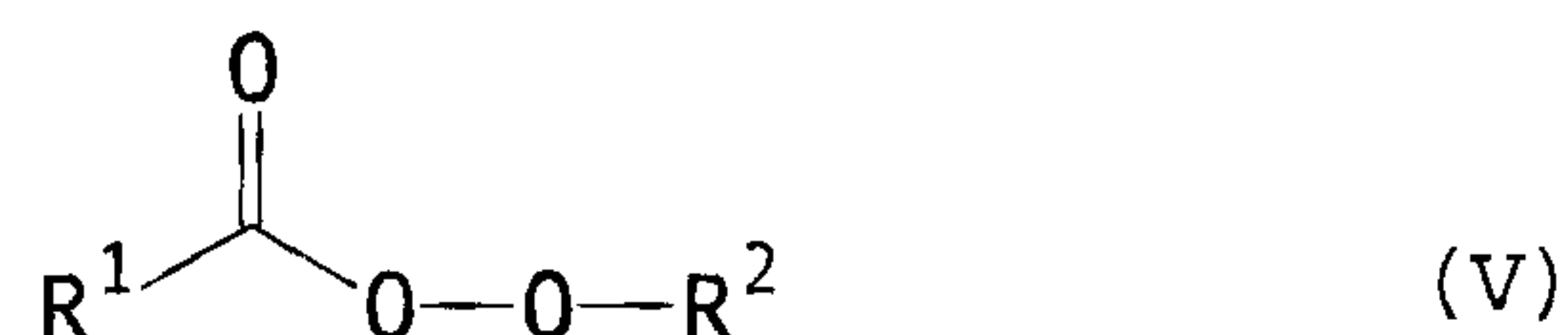
C₁-C₁₆ alkyl (linear or branched),

20 C₁-C₁₆ alkyl (linear or branched) in combination
with C₆-C₁₈ aryl,

C₆-C₁₈ aryl;

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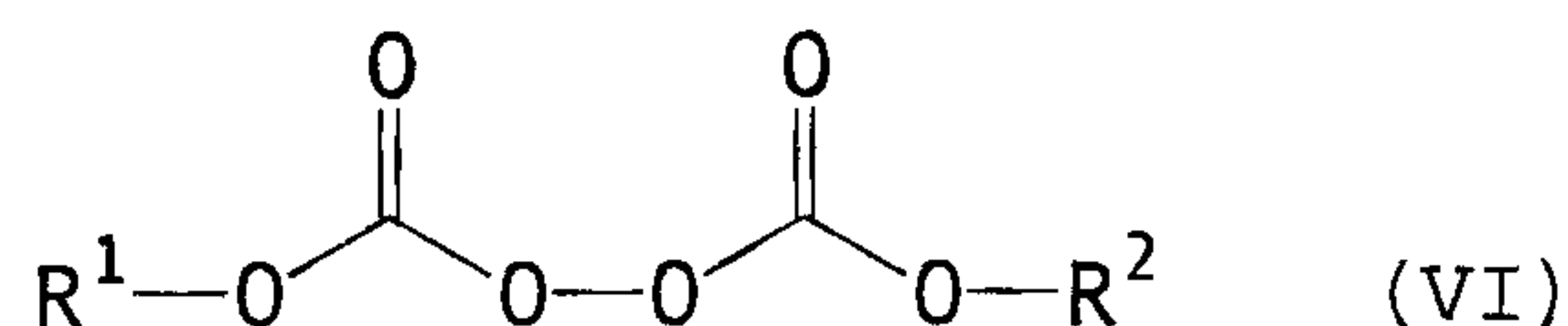
5. peroxocarboxylic esters of the general structural formula

in which R¹ and R² are identical or different and are one of
5 the following radicals:

C₁-C₁₆ alkyl (linear or branched),

C₁-C₁₆ alkyl (linear or branched) in combination
with C₆-C₁₈ aryl,

C₆-C₁₈ aryl;

10 6. peroxodicarbonates of the general structural formula

in which R¹ and R² are identical or different and are one of
the following radicals:

15 C₁-C₁₆ alkyl (linear or branched),

C₁-C₁₆ alkyl (linear or branched) in combination
with C₆-C₁₈ aryl,

C₆-C₁₈ aryl.

The invention relates to a process for the
20 preparation of a polymer latex, the polymer latex having a
glass transition temperature of from -30°C to 70°C, which
comprises polymerizing: using a sulfur-free and halogen-free
chain transfer agent and a separate polymerization initiator:

(A) from 10% by weight to 80% by weight of one or more
25 vinyl aromatic monomers;

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(B) from 0% by weight to 70% by weight of one or more conjugated diene monomers;

(C) from 0% by weight to 70% by weight of one or more acrylate monomers; and

- 5 (D) the remainder, if present, of one or more other copolymerizable comonomers, with the proviso that the sum of the percentages by weight of components (B) and (C) is greater than zero,

wherein the chain transfer agent is a peroxide
10 selected from the group consisting of:

1. hydroperoxides of the general structural formula



in which R is H or one of the following radicals:

C₁-C₁₆ alkyl (linear or branched),

- 15 C₁-C₁₆ alkyl (linear or branched) in combination with C₆-C₁₈ aryl,

C₆-C₁₈ aryl;

2. peroxides of the general structural formula



- 20 in which R¹ and R² are identical or different and are one of the following radicals:

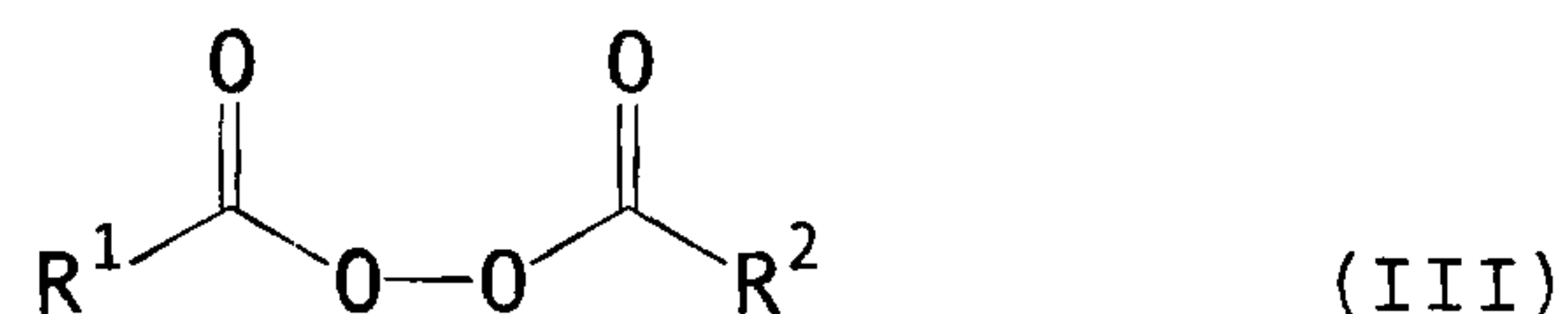
C₁-C₁₆ alkyl (linear or branched),

- C₁-C₁₆ alkyl (linear or branched) in combination with C₆-C₁₈ aryl,

- 25 C₆-C₁₈ aryl;

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3. peroxides of the general structural formula

in which R^1 and R^2 are identical or different and are one of
5 the following radicals:

C_1 - C_{16} alkyl (linear or branched),

C_1 - C_{16} alkyl (linear or branched) in combination
with C_6 - C_{18} aryl,

C_6 - C_{18} aryl;

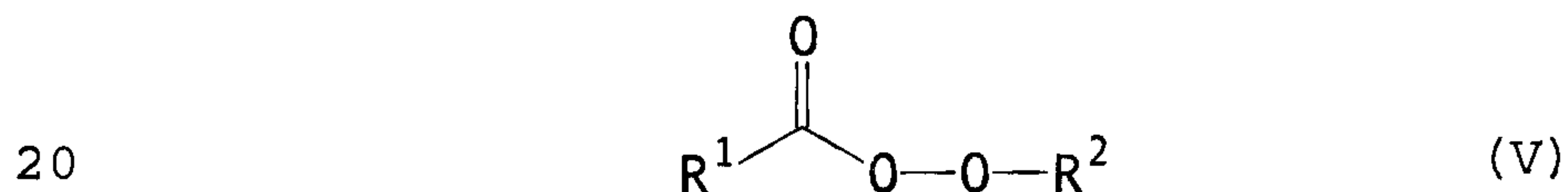
10 4. peroxocarboxylic acids of the general structural formula

in which R is H or one of the following radicals:

C_1 - C_{16} alkyl (linear or branched),

15 C_1 - C_{16} alkyl (linear or branched) in combination
with C_6 - C_{18} aryl,

C_6 - C_{18} aryl;

5. peroxocarboxylic esters of the general structural formula

in which R^1 and R^2 are identical or different and are one of
the following radicals:

C_1 - C_{16} alkyl (linear or branched),

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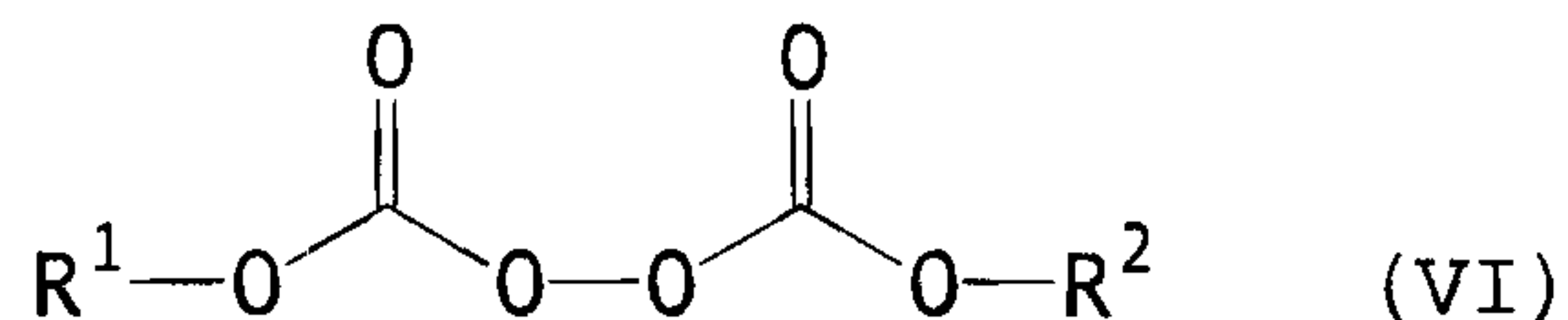
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C₁-C₁₆ alkyl (linear or branched) in combination with C₆-C₁₈ aryl,

C₆-C₁₈ aryl;

6. peroxodicarbonates of the general structural formula

5



in which R¹ and R² are identical or different and are one of the following radicals:

C₁-C₁₆ alkyl (linear or branched),

10

C₁-C₁₆ alkyl (linear or branched) in combination with C₆-C₁₈ aryl,

C₆-C₁₈ aryl.

The invention also relates to the use of the polymer latex for coating paper and cardboard and the use of peroxides for the preparation of these special latices.

Suitable peroxides are the abovementioned compounds according to the structural formulae, but in particular the hydroperoxides of the formula R-O-O-H. In this formula, preferably R is C₁-C₁₆ linear or branched alkyl or C₁-C₁₆ linear or branched alkyl in combination with C₆-C₁₈ aryl. More preferred are the hydroperoxides of the formula R-O-O-H in which R is C₃-C₈ branched alkyl or phenyl-C₃-C₈ branched alkyl.

tert-Butyl hydroperoxide and cumyl hydroperoxide are particularly preferred. Furthermore, peroxides of the general formula R¹-O-O-R² in which R¹ and R² are each C₃-C₈ branched alkyl such as di-tert-butyl peroxide; and

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peroxycarboxylic esters of the formula $R^1\text{-CO-O-O-R}^2$ in which R^1 is $C_6\text{-C}_{10}$ aryl or $C_5\text{-C}_{16}$ linear or branched alkyl and R^2 is $C_3\text{-C}_8$ branched alkyl, such as tert-butyl peroxybenzoate and tert-butyl peroxy-3,5,5-trimethylhexanoate are also
5 preferably used.

Typical amounts of the peroxides used are in the range of 0.1 - 10% by weight, preferably of 0.5 - 5% by weight, particularly preferably of from 0.5 to 3% by weight, based on the weight of the monomers. This makes it possible
10 to achieve a crosslinking density in the polymer which is analogous with that obtained with sulfur-containing regulators (measurable, for example, by determination of the gel content of the polymer). With respect to their performance characteristics, such as, for example, pick
15 resistance in the paper coat, the polymer latices obtained according to the present invention have very good properties which are comparable with those of polymer latices regulated by mercaptan. Of course, the peroxides used, according to the present invention, in particular tert-butyl
20 hydroperoxide and cumyl hydroperoxide, are not suitable, under the conditions described, for acting as an initiator in the polymerization. A separate initiator such as a persulfate, for example, ammonium persulfate or sodium persulfate, is required for this purpose. Without the
25 addition of an initiator, the polymerization would not function, which can serve as evidence that the peroxides used, in particular the tert-butyl hydroperoxide and cumyl hydroperoxide, act not as an initiator but as a molecular weight regulator under the polymerization conditions.
30 Therefore, only peroxides which exhibit substantially no thermal decomposition at the present polymerization temperatures are suitable for use as regulators in the context of the present invention. Moreover, it must be

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ensured that no strong reducing agent which might initiate spontaneous decomposition of the peroxide (i.e. redox initiator system) is present in the system.

The monovinyl aromatic monomers (A) include, for
5 example: styrene, α -methylstyrene, p-methylstyrene, tert-butylstyrene and vinyltoluene. Mixtures of one or more monovinyl aromatic monomers may also be used. Preferred monomers are styrene and α -methylstyrene. The monovinyl aromatic monomer is generally used in the range of from 10
10 to 80% by weight, preferably from 25 to 75% by weight, most preferably from 35 to 70% by weight, based on the total weight of the monomers.

The conjugated diene monomers (B) suitable for the preparation of the latices include, for example,
15 1,3-butadiene, isoprene and 2,3-dimethyl-1,3-butadiene. 1,3-Butadiene is preferred in the present invention. Typically, the amount of conjugated diene monomer which is present in the polymeric phase ranges from 0 to 70% by weight, preferably from 20 to 65% by weight, more preferably
20 from 20 to 58% by weight, more preferably from 30 to 50% by weight, most preferably from 30 to 45% by weight, based on the total weight of the monomers.

The acrylate monomers (C) which can be used in the present invention are esters of (meth)acrylic acid and
25 include, for example: n-, iso- or tert-alkyl esters of acrylic or methacrylic acid, in which the alkyl group has from 1 to 20 carbon atoms and may also contain one or more interrupting oxygen atoms (i.e. ether bonds). The acrylate monomers may be the reaction product of (meth)acrylic acid
30 with the glycidyl ester of a neo acid, such as versatic acids, neodecanoic acids or pivalic acid.

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Preferred acrylate monomers are C₁-C₁₀-alkyl (meth)acrylates, C₁-C₁₀-alkoxy-C₁-C₁₀-alkyl (meth)acrylates and C₁-C₁₀-alkoxy-C₁-C₁₀-alkoxy-C₁-C₁₀-alkyl (meth)acrylates, most preferably C₁-C₈-alkyl (meth)acrylates, C₁-C₆-alkoxy-C₁-C₈-alkyl (meth)acrylates and C₁-C₄-alkoxy-C₁-C₄-alkoxy-C₁-C₈-alkyl (meth)acrylates. Examples of such acrylate monomers include n-butyl acrylate, sec-butyl acrylate, ethyl acrylate, hexyl acrylate, tert-butyl acrylate, 2-ethylhexyl acrylate, isooctyl acrylate, 4-methyl-2-pentyl acrylate, 2-methylbutyl acrylate, methyl methacrylate, butyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, ethyl methacrylate, isopropyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate and cetyl methacrylate, methoxyethyl methacrylate, ethoxyethyl acrylate, butoxyethyl methacrylate, methoxybutyl acrylate and methoxyethoxyethyl acrylate.

Preferred acrylate monomers are n-butyl acrylate, butyl methacrylate, 2-ethylhexyl acrylate and methyl methacrylate. Methyl methacrylate and n-butyl acrylate are particularly preferred. Frequently, two or more acrylate monomers are used. The alkyl esters of acrylic or methacrylic acid and alkoxyalkyl (meth)acrylate monomers can be used as part of the monomer mixture.

The amount of acrylate monomers which are present in the polymeric phase depends on the monomer chosen, but the typical range is from 0 to 70% by weight, preferably from 0 to 60% by weight, most preferably from 0 to 51% by weight, based on the total weight of the monomers.

It is critical that the combined percentage by weight of conjugated diene monomer or monomers (component B) and acrylate monomer or monomers (component C) is greater than zero, preferably greater than 10%.

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As stated above, other polymerizable comonomers (D) may also be employed. These other comonomers include, for example: ethylenically unsaturated carboxylic acid monomers, nitrile monomers, vinyl ester monomers, hydroxyalkyl (meth)acrylate monomers, and (meth)acrylamide monomers, and are employed in their total amount, preferably 0 to 65% by weight.

The ethylenically unsaturated carboxylic acid monomers suitable for use in the present invention include monocarboxylic acid and dicarboxylic acid monomers and the monoesters thereof (other than the acrylate monomers (C) described above). It has been found that the addition of such an ethylenically unsaturated carboxylic acid monomer greatly improves the stability of the latex and the adhesion of the latex film, with the result that they are suitable for use in formulations for the coating of paper. For carrying out the present invention in practice, it is preferable to use ethylenically unsaturated aliphatic mono- or dicarboxylic acid(s) or anhydride(s) which contain from 3 to 5 carbon atoms. Examples of monocarboxylic acid monomers include, for example, acrylic acid and methacrylic acid, and examples of dicarboxylic acid monomers include, for example, fumaric acid, itaconic acid, crotonic acid, maleic acid and maleic anhydride.

The use of ethylenically unsaturated carboxylic acid monomers influences the properties of the polymer dispersion and of the coating produced therefrom. The type and the amount of these monomers are determined thereby. Typically, such an amount is from 0 to 20% by weight, preferably from 0 to 10% by weight, most preferably from 1 to 10% by weight, based on the total weight of the monomers.

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Nitrile monomers which can be used in this invention include polymerizable unsaturated aliphatic nitrile monomers which contain from 2 to 4 carbon atoms in a linear or branched arrangement which may be substituted
5 either by acetyl or additional nitrile groups. Such nitrile monomers include, for example, acrylonitrile, methacrylonitrile and fumaronitrile, acrylonitrile being preferred. These nitrile monomers (if used) may be included in amounts of up to about 25 parts by weight, preferably
10 from 0 to 15 parts by weight, based on 100 parts by weight of monomers.

Vinyl ester monomers which can be used here include vinyl acetate, vinyl propionate, vinyl butyrate, vinyl benzoate, vinyl 2-ethylhexanoate, vinyl stearate and
15 the vinyl esters of versatic acid. The most preferred vinyl ester monomer for use in the present invention is vinyl acetate. Typically, the amount of vinyl ester monomer (if used) which is present in the polymeric phase ranges from 0 to 45% by weight, preferably from 0 to 35% by weight,
20 based on the total weight of the monomers.

The hydroxyalkyl (meth)acrylate monomers which can be used here include hydroxyalkyl acrylate and methacrylate monomers which are based on ethylene oxide, propylene oxide and other higher alkylene oxides or mixtures thereof.
25 Examples are hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate and hydroxybutyl acrylate. Preferred hydroxyalkyl (meth)acrylate monomers are hydroxyethyl acrylate, hydroxypropyl acrylate and hydroxybutyl acrylate.
30 Typically, the amount of hydroxyalkyl (meth)acrylate monomers (if used) which is present in the polymeric phase depends on the monomer chosen, but the typical range is from 0 to 15% by weight, preferably from 0 to 10% by weight, most

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preferably from 1 to 10% by weight, based on the total weight of the monomers.

(Meth)acrylamide monomers which can be used here include the amides of α,β -olefinically unsaturated
5 carboxylic acids, such as, for example, acrylamide, methacrylamide and diacetoneacrylamide. The preferred (meth)acrylamide monomers is acrylamide. Typically, the amount of (meth)acrylamide monomers (if used) which is present in the polymeric phase depends on the monomer
10 chosen, but the typical range is from 0 to 10% by weight, preferably from 0 to 5% by weight, most preferably from 0 to 2% by weight, based on the total weight of the monomers.

In one embodiment, the polymer latex composition of the present invention comprises styrene, butadiene and
15 acrylic acid.

In another embodiment, the polymer latex composition of the present invention comprises styrene, butadiene, acrylonitrile and acrylic acid.

In general, the polymer latex composition of the
20 present invention can be prepared by polymerization processes which are known in the technical area, and in particular by the known latex emulsion polymerization processes, including a latex polymerization carried out with or without seeds (seed latex). Representative processes
25 include those which are described in U.S. Patent Nos. 4,478,974; 4,751,111; 4,968,740; 3,563,946; and 3,575,913 and German Offenlegungsschrift (DE-A) 19 05 256. Such processes can, if required, be adapted for the polymerization of the monomers described above. The method
30 for introducing the monomers and other ingredients, such as polymerization assistants, is not particularly critical. The polymerization is then carried out under conventional

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conditions until the desired degree of polymerization has been reached. Crosslinking agents and the well known assistants for latex polymerization, such as initiators, surfactants and emulsifiers, can be used depending on
5 requirements.

The invention relates to a process for the preparation of a polymer latex having a glass transition temperature of from -30° to 70°C , which comprises co-polymerizing, in the presence of a sulfur- and halogen-
10 free chain transfer agent, the above-mentioned monomers, at temperatures of from 0 to 130°C , preferably from 60 to 130°C , particularly preferably from 60 to 100°C , very particularly preferably from 75 to 100°C , in the further presence of one or more emulsifiers and one or more
15 initiators, such as, for example, sodium persulfate or ammonium persulfate.

Initiators which can be used when carrying out the present invention include water-soluble and/or oil-soluble initiators which are effective for the purposes of the
20 polymerization. Representative initiators are well known in the technical area and include, for example: azo compounds (such as, for example, AIBN) and persulfates (such as, for example, potassium persulfate, sodium persulfate and ammonium persulfate).

25 The initiator is used in a sufficient amount to initiate the polymerization reaction at a desired rate. In general, an amount of initiator of from 0.05 to 5, preferably from 0.1 to 4, % by weight, based on the weight of the total polymer, is sufficient. The amount of
30 initiator is most preferably from 0.1 to 3% by weight, based on the total weight of the polymer.

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Surfactants or emulsifiers which are suitable here for stabilizing the latex particles include those conventional surface-active agents which are known as being typical in the technical area for polymerization processes.

5 The surfactant or surfactants can be added to the aqueous phase and/or the monomer phase. An effective amount of surfactant in a seed process is the amount which was chosen for supporting the stabilization of the particle as a colloid, the minimization of contact between the particles

10 and the prevention of coagulation. In a non-seed process, an effective amount of surfactant is the amount which was chosen for influencing the particle size.

Representative surfactants include saturated and ethylenically unsaturated sulfonic acids or salts thereof,

15 including, for example, hydrocarbonsulfonic acid, such as vinylsulfonic acid, allylsulfonic acid and methallylsulfonic acid, and salts thereof; aromatic hydrocarbon acids, such as, for example, p-styrenesulfonic acid, isopropenylbenzenesulfonic acid and vinyloxybenzenesulfonic

20 acid and salts thereof; sulfoalkyl esters of acrylic acid and methacrylic acid, such as, for example, sulfoethyl methacrylate and sulfopropyl methacrylate and salts thereof, and 2-acrylamido-methylpropanesulfonic acid and salts thereof; alkylated diphenyl oxide disulfonates, sodium

25 dodecylbenzenesulfonates and dihexyl esters of sodium sulfosuccinate, ethoxylated alkylphenols and ethoxylated alcohols; fatty alcohol (poly)ethersulfates.

The type and the concentration of the surfactant depend typically on the content of polymer solids. A higher

30 content of polymer solids generally increases the necessity for surfactant. Typically, the surfactant is used in amounts of from 0.05 to 20, preferably from 0.05 to 10, more

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preferably from 0.05 to 5, parts by weight, based on the total weight of monomers.

Various protective colloids can also be used instead of or in addition to the surfactants described above. Suitable colloids include partially acetylated polyvinyl alcohol, casein, hydroxyethyl starch, carboxymethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose and gum arabic. The preferred protective colloids are carboxymethylcellulose, hydroxyethylcellulose and hydroxypropylcellulose. In general, these protective colloids are used in contents of from 0 to 10, preferably from 0 to 5, more preferably from 0 to 2, parts by weight, based on the total weight of the monomers.

Polymer particles in the polymer latex thus prepared have a glass transition temperature of -30°C to $+70^{\circ}\text{C}$, preferably 0 to $+40^{\circ}\text{C}$, a particle size typically in the range of 20 to 1,000 nm, preferably 100 to 300 nm, and a gel content insoluble in toluene typically in the range of 65 to 99% by weight.

Various other additives and ingredients which are known to a person skilled in the art can be added in order to use the latex composition of the present invention in coating paper or cardboard. Such additives include, for example: antifoams, wetting agents, thickeners, plasticizers, fillers, pigments, crosslinking agents, antioxidants and metal chelating agents. Known antifoams include silicone oils and acetylene glycols. Customary known wetting agents include alkylphenol ethoxylates, alkali metal dialkylsulfosuccinates, acetylene glycols and alkali metal alkylsulfate. Typical thickeners include polyacrylates, polyacrylamides, xanthan gums, modified

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celluloses or particulate thickeners, such as silicas. Typical plasticizers include mineral oil, liquid polybutenes, liquid polyacrylates and lanolin. Zinc oxide, titanium dioxide, aluminum hydroxide, calcium carbonate and
5 clay are the filler typically used.

The polymer latex of the present invention is to be used for coating paper or cardboard. Typically, fillers such as clay and calcium carbonate are mixed with the polymer latex produced by the process described above, to
10 obtain coating slip formulations. Such coating slip formulations typically have a solids content of 60-70% by weight and are applied to the paper or cardboard at a coat weight of 5-20 g/m².

The coating step involves applying the slip
15 formulations to a surface of the paper or cardboard and drying the applied formulation.

The following examples serve for illustrating the invention.

Measuring methods used

Glass transition temperature:

The glass transition temperature is determined with the aid of a differential scanning calorimeter of the "Perkin-Elmer* DSC 7" type. For this purpose, the polymer latex is dried in a Teflon* mold at room temperature for three days and then for a further 20 hours at 65°C. The measurements are carried out in a temperature range from -60°C to 100°C at a heating rate of 20 K/min. The glass transition temperature is specified as the point of inflection of the DSC curve.

Gel content:

10 The insoluble fraction of a polymer in a specific solvent is determined with the aid of the gel content. In the present case, the measurement of the gel content serves for determining the crosslinking of the polymer latex. The solvent used here is toluene. The swelling is effected using films which are produced as described above. The gel insoluble in toluene is separated off by filtration, dried and weighed. The gel content is defined as the quotient of the weight of
15 the dried gel and the weight of the original latex film (before swelling with toluene) and is stated in percent.

Gel permeation chromatography (GPC):

With the aid of GPC, it is possible to determine the molar mass of polymers. For this purpose,
20 it is necessary for the polymers to dissolve completely in the solvent used. In the present case, tetrahydrofuran is used as the solvent. The flow rate is 1 ml/min. Polystyrene standards are used for calibrating the columns.

Preparation of coating slip formulations for coating paper and cardboard:

25 11 parts by weight of each of the latices are used in a formulation of 30 parts by weight of clay and 70 parts by weight of calcium carbonate. The pH of the formulation is 8.5 and the solids content is 65%. Each formulation is applied to a wood-free base paper having a weight of 67 g/m² in a coat weight of 12 g/m².

*Trade-mark

Paper gloss:

The paper gloss is determined using a gloss measuring instrument of the type "LGDL-03 Labor^{*}" from Lehmann. The measuring head has a 75° geometry (Tappi standard). The paper to be measured rests flat on a smooth surface. Three sheets are chosen for each test, five individual measurements being carried out on each sheet. The stated value for the paper gloss is the mean value of the individual measurements.

Print gloss:

The coated paper is printed on a multipurpose proof press from Prüfbau with the ink "Reflecta-schwarz^{*} 49 N 8000" from Huber. The impression pressure of the rollers is 500 N and the printing speed is 0.5 m/s. The measurement of the gloss on the printed paper is carried out analogously to the paper gloss measurement described above.

Dry pick resistance:

The dry pick resistance is determined using a multipurpose proof press from Prüfbau. At least three test strips are printed for each test with the ink 408004 from Huber at a speed of 2 m/s (increasing). The stated measured value for the dry pick resistance is the mean value of the individual measurements.

Offset test:

The offset test is performed using a multipurpose proof press from Prüfbau. For each test, a test strip is printed with the ink 520068 from Huber at a speed of 0.5 m/s. The same strip is printed again after 10 s with the same roller. The process is repeated until the paper has picks. The number of printing processes until the occurrence of picks gives the measured value for the offset test.

Printing ink setting:

The speed of the printing ink setting is determined using a multipurpose proof press from Prüfbau. For each test, a test strip is printed with the ink 520068 from Huber at a speed of 0.5 m/s. The strip is covered with a counterstrip immediately after the printing process and is passed through the printing unit after 15 s over a distance of 5 cm. After further time intervals

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(e.g. 30 s, 60 s, 180 s), the print medium is conveyed a further 5 cm in each case. In this way, ink is transferred from the printed strip to the counterstrip. The ink density is evaluated using a densitometer of the type "RD 918" from Macbeth. The ink density on the counterstrip as a function of the time interval is a measure of the speed of the printing ink setting.

5

Preparation of the model latices:

For investigating the regulator efficiency of the peroxides described, model latices are synthesized (based on styrene and acrylic acid). These are prepared by emulsion polymerization of a monomer composition comprising 96% by weight of styrene and 4% by weight of acrylic acid in the presence of 1% by weight of emulsifier (sodium dodecylbenzenesulfonate) and varying amounts and types of peroxide chain transfer agents. This polymerization is carried out as a seeded free radical emulsion polymerization with a particle size of from 150 to 160 nanometers (nm) at a temperature of from 75°C to 95°C. The molar mass of the polymers can be investigated with the aid of gel permeation chromatography (GPC).

Preparation of the latices:

The polymer latices described are prepared by emulsion polymerization of a monomer composition comprising 56% by weight of styrene, 40% by weight of butadiene and 4% by weight of acrylic acid in the presence of 0.6% by weight of emulsifier (sodium dodecylbenzenesulfonate) and varying amounts and types of peroxide chain transfer agents. This polymerization is carried out as a seeded free radical emulsion polymerization with a particle size of 150 to 160 nanometers at a temperature of from 75°C to 95°C.

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Examples

Table 1: Properties of the model latices

Latex	Regulator type	Amount of regulator (pph)	Particle size (nm)	M_n (g/mol)	M_w (g/mol)	M_w / M_n
M1	---	---	155	112400	689600	6.14
M2	tert-Butyl hydroperoxide	1.0	155	46500	194400	4.18
M3	Cumyl hydroperoxide	1.0	155	30700	88300	2.88

- 5 In the present example, the peroxides used prove to be efficient as regulators at the lower molar mass and at the lower polydispersity of the latices M2 and M3 in comparison with latex M1.

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Table 2: Latex properties

Latex	Regulator type	Amount of regulator (pph)	Polym. temp. (°C)	Particle size (nm)	Glass transition temp. (°C)	Gel content (%)
Ref.*	t-DDM	1.1	85	165	18	74
1	---	---	85	155	14	98
2	t-Butyl hydroperoxide	0.5	75	155	14	88
3	t-Butyl hydroperoxide	0.5	80	155	14	90
4	t-Butyl hydroperoxide	1.0	75	155	14	79
5	t-Butyl hydroperoxide	1.0	80	150	14	83
6	Cumyl hydroperoxide	1.0	85	160	14	93
7	Cumyl hydroperoxide	1.5	85	155	14	83
8	Cumyl hydroperoxide	2.0	85	160	14	72
9	Di-tert-butyl peroxide	1.0	95	160	14	98
10	t-Butyl peroxybenzoate	1.0	85	160	14	96
11	t-Butyl peroxy-3,5,5- trimethylhexanoate	1.0	85	155	14	96

*) Standard XSBR latex with wide application range

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Table 3: Properties of the coated paper

Latex	Paper gloss (%)	Print gloss (%)	Pick resistance (cm/s)	Offset test (number of printing processes)	Printing ink setting (color density of counterstrip after 15 s)
Ref.*	67	73	84	6	0.74
1	67	60	40	2	0.40
2	63	69	93	4	0.56
3	64	69	80	4	0.57
4	67	71	97	3	0.61
5	66	72	88	4	0.66
6	65	71	69	3	0.59
7	65	75	72	4	0.65
8	66	78	85	5	0.78
9	66	60	51	3	0.39

*) Standard XSBR latex with wide application range

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CLAIMS:

1. A polymer latex for use in coating paper or cardboard, the polymer latex having a glass transition temperature of from -30°C to 70°C , being prepared by using a
 5 sulfur- and halogen-free chain transfer agent, and comprising, in polymerized form:

(A) from 10% by weight to 80% by weight of one or more monovinyl aromatic monomers;

(B) from 20% by weight to 70% by weight of one or more
 10 conjugated diene monomers;

(C) from 0% by weight to 70% by weight of one or more acrylate monomers; and

(D) if present, the remainder being one or more other copolymerizable comonomers,

15 wherein the chain transfer agent is a peroxide selected from the group consisting of:

1. a hydroperoxide of the general formula (I):



wherein R is H, linear or branched $\text{C}_1\text{-C}_{16}$ alkyl, linear or
 20 branched $\text{C}_1\text{-C}_{16}$ alkyl- $\text{C}_6\text{-C}_{18}$ aryl or $\text{C}_6\text{-C}_{18}$ aryl;

2. a peroxide of the general formula (II):

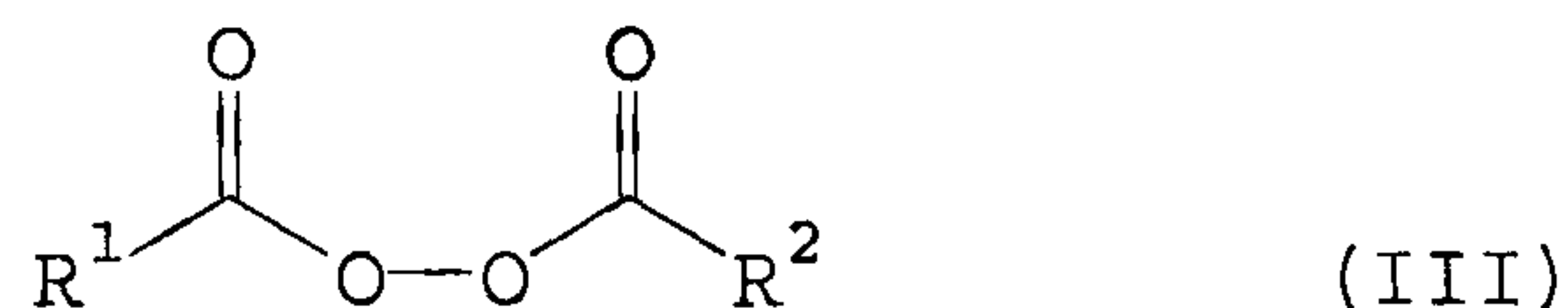


wherein R^1 and R^2 are identical or different and are each linear or branched $\text{C}_1\text{-C}_{16}$ alkyl, linear or branched $\text{C}_1\text{-C}_{16}$
 25 alkyl- $\text{C}_6\text{-C}_{18}$ aryl or $\text{C}_6\text{-C}_{18}$ aryl;

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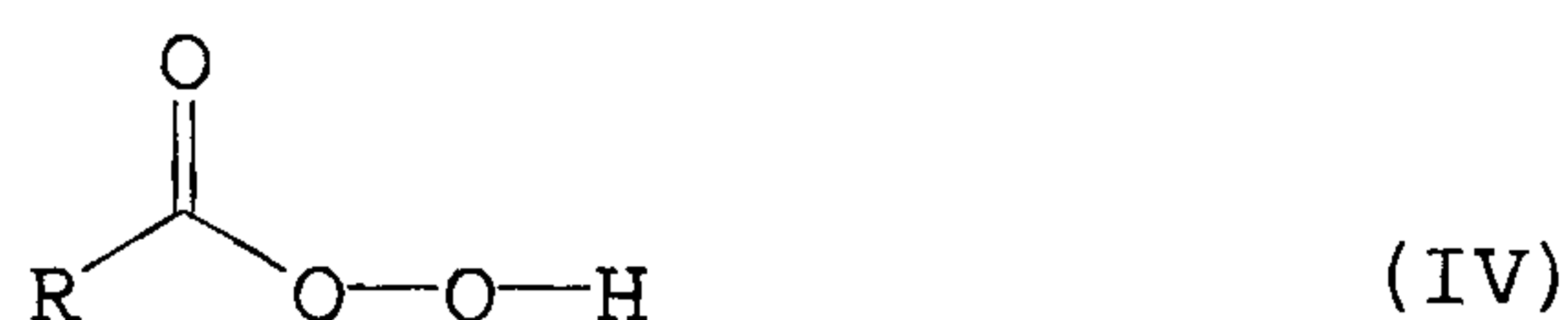
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3. a peroxide of the general formula (III):



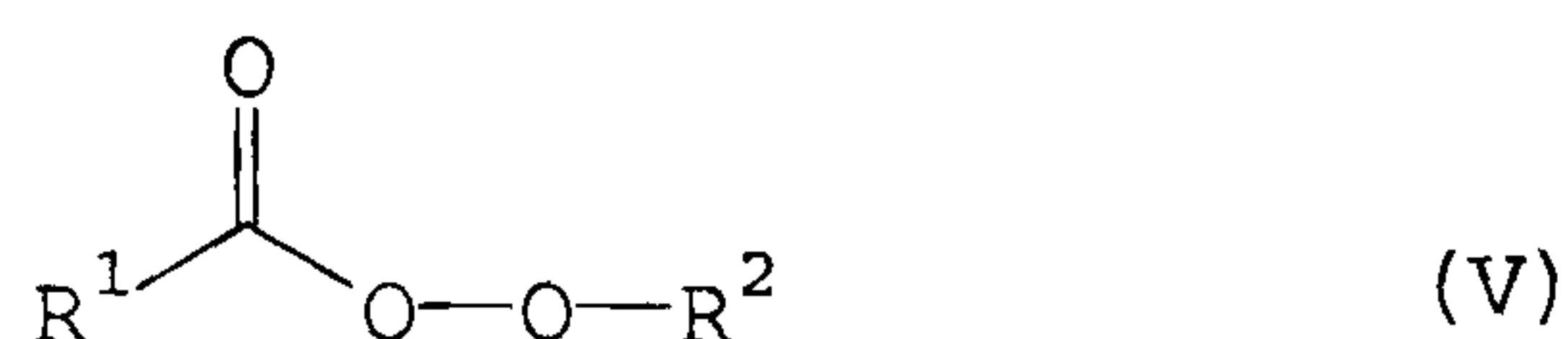
wherein R^1 and R^2 are as defined above;

5 4. a peroxocarboxylic acid of the general structural formula (IV):



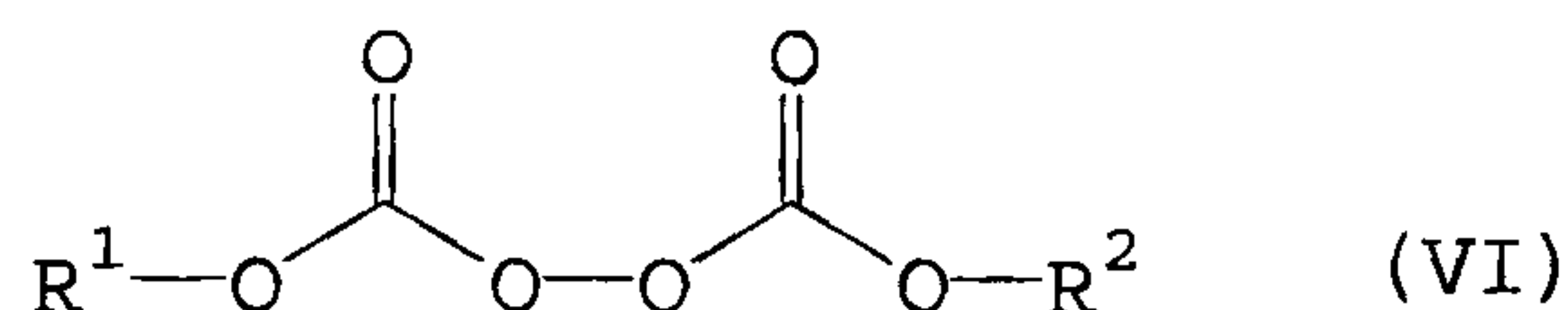
wherein R is as defined above;

10 5. a peroxocarboxylic ester of the general formula (V):



wherein R^1 and R^2 are as defined above; and

15 6. a peroxodicarbonate of the general formula (VI):



wherein R^1 and R^2 are as defined above.

2. The polymer latex as claimed in claim 1, wherein the
20 peroxide is a hydroperoxide of the general formula $\text{R}-\text{O}-\text{O}-\text{H}$ (I).

3. The polymer latex as claimed in claim 2, wherein the peroxide is tert-butyl hydroperoxide or cumyl hydroperoxide.

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4. The polymer latex as claimed in claim 1, wherein the peroxide is di-tert-butyl peroxide, tert-butyl peroxybenzoate or tert-butyl peroxy-3,5,5-trimethylhexanoate.

5. The polymer latex as claimed in any one of claims 1 to 4, which contains, as the component (A), styrene; as the component (B), butadiene; and as the component (D), an ethylenically unsaturated carboxylic acid.

6. The polymer latex as claimed in any one of claims 1 to 4, which, in polymerized form, comprises: styrene, butadiene and acrylic acid.

7. The polymer latex as claimed in any one of claims 1 to 6, which further contains, as the component (D), a nitrile monomer in an amount of from 1 to 20% by weight.

8. The polymer latex as claimed in claim 7, wherein the nitrile monomer is acrylonitrile.

9. The polymer latex as claimed in claim 8, which, in polymerized form, comprises: styrene, butadiene, acrylonitrile and acrylic acid.

10. Use of the polymer latex as claimed in any one of claims 1 to 9, in a composition for coating paper or cardboard.

11. A process for preparing a polymer latex having a glass transition temperature of from -30°C to 70°C and comprising, in polymerized form:

(A) from 10% by weight to 80% by weight of one or more monovinyl aromatic monomers;

(B) from 20% by weight to 70% by weight of one or more conjugated diene monomers;

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(C) from 0% by weight to 70% by weight of one or more acrylate monomers; and

(D) if present, the remainder being one or more other copolymerizable comonomers,

5 which comprises polymerizing the monomers using a sulfur- and halogen-free chain transfer agent, wherein the chain transfer agent is a peroxide selected from the group consisting of:

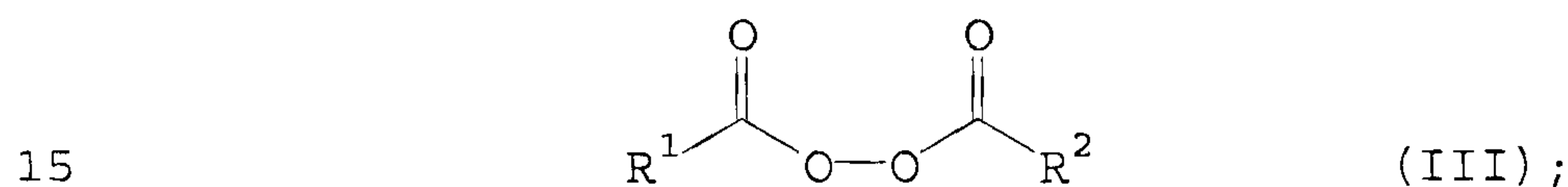
1. a hydroperoxide of the general formula (I):



2. a peroxide of the general formula (II):



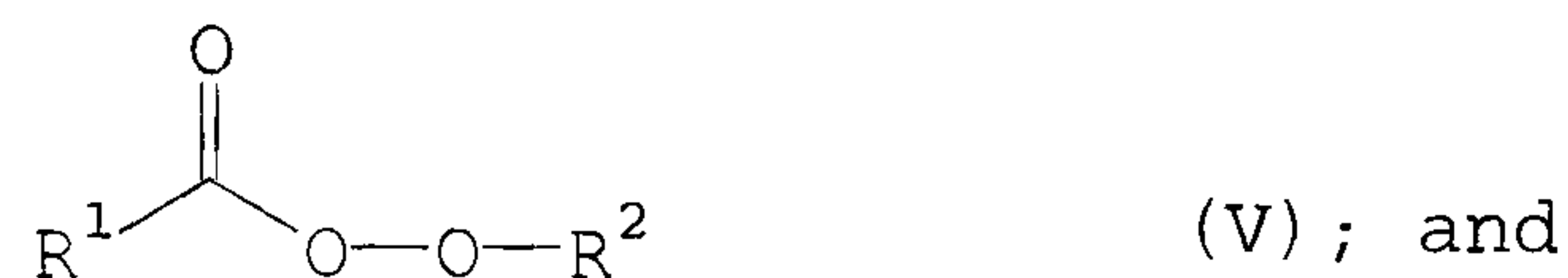
3. a peroxide of the general formula (III):



4. a peroxocarboxylic acid of the general formula (IV):



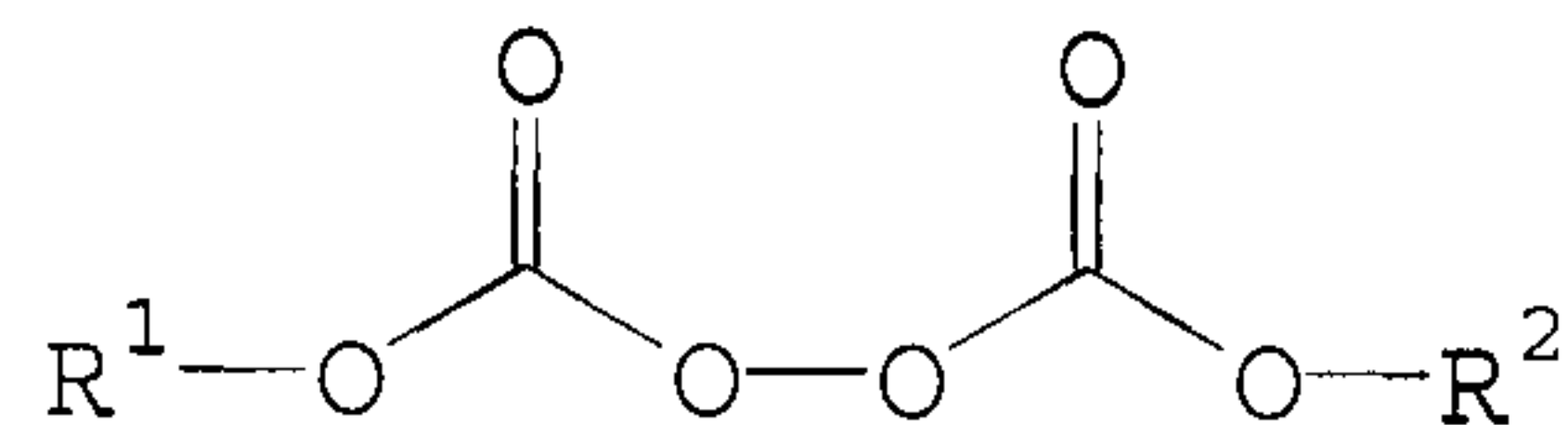
20 5. a peroxocarboxylic ester of the general structural formula (V):



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6. a peroxodicarbonate of the general formula
(VI) :



(VI)

5 wherein R, R¹ and R² are as defined in claim 1.

12. The process as claimed in claim 11, wherein the polymerization is conducted at a temperature of 0 to 130°C, in the presence of one or more emulsifiers and one or more initiators.

10 13. The process as claimed in claim 12, wherein the temperature is 60 to 130°C.

14. The process as claimed in claim 13, wherein the temperature is 60 to 100°C.

15 15. The process as claimed in claim 14, wherein the temperature is 75 to 100°C.

16. Use of the hydroperoxide of the general formula (I) as defined in claim 1, as a chain transfer agent for the preparation of a polymer latex according to any one of claims 1 to 9.