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Binder polymer obtainable by copolymerizing a monomer mixture comprising a vinyl monomer and a butenolide monomer

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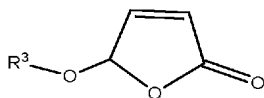
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(54) Title: BINDER POLYMER OBTAINABLE BY COPOLYMERIZING A MONOMER MIXTURE COMPRISING A VINYL MONOMER AND A BUTENOLIDE MONOMER



(57) Abstract: The invention relates to a binder polymer obtainable by copolymerizing a monomer mixture comprising a vinyl monomer M1 and a butenolide monomer M2, wherein the vinyl monomer M1 is a vinyl ether of general formula $R^1-O-CH=CH_2$, a vinyl ester of general formula $R^2-C(O)-CH=CH_2$, or a combination thereof, wherein each of R^1 and R^2 is, independently, an organic radical containing in the range of from 4 to 18 carbon atoms, and wherein the butenolide monomer M2 is a 5-alkoxy-2(5H)-furanone of general formula (III) wherein R^3 is an alkyl radical containing in the range of from 1 to 12 carbon atoms. The invention further relates to a coating composition comprising such binder polymer and to a substrate coated with a coating deposited from such coating composition.



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BINDER POLYMER OBTAINABLE BY COPOLYMERIZING A MONOMER
MIXTURE COMPRISING A VINYL MONOMER AND A BUTENOLIDE
MONOMER

5 Field of the Invention

The present invention relates to binder polymer obtainable by copolymerizing a monomer mixture comprising a vinyl monomer and a butenolide monomer, to a coating composition comprising such binder polymer, and to a substrate coated with a coating deposited from such coating composition.

10

Background of the Invention

Polyacrylates or other addition polymers are widely used as film-forming polymers in paints and coatings. Film-forming polymers are also referred to as binder polymers since such polymers have the role to bind any particulate material such as color pigments and extender pigments together.

15

Polyacrylates or other addition polymers are typically prepared by radical polymerization of monomers with an ethylenically unsaturated group, such as an acrylic, methacrylic, or vinyl group. Examples of such monomers include acrylic acid, methacrylic acid, alkyl esters of (meth)acrylic acid, styrene, alkyl-substituted styrene, vinyl esters, and vinyl ethers. The monomers are usually prepared from petrochemical raw materials.

20

There is an increasing demand for chemical products prepared from renewable feedstock. Binder polymers at least partly prepared from renewable feedstock are known in the art. Alkyd resins for example comprise a relatively high content of fatty acids obtained from vegetable oil.

25

In WO 2009/080599 is disclosed a process for preparing polymerizable ethylenically unsaturated macromonomers from vegetable oil that can be used to prepare an addition polymer for use in coating compositions.

30

Butenolides are ethylenically unsaturated furanoic compounds that can be prepared from carbohydrates, i.e. a renewable feedstock. Carbohydrate feedstock such as starch, cellulose or carbohydrate-containing bio-waste can be converted into furfural, hydroxymethylfurfural, or related furan derivatives by dehydration and then oxidized into lactones or other butenolides. Preparation of butenolides is for example described in Chapter II of J.C. de Jong, Asymmetric Diels-Alder reactions with 5-menthyloxy-2(5H)-furanones, Thesis University of Groningen, 2006, accessible via [https://www.rug.nl/research/portal/en/publications/asymmetric-dielsalder-reactions-with-5menthyloxy25hfuranones\(f0ab6c00-8c6c-4ccc-90aa-3ef05f759fa4\).html](https://www.rug.nl/research/portal/en/publications/asymmetric-dielsalder-reactions-with-5menthyloxy25hfuranones(f0ab6c00-8c6c-4ccc-90aa-3ef05f759fa4).html).

Poskonin et al. have disclosed in *Russian Journal of Organic Chemistry* 35 (1999) 721-726 copolymers prepared by radical polymerization of 4-alkoxy-2-butenolide (5-alkoxy-2(5H)-furanone) and styrene, methyl methacrylate, or vinyl acetate. Use of such copolymers for synthesis of physiologically active substances is suggested.

There is a need for binder polymers that can be obtained from renewable feedstock.

Summary of the Invention

It has now been found that if 5-alkoxy-2(5H)-furanones are copolymerized with specific vinyl monomers, copolymers can be prepared that can suitably be used as binder polymer in coating compositions.

Accordingly, the invention provides in a first aspect a binder polymer obtainable by copolymerizing a monomer mixture comprising a vinyl monomer M1 and a butenolide monomer M2, wherein the vinyl monomer M1 is a vinyl ether of general formula (I)



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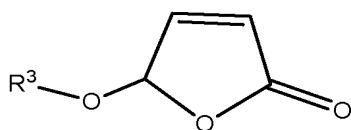
a vinyl ester of general formula (II)



or a combination thereof,

wherein each of R^1 and R^2 is, independently, an organic radical containing in the
5 range of from 4 to 18 carbon atoms,

and wherein the butenolide monomer M2 is a 5-alkoxy-2(5H)-furanone of
general formula (III)



(III),

10 wherein R^3 is an alkyl radical containing in the range of from 1 to 12 carbon
atoms.

The binder polymer has been found to provide a tack-free coating film with good
hardness properties if applied to a substrate and allowed to dry.

15

The binder polymer has a polymer backbone with acetal functionality, which
advantageously provides possibilities for crosslinking.

20 Accordingly, the invention provides in a second aspect a coating composition
comprising a binder polymer according to the first aspect of the invention.

In a final aspect, the invention provides a substrate coated with a coating
deposited from a coating composition according to the second aspect of the
invention.

25

Detailed Description of the Invention

The binder polymer according to the invention is obtainable by copolymerizing a
monomer mixture comprising a vinyl monomer M1 and a butenolide monomer
M2.

Vinyl monomer M1 is a vinyl ether of general formula (I) or a vinyl ester of general formula (II) or a combination thereof. General formula (I) is



5 and general formula (II) is



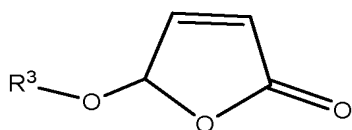
wherein each of R¹ and R² is, independently, an organic radical containing in the range of from 4 to 18 carbon atoms, preferably in the range of from 4 to 12 carbon atoms. Each of R¹ and R² may be an aromatic or aliphatic organic radical and may be branched or unbranched. Preferably, each of R¹ and R² is a hydrocarbon radical, optionally substituted with an OH group, more preferably a branched or unbranched aliphatic hydrocarbon radical, optionally substituted with an OH group. Preferably, vinyl monomer M1 is vinyl neodecanoate, vinyl neononanoate, vinyl decanoate, n-butyl vinyl ether, iso-butyl vinyl ether, 10 cyclohexyl vinyl ether, phenyl vinyl ether, 2-ethylhexyl vinyl ether, n-dodecyl vinyl ether, octadecyl vinyl ether, 4-hydroxybutyl vinyl ether, or a mixture of two or more thereof.

In one embodiment, vinyl monomer M1 is vinyl neodecanoate or a mixture of 20 vinyl neodecanoate and vinyl neononanoate.

In another embodiment, vinyl monomer M1 is a vinyl ether, preferably n-butyl vinyl ether, iso-butyl vinyl ether, cyclohexyl vinyl ether, phenyl vinyl ether, 2-ethylhexyl vinyl ether, n-dodecyl vinyl ether, 4-hydroxybutyl vinyl ether, or a mixture of two or more thereof. It has been found that vinyl monomer M1 of 25 general formula (I), i.e. vinyl ethers, copolymerize at a higher reaction rate with butenolide monomer M2 compared to vinyl monomer M1 of general formula (II), i.e. vinyl esters.

30 Butenolide monomer M2 is a 5-alkoxy-2(5H)-furanone of general formula (III)

5



(III),

wherein R³ is an alkyl radical containing in the range of from 1 to 12 carbon atoms. The alkyl radical may be branched, unbranched, linear, or cyclic.

- 5 Examples of suitable alkyl radicals are methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, sec-butyl, isobutyl, hexyl, menthyl (2-isopropyl-5-methylcyclohexan-1-yl). Preferably, the alkyl radical has in the range of from 1 to 6 carbon atoms, more preferably of from 1 to 4 carbon atoms. A particularly preferred monomer M2 is 5-methoxyfuran-2(5H)-one (R³ is CH₃).

10

The monomer mixture may have any suitable molar ratio of vinyl monomer M1 to butenolide monomer M2. Preferably, the molar ratio of vinyl monomer M1 to butenolide monomer M2 is in the range of from 1:10 to 10:1, more preferably of from 1:5 to 5:1, even more preferably of from 1:3 to 3:1, still more preferably of
15 from 1:2 to 2:1, or even of from 1:1.5 to 1.5:1 .

The monomer mixture may comprise further ethylenically unsaturated monomers other than vinyl monomers M1 and butenolide monomers M2 that can be copolymerized by radical polymerization. Examples of such further
20 monomers are acrylic acid, methacrylic acid, alkyl esters of (meth)acrylic acid, styrene, methylene malonates, itaconic acid, vinyl acetate, divinyl ethers such as ethyleneglycol divinyl ether, diethyleneglycol divinyl ether, triethyleneglycol divinyl ether, 1,4-butanediol divinyl ether, and trivinyl ethers such as trimethylolpropane trivinyl ether. The presence of divinyl ethers in the monomer
25 mixture provides a binder polymer with crosslinking functional groups.

Preferably, the monomer mixture comprises less than 50 mole% of further ethylenically unsaturated monomers, more preferably less than 30 mole%, even more preferably less than 20 mole %, or even less than 10 mole%. In one

embodiment, the monomer mixture comprises in the range of from 1 to 50 mole% of further ethylenically unsaturated monomers, preferably of from 2 to 30 mole%, more preferably of from 5 to 20 mole%.

- 5 In another embodiment, the monomer mixture is free of further ethylenically unsaturated monomers.

The copolymerizing is a radical polymerization process. Conditions that allow the monomers to copolymerize into an addition polymer by radical
10 polymerization are well-known in the art. Suitable conditions typically include the presence of an initiator.

The co-polymerization may be carried out in an organic solvent (solvent polymerization). In solvent polymerization, the monomer mixture is dissolved in
15 a suitable organic solvent, heated to the desired reaction temperature and a suitable initiator is added in a suitable amount. Typically, the temperature during solvent polymerization is in the range of from 50 °C to 180 °C, preferably of from 70 °C to 160 °C. It will be appreciated that the optimum polymerization temperature will depend on the decomposition temperature of the initiator used
20 and the boiling temperature of the any monomers at the pressure at which the polymerization is carried out. The monomer mixture may be dissolved in any suitable solvent during the copolymerization. Suitable organic solvents are solvents in which all monomers in the monomer mixture and the resulting copolymer dissolve at polymerization conditions. Preferably, the organic solvent
25 is an oxygenated organic solvent such as for example an alcohol, glycol ether, glycol ester, alkyl acetate, ketone, ester, or glycol ether/ester. More preferably, the solvent is a glycol ether or an alkyl acetate. 1-Methoxy-2-propanol and butyl acetate are particularly preferred solvents.

- 30 Alternatively, the copolymerization may be carried out as an emulsion polymerization process wherein monomers are emulsified in an aqueous phase

and then copolymerized. Emulsion polymerization is typically may be carried out at a temperature in the range of from 15 °C to 90 °C.

Any suitable initiator may be used. Suitable initiators are known in the art and include organic peroxides and azo initiators. Examples of azo initiators include azobisisobutyronitrile (AIBN) and 2,2'-azodi(2-methylbutyronitrile) (AMBN). Examples of suitable organic peroxides include tert-butyl peroxy-3,5,5-trimethylhexanoate, benzoyl peroxide, lauroyl peroxide, di-t-butyl peroxide, acetyl peroxide, t-butyl peroxy 2-ethylhexyl carbonate, t-butyl peroxy octanoate, t-amyl peroxy octanoate, and t-butyl peroxy benzoate. The initiator may be added in any suitable amount, typically up to 6 mole% based on the total moles of ethylenically unsaturated monomers, preferably in the range of from 1 to 4 mole%. The total amount of initiator may be added in two or three steps, i.e. a first amount at the start of the polymerization and a further amount during the polymerization reaction.

Optionally, a chain transfer agent is used during polymerization. Any suitable chain transfer agent may be used in a suitable amount. Suitable chain transfer agents are known in the art and include methyl mercaptopropionate, 1-dodecanethiol, 1-octanethiol, thioglycolic acid, 2-hydroxy-1-ethanethiol, and butenediol.

The copolymerization may be carried out batch-wise, i.e. by dosing all monomers and initiator at the start of the polymerization, or by gradually dosing part of the monomers and/or initiator during copolymerization, i.e. at so-called starve-fed conditions.

It has been found that the copolymer thus-obtained has properties that makes it suitable to be used as binder polymer in coating compositions. The binder polymer has a relatively high content of butenolide, a component that can be obtained from renewable feedstock. In particular, a binder polymer with a glass transition temperature in the range of from +5 °C to + 80 °C, as measured by

differential scanning calorimetry (DSC) according ISO 11357- 2 using a heating rate of 20 K/min, can be obtained. A further advantageous property of the binder polymer is that it has a polymer backbone with acetal functionality (at the butenolide monomer). Such acetal group can be used for crosslinking, for
5 example with a hydroxyl or thiol functional crosslinker or with a polymer with hydroxyl or thiol functionality.

Accordingly, the invention provides a coating composition comprising the binder polymer obtainable by copolymerizing a monomer mixture comprising a vinyl
10 monomer M1 and a butenolide monomer M2 as specified above.

The coating composition may be a solventborne or waterborne liquid coating composition, or a powder coating composition, preferably a liquid coating composition, more preferably a waterborne liquid coating composition wherein
15 the binder polymer is emulsified in an aqueous liquid phase.

The coating composition may comprise further ingredients commonly used in coating compositions such as color pigments, extender pigments, coalescing solvents, and one or more additives such as for example surfactants, defoaming
20 agents, thickeners, leveling agents, and biocides.

In a final aspect, the invention relates to a substrate coated with a coating deposited from a coating composition according to the invention. The substrate may be any suitable substrate, such as for example wood, polymer, composite,
25 metal or mineral substrate. The substrate may be a primed or bare substrate.

The invention is further illustrated by means of the following non-limiting examples.

30 Examples

The following vinyl ester and vinyl ether monomers were used:

- vinyl neodecanoate (ex. Hexion) VeoVa 10
- vinyl neononanoate (ex. Hexion) VeoVa 9
- 4-hydroxybutyl vinyl ether C4-OH vinyl ether
- n-dodecyl vinyl ether C12 vinyl ether
- 5 - vinyl acetate VAc

The following other ethylenically unsaturated monomers were used:

- butylacrylate BA
 - methylmethacrylate MMA
 - styrene STY
- 10 The following butenolide monomers were used:
- 5-methoxy-2(5H)-furanone 5-methoxy
 - 5-menthoxy-2(5H)-furanone 5-menthoxy
 - 5-methyl-5-methoxy-2(5H)-furanone 5-methyl, 5-methoxy
 - 5-hydroxy-2(5H)-furanone 5-hydroxy
 - 15 - 2(5H)-furanone
 - 5-hexyloxy-2(5H)-furanone 5-hexyloxy

The following solvents were used:

- butyl acetate BuAc
 - 1-methoxy-2-propanol (Dowanol™ PM) DowPM
- 20 The following initiators were used:
- 2,2'-azodi(2-methylbutyronitrile) AMBM
 - t-butyl peroxy-3,5,5-trimethylhexanoate T42S

EXAMPLE 1 - Binder polymers from vinyl ester or vinyl ether and butenolide

- 25 Binder polymers were prepared by charging butenolide monomer and solvent in a three-neck round-bottom flask equipped with a reflux condenser. The mixture was heated to a temperature of 125 °C and vinyl monomer and t-butyl peroxy-3,5,5-trimethylhexanoate (Trigonox 42S, ex. Nouryon) in further solvent was
- 30 dosed in two hours whilst keeping the temperature at 125 °C under reflux conditions under a nitrogen blanket. Some further initiator was then added, and the reaction continued for one hour; then still further initiator was added and the

reaction continued for another hour. The reaction mixture was cooled to room temperature. The calculated solids content (weight of monomers and initiator based on total weight of monomers, initiator, and solvent) was 43 wt%.

- 5 Different binder polymers were prepared using different monomers. Binder polymers 1 to 8 are binder polymers according to the invention; binder polymers A to D are comparison binder polymers.

The solids content of the resulting polymer solutions was determined in accordance with ISO 3251 with an initial sample mass of 1.0 g, test duration of 10 60 minutes, at a temperature of 125 °C. The monomer conversion was calculated based on the measured solids content. Remaining monomers evaporate under the test conditions, whilst any polymer formed does not evaporate.

15 Solvent was evaporated from the polymer solutions obtained in a rotary evaporator (rotavapor) under reduced pressure (50 mbar), at 80 °C. The thus-obtained samples were subjected to ¹H NMR spectroscopy. The ¹H NMR spectrum in combination with the polymer content of the polymer solution (from the solids content determination) gives a good indication of the conversion of 20 specific monomers.

For some of the binder polymers, the number average and weight average molecular weights were determined using gel permeation chromatography (GPC) with tetrahydrofuran (THF) (+ 1% acetic acid) as eluent (1 ml/min) on a styrene-25 divinylbenzene column using polystyrene standards for calibration.

In Table 1 is shown for the different binder polymers prepared, the type and molar ratio of monomers used, and the solvent and initiator used.

EXAMPLE 2 - Binder polymers from other ethylenically unsaturated monomers and butenolide (comparison)

Comparison binder polymers E and F were prepared as described in Example 1, using 5-methoxy-2(5H)-furanone as butenolide monomer and ethylenically unsaturated monomers other than vinyl monomers M1 as copolymers. Butylacetate was used as solvent and Trigonox 42S as initiator. In Table 2 is shown the type and ratio of monomers used.

In Table 3 is shown for binder polymers 1 to 8 (invention) and for binder polymers A to F (comparison): the monomer conversion; the solids content of the binder polymer solution prepared; and observations on monomer built-in from the ¹H-NMR spectra. The number average and weight average molecular weights (M_n and M_w ; both in g/mole) and the polydispersity index (PDI), i.e. M_w/M_n , is given for binder polymers 1 to 5, E and F.

Table 1 Example 1 - Preparation of binder polymers (invention and comparison)

	vinyl monomer	butenolide monomer	Molar ratio vinyl : butenolide	solvent	initiator
1	Veova 10	5-methoxy	1 : 1	DowPM	T42S
2	Veova 10	5-methoxy ^a	1 : 1	DowPM	T42S
3	Veova 10/9 (1:1)	5-methoxy	1 : 1	DowPM	T42S
4	Veova 10	5-methoxy	1.1 : 1	DowPM	T42S
5	C12 vinyl ether	5-methoxy	1 : 1	DowPM	T42S
6	C12 vinyl ether	5-methoxy	1 : 1	BuAc	T42S
7	C4-OH vinyl ether	5-methoxy	1.:1	DowPM	T42S
8	Veova 10	5-menthyloxy	1 : 1	DowPM	T42S
A ^b	VAc	5-methoxy	1.1 : 1	BuAc	AMBn
B	Veova 10	5-methyl, 5-methoxy	1 : 1	DowPM	T42S
C	C12 vinyl ether	5-methyl, 5-methoxy	1 : 1	DowPM	T42S
D	Veova 10	5-hydroxy	1 : 1	DowPM	T42S

^a monomer purified to 98% purity.

^b polymerization carried out at 80 °C.

Table 2 Example 2 - Preparation of comparison binder polymers

	non-butenolide monomers	butenolide monomer	molar ratio	solvent	initiator
E	BA/MMA	5-methoxy	BA/MMA/butenolide 9/23/13	BuAc	T42S
F	BA/STY	5-methoxy	BA/STY/ butenolide 6/23/13	BuAc	T42S

5 Table 3 Characteristics of binder polymers prepared in Examples 1 and 2

	solids content (wt%)	conversion (wt%)	M _n	M _w	PDI	built-in of monomers ^c
1	41.6	96.1	1,074	2,230	2.1	butenolide built-in
2	43.2	99.7	1,020	1,920	2.0	butenolide built-in
3	40.8	95.4				butenolide built-in
4	41.8	93.2	1,098	2,462	2.2	butenolide built-in
5	34.0	76.6	1,047	2,770	2.6	butenolide built-in
6	34.7	78.1				butenolide built-in
7	29.9	83.0				butenolide built-in
8	25.8	56.9				most butenolide built-in
A	7.9	22				unreacted vinyl and butenolide monomers visible in NMR
B	12.6	28.3				unreacted vinyl and butenolide monomers in 1:1 ratio
C	18.0	39.5				unreacted vinyl and butenolide monomers in 3:7 ratio
D	7.3	16.4				Unreacted vinyl monomer visible; butenolide monomer seems to have decomposed
E	32.9	70.6	3,412	9,346	2.7	butenolide not copolymerized
F	32.6	62.2	4,647	10,384	2.2	butenolide not copolymerized

^c Based on ¹H-NMR of polymer solution after evaporation of solvent.

EXAMPLE 3 - Preparation of coating

A 200 µm wet film of binder polymer solution no. 3 was drawn on a glass plate using a drawing bar. The wet film was allowed to dry at 23 °C and 50 % relative humidity for 7 days. A tack-free, transparent coating was obtained within 4
5 hours. Pendulum hardness (Persoz hardness) after two weeks storage at 23 °C and 50 % relative humidity was determined according to ISO 1522. The time for the amplitude of the pendulum to decrease from 12 to 4 degrees was 60 seconds.

10 This example shows that the binder polymer film forms and can form a coating that is tack-free and has acceptable hardness for many coating applications.

EXAMPLE 4 – Reaction kinetics for different monomer combinations

The reaction kinetics (polymerization rate constant and maximum conversion)
15 for different combinations of vinyl monomer and butanolide monomer were determined by means of ¹H-NMR spectroscopy as follows.

To a 4mL vial with screwcap with septum were added 2 mmol of a vinyl
monomer and 2 mmol of a butanolide monomer, 1 mL 1DowPM as solvent and
20 1 mmol 1,3,5-trimethoxybenzene as internal standard. The mixture was heated to 120 °C and 30 mg T42S was added as initiator. The mixture was refluxed for 2 to 4 hours. At intervals of 5 minutes, a sample of 50 µL was taken and flash frozen to stop polymerization. The absolute concentration of monomers was
25 determined by ¹H-NMR spectroscopy using ¹H-NMR shifts specific for each monomer. From the decrease of monomer concentration over time, the overall polymerization rate constant (in s⁻¹) and the maximum monomer conversion (%) achieved were determined. The results are given in Table 4.

Table 4 – reaction kinetics of polymerization for different monomer combinations

	monomers		overall polymerization rate constant (s ⁻¹)	maximum conversion (%)
	vinyl monomer	butanolide monomer		
G*	C12 vinyl ether	2(5H)-furanone	3.10 ⁻⁴	58
H*	Veova 10	2(5H)-furanone	8.10 ⁻⁵	37
9	C12 vinyl ether	5-methoxy	1.4.10 ⁻³	95
10	Veova 10	5-methoxy	6.10 ⁻⁴	100
11	C12 vinyl ether	5-hexyloxy	2.1.10 ⁻³	100
12	Veova 10	5-hexyloxy	4.10 ⁻⁵	90
13	C12 vinyl ether	5-menthoxy	1.1.10 ⁻³	100
14	Veova 10	5-menthoxy	3.10 ⁻⁴	90

* comparison example

- 5 In sample G, more vinyl monomer than butanolide monomer was built into the polymer.

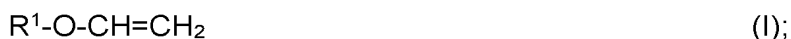
This example shows that the 5-alkoxy-2(H)-furanones polymerize with vinyl monomers of general formula (I) at a higher polymerization rate compared to
 10 2(5H)-furanone. Moreover, higher monomer conversion and better built-in of butanolide monomer is achieved.

Claims

1. A binder polymer obtainable by copolymerizing a monomer mixture comprising a vinyl monomer M1 and a butenolide monomer M2,

5 wherein the vinyl monomer M1 is:

a vinyl ether of general formula (I)



a vinyl ester of general formula (II)

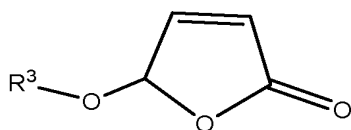


10 or a combination thereof,

wherein each of R^1 and R^2 is, independently, an organic radical containing in the range of from 4 to 18 carbon atoms,

and wherein the butenolide monomer M2 is a 5-alkoxy-2(5H)-furanone of general formula (III)

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(III),

wherein R^3 is an alkyl radical containing in the range of from 1 to 12 carbon atoms.

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2. A binder polymer according to claim 1, wherein R^3 is an alkyl radical containing in the range of from 1 to 6 carbon atoms, preferably of from 1 to 4 carbon atoms.

- 25 3. A binder polymer according to claim 2, wherein the butenolide monomer M2 is 5-methoxy-2(5H)-furanone.

4. A binder polymer according to any one of the preceding claims, wherein each of R¹ and R² is, independently, a hydrocarbon radical containing 4 to 12 carbon atoms, optionally substituted with an OH group.
- 5 5. A binder polymer according to any one of the preceding claims, wherein vinyl monomer M1 is vinyl neodecanoate or a mixture of vinyl neodecanoate and vinyl neononanoate.
6. A binder polymer according to any one of claims 1 to 4, wherein vinyl
10 monomer M1 is a vinyl ether of general formula (I).
7. A binder polymer according to claim 6, wherein vinyl monomer M1 is n-butyl vinyl ether, iso-butyl vinyl ether, cyclohexyl vinyl ether, phenyl vinyl ether, 2-ethylhexyl vinyl ether, n-dodecyl vinyl ether, 4-hydroxybutyl vinyl
15 ether, or a mixture of two or more thereof.
8. A binder polymer according to any one of the preceding claims, wherein the monomer mixture comprises vinyl monomer M1 and butenolide M2 in a molar ratio in the range of from 1:5 to 5:1, preferably of from 1:2 to 2:1.
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9. A binder polymer according to any one of the preceding claims, wherein the monomer mixture comprises in the range of from 1 to 50 mole% of further ethylenically unsaturated monomers, preferably of from 2 to 30 mole%.
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10. A binder polymer according to any one of claims 1 to 8, wherein the monomer mixture is free of further ethylenically unsaturated monomers.
11. A coating composition comprising a binder polymer according to any one
30 of the preceding claims.

12. A coating composition according to claim 11, wherein the coating composition is an aqueous liquid coating composition comprising the binder polymer emulsified in an aqueous phase.
- 5 13. A substrate coated with a coating deposited from a coating composition according to claim 11 or 12.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/080505

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08F216/14 C08F218/08 C08F218/10 C08F220/26 C09D129/10
 C09D131/02 C09D131/04 C09D133/14
 ADD. C07D307/32
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 C09J C08F C09D C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2003 335826 A (JSR CORP) 28 November 2003 (2003-11-28) paragraph [0068]	1-13
A	----- US 2009/191399 A1 (MOORE DAVID ROGER [US] ET AL) 30 July 2009 (2009-07-30) claims 1,7 paragraph [0030] -----	1-13

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>
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Date of the actual completion of the international search 6 November 2020	Date of mailing of the international search report 16/11/2020
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Rodríguez, Luis
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2003335826	A	28-11-2003	NONE

US 2009191399	A1	30-07-2009	
		CN 101492559 A	29-07-2009
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