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(54) Title: PHOSPHONIC COPOLYMER AND COSMETIC USE THEREOF

(57) Abstract: The invention relates to a copolymer derived from the polymerization of: (i) 70% to 95% by weight, of the total weight of the monomers, of tetrahydrofurfuryl (meth)acrylate; (ii) 1% to 30 % by weight of vinylphosphonic acid monomer; (iii) 0 to 20% by weight of an additional monomer. Cosmetic composition comprising the copolymer and cosmetic process for making up or caring for keratin materials, more particularly the nails, comprising the topical application of the composition to the keratin materi-

Phosphonic copolymer and cosmetic use thereof

The present invention relates to a phosphonic acid group-containing copolymer, a cosmetic composition comprising such a copolymer and the use thereof as a nail varnish.

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Documents FR2868784, EP522756, US2003/0118629 and FR2746640 describe nail varnish compositions comprising acrylic monomers containing anionic monomers such as acrylic acid or 2-acrylamido-2-methylpropanesulfonic acid.

- Nonetheless, as demonstrated in the comparative examples below, some copolymers containing acrylic acid or vinylphosphonic acid do not enable nail varnish films with good cosmetic properties to be obtained; the film is not uniform, having cracks or trapped bubbles of air, or else is white and not transparent.
- 15 There is therefore a need for polymers which allow films with improved cosmetic properties to be obtained.

The inventors have discovered that copolymers of tetrahydrofurfuryl (meth)acrylate and of phosphonic acid group-containing monomers make it possible to obtain a uniform transparent film which does not chip, unlike similar copolymers containing acrylic acid instead of the phosphonic acid monomer. The film obtained has good properties of adhesion.

More precisely, a subject of the present invention is a copolymer derived from the polymerization of:

- (i) 70% to 95% by weight, of the total weight of the monomers, of tetrahydrofurfuryl (meth)acrylate;
- (ii) 1% to 30 % by weight of vinylphosphonic acid monomer of formula (I) defined hereinafter;
- 30 (iii) 0 to 20% by weight of an additional monomer.

Such a copolymer is referred to hereinbelow as a phosphonic polymer.

A subject of the invention is also a composition comprising, in a physiologically acceptable medium, a phosphonic polymer as described previously.

A subject of the invention is also a cosmetic process for making up and/or nontherapeutically caring for the nails, comprising the application to the nails of a composition as defined previously. The phosphonic polymer according to the invention comprises a tetrahydrofurfuryl (meth)acrylate, a vinylphosphonic acid monomer of formula (I) and optionally an additional monomer as defined hereinafter.

The vinylphosphonic acid monomer corresponds to the following formula (I):

$$\begin{array}{c} H_{2}C = C - X - \left[-CH_{2} \right]_{n} - PO_{3}H_{2} \\ R1 \end{array}$$

10 in which:

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R1 denotes H or -CH₃;

X denotes a covalent bond and n denotes an integer ranging from 0 to 14; or X denotes a –COO- group and n denotes an integer ranging from 2 to 6.

Advantageously, for the monomer of formula (I), X denotes a covalent bond and n is an integer ranging from 0 to 6 or X denotes a –COO- group and n is an integer ranging from 2 to 4.

Preferably, for the monomer of formula (I):

20 R1 = H

X denotes a covalent bond and n denotes an integer ranging from 0 to 4.

As examples of monomer of formula (I), the following can be cited:

vinylphosphonic acid;

25 3-butenylphosphonic acid;

4-pentenylphosphonic acid;

10-undecenylphosphonic acid;

11-dodecenylphosphonic acid;

2-phosphonoethyl ester of 2-methyl-2-propenoic acid;

30 2-phosphonoethyl ester of 2-propenoic acid.

Preferably, monomer (I) is vinylphosphonic acid.

The additional monomer optionally present is different to the tetrahydrofurfuryl (meth)acrylate monomers and the vinylphosphonic acid monomer of formula (I).

In particular, the additional monomer may be chosen from the monomers of formula (II):

in which:

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R1 denotes a hydrogen atom or a methyl radical;

5 X denotes O or NH or NR₃;

R2 denotes a linear C_1 - C_{22} or branched C_3 - C_{10} or cyclic C_5 - C_7 alkyl radical, or a linear C_3 - C_{20} or branched C_6 - C_{20} or cyclic C_5 - C_7 unsaturated hydrocarbon-based radical or a $-(CH_2$ - CH_2 - $O)_a$ -H radical, with a ranging from 9 to 115, or an $-(Si(CH_3)_2 O)_b$ - CH_3 radical, with b ranging from 5 to 70, it being understood that X = O when R2 is a radical of formula $-(CH_2$ - CH_2 - $O)_a$ -H or $-(Si(CH_3)_2 O)_b$ - CH_3 ;

R3 denotes a linear C₁-C₁₂ or branched C₃-C₁₂ alkyl radical.

As alkyl radical, mention may be made of the methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, pentyl, isopentyl, hexyl, heptyl, octyl, isooctyl, nonyl, decyl, undecyl, lauryl, myristyl, palmityl, stearyl, eicosyl and behenyl radicals.

According to one preferred embodiment, the copolymer is free of any additional monomer.

Advantageously, the copolymer is chosen from copolymers of tetrahydrofurfuryl (meth)acrylate and of vinylphosphonic acid.

The polymer according to the invention is preferably chosen from the copolymers derived from the polymerization of:

- 70% to 95% by weight, of the total weight of the monomers, of tetrahydrofurfuryl (meth)acrylate;
- 5% to 30 % by weight of vinylphosphonic acid monomer of formula (I) as described previously.

Preferably, the polymer according to the invention is chosen from the copolymers derived from the polymerization of:

- 75% to 95% by weight, of the total weight of the monomers, of tetrahydrofurfuryl (meth)acrylate;
- 5% to 25 % by weight of vinylphosphonic acid monomer of formula (I) as described previously.

According to one preferred mode of the invention, the polymer is chosen from the copolymers derived from the polymerization of:

- 70% to 95% by weight, of the total weight of the monomers, of tetrahydrofurfuryl (meth)acrylate;
- 5% to 30% by weight of vinylphosphonic acid; and preferably of:
- 5 75% to 95% by weight, of the total weight of the monomers, of tetrahydrofurfuryl (meth)acrylate;
 - 5% to 25% by weight of vinylphosphonic acid.

As examples of copolymers according to the invention, mention may be made of tetrahydrofurfuryl methacrylate/vinyphosphonic acid copolymers, in particular (80/20) or (90/10) (weight/weight) tetrahydrofurfuryl methacrylate/vinylphosphonic acid copolymers.

The copolymer may be a random, alternating (block) or gradient polymer. Preferably, the copolymer is random.

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The copolymer according to the invention may be prepared by radical polymerization of the monomers described previously, especially as a mixture or sequentially added during the polymerization, especially using an organic solvent with a boiling point of greater than or equal to 60°C, for instance isododecane, ethanol, ethyl acetate, tetrahydrofuran, methyltetrahydrofuran or methyl ethyl ketone. The organic solvent makes it possible to dissolve the monomers used and the polymer formed.

The polymerization is especially performed in the presence of a radical initiator especially of peroxide type (for example tert-butyl peroxy-2-ethylhexanoate: Trigonox® 21S; 2,5-dimethyl-2,5-bis(2-ethylhexanoylperoxy)hexane:Trigonox® 141; tert-butyl peroxypivalate: Trigonox® 25C75 from Akzo Nobel) or of azo type (for example AIBN: azobisisobutyronitrile; V50: 2,2'-azobis(2-amidinopropane) dihydrochloride).

The polymerization may be performed at a temperature ranging from 60 to 100°C, and preferably ranging from 60 to 85°C.

30 The polymerization time may be about 24 hours.

Preferably, the phosphonic polymer according to the invention has a weight-average molecular weight ranging from 5000 to 1 000 000 daltons, more preferably ranging from 10 000 to 500 000 daltons, and even more preferably ranging from 15 000 to 350 000 daltons.

The phosphonic polymer as defined previously may be present in the composition in a content ranging from 0.1% to 60% by weight and preferably ranging from 0.1% to 40% by weight, relative to the total weight of the composition.

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The composition according to the invention may also comprise an additional film-forming polymer, commonly referred to as resin, such as sulfonamide resins, alkyd resins,

nitrocellulose, cellulose esters such as cellulose acetobutyrate, cellulose acetate, cellulose acetopropionate.

The additional film-forming polymer may be present in a content ranging from 0.01% to 50% by weight and preferably ranging from 1% to 30% by weight, relative to the total weight of the composition.

The composition according to the invention may comprise an auxiliary film-forming agent to improve the film-forming properties of the composition.

The auxiliary film-forming agent may be chosen from any compound known to those skilled in the art as being capable of performing the desired function, and may be chosen especially from plasticizers.

As examples of plasticizer, the following can be cited:

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citrates such as triethyl citrate, tributyl citrate, triethyl acetylcitrate, tributyl acetylcitrate, 2triethylhexyl acetylcitrate,

phthalates such as diethyl phthalate, dibutyl phthalate, dioctyl phthalate, dipentyl phthalate, dimethoxyethyl phthalate,

tricresyl phosphate, benzyl benzoate, tributyl phosphate, butyl acetyl ricinoleate, glyceryl acetyl ricinoleate, butyl glycolate, tributoxyethyl phosphate, triphenyl phosphate, dibutyl tartrate, camphor, glyceryl triacetate, N-ethyl-o,p-toluenesulfonamide, and mixtures thereof.

The plasticizer may be present in the composition in a content ranging from 0.01% to 10% by weight and preferably ranging from 0.1% to 5% by weight, relative to the total weight of the composition. Advantageously, the plasticizer is present in the composition in a weight ratio of film-forming polymer/plasticizer ranging from 1.5 to 3.

The composition according to the invention may comprise an organic solvent medium.

The composition may especially be anyhdrous.

The organic solvent medium of the composition may comprise one or more organic solvents chosen from:

- ketones that are liquid at room temperature (25°C), such as methyl ethyl ketone, methyl isobutyl ketone, diisobutyl ketone, isophorone, cyclohexanone or acetone;
- alcohols that are liquid at room temperature, such as ethanol, isopropanol, n-propanol, n-butanol, diacetone alcohol, 2-butoxyethanol or cyclohexanol;
- glycols that are liquid at room temperature, such as ethylene glycol, propylene glycol, pentylene glycol or glycerol;
- propylene glycol ethers that are liquid at room temperature, such as propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate or dipropylene glycol nbutyl monoether;

- short-chain esters (having from 3 to 8 carbon atoms in total), such as ethyl acetate, methyl acetate, propyl acetate, n-butyl acetate or isopentyl acetate;
- ethers that are liquid at room temperature, such as diethyl ether, dimethyl ether or dichlorodiethyl ether;
- 5 alkanes that are liquid at room temperature, such as decane, heptane, dodecane, isododecane or cyclohexane;
 - aromatic cyclic compounds that are liquid at room temperature, such as toluene and xylene;
 - aldehydes that are liquid at room temperature, such as benzaldehyde or acetaldehyde.
- 10 mixtures thereof.

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The organic solvent is preferably chosen from the short-chain esters described previously.

The organic solvent content in the composition may range from 10% to 95% by weight, preferably from 40% to 90% by weight and better still from 60% to 85% by weight, relative to the total weight of the composition.

The composition may comprise a thickener, especially for imparting a consistency to the composition which enables good application of the composition to the nails. The thickener is more particularly an organic solvent thickener and may be chosen from the hydrophobic silicas such as those described in document EP-A-898960, and for example sold under the references "AEROSIL R812®" by the company Degussa, "CAB-O-SIL TS-530®", "CAB-O-SIL TS-610®" and "CAB-O-SIL TS-720®" by the company Cabot, "AEROSIL R972®" and "AEROSIL R974®" by the company Degussa; clays such as montmorillonite, stearalkonium hectorite, stearalkonium bentonite; polysaccharide alkyl ethers (especially those in which the alkyl group comprises from 1 to 24 carbon atoms, preferably from 1 to 10, better still from 1 to 6 and more especially from 1 to 3) such as those dscribed in document EP-A-898958, and for example sold under the names "N-HANCE-AG 200®" and "N-HANCE AG 50®" by the company Aqualon.

The thickener may be present in the composition according to the invention in a content ranging from 0.05% to 10% by weight and preferably ranging from 0.1% to 3% by weight, relative to the total weight of the composition.

The composition according to the invention may also comprise any cosmetic adjuvant known to those skilled in the art as being able to be incorporated into such a composition, such as fillers, spreading agents, wetting agents, dispersants, antifoams, preservatives, UV-screening agents, active agents, surfactants, moisturizers, fragrances, neutralizing agents, stabilizers, antioxidants or colorants. Needless to say, a person skilled in the art will take care to select this or these optional additional compound(s), and/or the amount thereof, such that the advantageous properties of the corresponding composition

according to the invention are not, or are not substantially, adversely affected by the envisaged addition.

The composition according to the invention is preferably in the form of a nail varnish.

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The invention is illustrated in more detail in the following examples.

Example 1: (90/10 by weight) Tetrahydrofurfuryl methacrylate/vinylphosphonic acid copolymer

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180 g of tetrahydrofurfuryl methacrylate, 20 g of vinylphosphonic acid and 200 g of ethyl acetate were introduced into a reactor. The reaction medium was degassed under argon for 20 minutes. Then, 2 g of

2,5-Dimethyl-2,5-di(2-ethylhexanoylperoxy)hexane initiator (Trigonox® T141 from Akzo Nobel) were added. The reaction medium was heated at reflux of the ethyl acetate for 24 hours with stirring. After cooling to room temperature (25°C), the reaction medium was diluted with 300 g of a (50/50 by weight) mixture of butanone and methyltetrahydrofuran.

The product obtained was precipitated from cyclohexane, recovered and dried in an oven at 60°C under vacuum.

20 145 g (72.5% yield) of a white powder were obtained after drying.

Example 2: (80/20 by weight) Tetrahydrofurfuryl methacrylate/vinylphosphonic acid copolymer

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The copolymer was prepared according to the procedure from Example 1 using 160 g of tetrahydrofurfuryl methacrylate and 40 g of vinylphosphonic acid.

175 g (87.5% yield) of a white powder were obtained.

30 The acid number is 176 mg/g.

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Example 3: (80/10/10 by weight) Tetrahydrofurfuryl methacrylate/vinylphosphonic acid/methyl methacrylate copolymer

The copolymer was prepared according to the procedure from Example 1 using 160 g of tetrahydrofurfuryl methacrylate, 20 g of vinylphosphonic acid and 20 g of methyl methacrylate.

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160 g (80% yield) of a white powder were obtained.

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Example 4: (70/10/20 by weight) Tetrahydrofurfuryl methacrylate/vinylphosphonic acid/methyl methacrylate copolymer

The copolymer was prepared according to the procedure from Example 1 using 140 g of tetrahydrofurfuryl methacrylate, 20 g of vinylphosphonic acid and 40 g of methyl methacrylate.

5 155 g (85% yield) of a white powder were obtained.

Example 5 (outside the invention): (90/10 by weight) Methyl

10 methacrylate/vinylphosphonic acid copolymer

The copolymer was prepared according to the procedure from Example 1 using 180 g of methyl methacrylate and 20 g of vinylphosphonic acid.

15 170 g (85% yield) of a white powder were obtained.

Example 6 (outside the invention): (80/20 by weight) Methyl

methacrylate/vinylphosphonic acid copolymer

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The copolymer was prepared according to the procedure from Example 1 using 160 g of methyl methacrylate and 40 g of vinylphosphonic acid.

170 g (85% yield) of a white powder were obtained.

The acid number is 149 mg/g.

<u>Example 7 (outside the invention)</u>: (90/10 by weight) Cyclohexyl methacrylate/vinylphosphonic acid copolymer

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The copolymer was prepared according to the procedure from Example 1 using 180 g of cyclohexyl methacrylate and 20 g of vinylphosphonic acid.

125 g (62.5% yield) of a white powder were obtained.

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<u>Example 8 (outside the invention)</u>: (80/20 by weight) Cyclohexyl methacrylate/vinylphosphonic acid copolymer

The copolymer was prepared according to the procedure from Example 1 using 160 g of cyclohexyl methacrylate and 40 g of vinylphosphonic acid.

120 g (60% yield) of a white powder were obtained. The acid number is 138 mg/g.

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Example 9 (outside the invention): (90/10 by weight) Tetrahydrofurfuryl methacrylate/acrylic acid copolymer

The copolymer was prepared according to the procedure from Example 1 using 180 g of tetrahydrofurfuryl methacrylate and 20 g of acrylic acid.

150 g (75% yield) of a white powder were obtained.

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Example 10 (outside the invention): (80/20 by weight) Tetrahydrofurfuryl methacrylate/acrylic acid copolymer

The copolymer was prepared according to the procedure from Example 1 using 160 g of tetrahydrofurfuryl methacrylate and 40 g of acrylic acid.

105 g (82.5% yield) of a white powder were obtained.

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Example 11 (comparative):

The quality of the films obtained, with the polymers from Examples 1 to 4 according to the invention and also with the polymers from Examples 5 to 10 outside the invention, was evaluated.

Each polymer was placed in solution at 30% AM in a (50/50) mixture of ethyl acetate/ethanol.

Each polymer solution was applied using a brush to a plate sold under the name VITRO-NAILS® by the company IMS Inc. which had been filed beforehand using a nail file then cleaned with a (50/30/20 by weight) mixture of isopropanol/acetone/ethyl acetate.

The appearance of the film obtained after a drying time of 24 hours at room temperature 30 (25°C) was observed. The following results were obtained:

Example	Appearance of the film obtained
1	Transparent, uniform film
2	Transparent, uniform film
3	Transparent, uniform film
4	Transparent, uniform film
5	Rigid, brittle film containing air bubbles
6	Rigid, brittle film containing air bubbles
7	Rigid, brittle film containing air bubbles
8	Rigid, brittle film containing air bubbles
9	White, non-transparent, non-uniform (cracked) film
10	White, non-transparent, non-uniform (cracked) film

The results obtained show that the polymers according to the invention (Examples 1 to 4) make it possible to obtain a transparent and uniform film, whereas the polymers which are not part of the invention (Examples 5 to 10) form non-uniform (cracking, air bubbles), brittle or non-transparent films.

Example 12:

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40 A nail varnish having the following composition was prepared:

- polymer of Example 1	25 g
- disteardimonium hectorite/propylene carbonate in isododecane	
(bentone gel ® ISDV from Elementis)	1.5 g
- Preservatives qs	
- Ethanol	33.5 g
- Ethyl acetate	40 g

A similar composition was also prepared using the polymer of Example 2 or 3 or 4.

The composition obtained, applied to the nails, makes it possible to obtain, after drying, a transparent and uniform film which is glossy and has no cracking.

Example 13 (comparative):

The wear property of the gloss of the films obtained with the polymer of Example 1 (invention) and the polymer of Example 10 (outside the invention) was measured.

A solution at 25% AM of the polymer in a (50/50 by weight) mixture of ethyl acetate/ethanol was prepared. Each solution was poured onto a metal (steel) support to obtain, after drying for 5 days at 23±2°C and at 55±5% relative humidity, a film with a thickness of approximately 100 µm (after drying). The gloss of the film obtained after drying (gloss T0 measured at 60° with the LZM 151 Ref 3 glossmeter from Dr Lange) was measured. The film was then subjected to abrasion for 10 revolutions using a Taber abrasion tester (reference 5130 Abraser) equipped with two abrasive discs, sold under the name CS10F by the company Taber Industries, with application of a force of 2.5 N to each disc. After the abrasion operation, the gloss of the film was measured (gloss T1).

The following results were obtained:

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Polymer	Gloss T0	Gloss T1
Example 1 (invention)	80	63
Example 9 (outside the	80	50
invention)		

The results show that the polymer of Example 1 according to the invention forms a film having a better wear property of the gloss than that of the film obtained with the polymer of Example 9. This better wear property of the gloss is due to the presence of the vinylphosphonic acid monomer in the polymer.

CLAIMS

- 5 1. Copolymer derived from the polymerization of:
 - (i) 70% to 95% by weight, of the total weight of the monomers, of tetrahydrofurfuryl (meth)acrylate;
 - (ii) 1% to 30 % by weight of vinylphosphonic acid monomer of formula (I):

$$H_2C = C - X - \left[-CH_2 \right]_n - PO_3H_2$$
R1

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in which:

R1 denotes H or -CH₃;

X denotes a covalent bond and n denotes an integer ranging from 0 to 14; or X denotes a –COO- group and n denotes an integer ranging from 2 to 6;

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- (iii) 0 to 20% by weight of an additional monomer.
- 2. Copolymer according to Claim 1, characterized in that, for monomer (I):

X denotes a covalent bond and n is an integer ranging from 0 to 6 or X denotes a –COOgroup and n is an integer ranging from 2 to 4.

3. Copolymer according to either of the preceding claims, characterized in that, for monomer (I), R1 = H and X denotes a covalent bond and n is an integer ranging from 0 to 4.

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4. Copolymer according to one of the preceding claims, characterized in that monomer (I) is chosen from:

vinylphosphonic acid;

- 3-butenylphosphonic acid;
- 30 4-pentenylphosphonic acid;

10-undecenylphosphonic acid;

11-dodecenylphosphonic acid;

2-phosphonoethyl ester of 2-methyl-2-propenoic acid;

2-phosphonoethyl ester of 2-propenoic acid;

- 35 and preferably vinylphosphonic acid.
 - 5. Copolymer according to one of the preceding claims, characterized in that the additional monomer is a monomer of formula (II):

in which:

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R1 denotes a hydrogen atom or a methyl radical;

X denotes O or NH or NR₃;

- R2 denotes a linear C_1 - C_{22} or branched C_3 - C_{10} or cyclic C_5 - C_7 alkyl radical, or a linear C_3 - C_{20} or branched C_6 - C_{20} or cyclic C_5 - C_7 unsaturated hydrocarbon-based radical or a $-(CH_2$ - CH_2 - $O)_a$ -H radical, with a ranging from 9 to 115, or an $-(Si(CH_3)_2 O)_b$ - CH_3 radical, with b ranging from 5 to 70, it being understood that X = O when R2 is a radical of formula $-(CH_2$ - CH_2 - $O)_a$ -H or $-(Si(CH_3)_2 O)_b$ - CH_3 ;
- 10 R3 denotes a linear C₁-C₁₂ or branched C₃-C₁₂ alkyl radical.
 - 6. Copolymer according to one of the preceding claims, characterized in that it is derived from the polymerization of:
 - 70% to 95% by weight, of the total weight of the monomers, of tetrahydrofurfuryl (meth)acrylate;
 - 5% to 30% by weight of vinylphosphonic acid; and preferably of:
 - 75% to 95% by weight, of the total weight of the monomers, of tetrahydrofurfuryl (meth)acrylate;
- 20 5% to 25% by weight of vinylphosphonic acid.
 - 7. Copolymer according to any one of the preceding claims, characterized in that it is chosen from (80/20) or (90/10) (weight/weight) tetrahydrofurfuryl methacrylate/vinylphosphonic acid copolymers.

8. Composition comprising, in a physiologically acceptable medium, a copolymer according to any one of the preceding claims.

- 9. Composition according to the preceding claim, characterized in that the copolymer is present in a content ranging from 0.1% to 60% by weight and preferably ranging from 0.1% to 40% by weight, relative to the total weight of the composition.
 - 10. Composition according to either of Claims 8 and 9, characterized in that it comprises an organic solvent, preferably an ester having from 3 to 8 carbon atoms.
 - 11. Composition according to any one of Claims 8 to 10, characterized in that it comprises a cosmetic adjuvant chosen from additional film-forming polymers, plasticizers, thickeners,

fillers, spreading agents, wetting agents, dispersants, antifoams, preservatives, UV-screening agents, active agents, surfactants, moisturizers, fragrances, neutralizing agents, stabilizers, antioxidants and colorants.

- 5 12. Composition according to any one of Claims 8 to 11, characterized in that it is in the form of a nail varnish.
 - 13. Cosmetic process for making up and/or non-therapeutically caring for the nails, comprising the application to the nails of a composition according to any one of Claims 8 to 12.
 - 14. Use of a composition according to any one of Claims 8 to 12, for obtaining a transparent, uniform film applied to the nails.

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INTERNATIONAL SEARCH REPORT

International application No PCT/EP2015/076051

A. CLASSI INV. ADD.	FICATION OF SUBJECT MATTER C08F220/28 A61Q3/02 A61K8/8	1	
According to	o International Patent Classification (IPC) or to both national classifica	ation and IPC	
B. FIELDS	SEARCHED		
	poumentation searched (classification system followed by classification $A61Q-A61K$	on symbols)	
Documentat	tion searched other than minimum documentation to the extent that su	uch documents are included in the fields sea	arched
Electronic d	ata base consulted during the international search (name of data bas	se and, where practicable, search terms use	ed)
EPO-In	ternal, WPI Data		
C. DOCUME	ENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the rele	evant passages	Relevant to claim No.
А	EP 0 085 370 A2 (WICKHEN PRODUCTS [US]) 10 August 1983 (1983-08-10) pages 3-6; examples 2,9-12		1-14
А	EP 0 522 756 A1 (CALGON CORP [US] 13 January 1993 (1993-01-13) cited in the application page 2, lines 5-6,22-25 page 6, lines 38-40 page 7, lines 10-12])	1-14
А	US 2013/263875 A1 (BURGESS TAMAR/AL) 10 October 2013 (2013-10-10) paragraphs [0002], [0058]	A [US] ET	1-14
Furth	her documents are listed in the continuation of Box C.	X See patent family annex.	
"A" docume to be control to be	ent which may throw doubts on priority claim(s) or which is o establish the publication date of another citation or other al reason (as specified) ent referring to an oral disclosure, use, exhibition or other sent published prior to the international filing date but later than ority date claimed	"T" later document published after the inter date and not in conflict with the applicathe principle or theory underlying the in "X" document of particular relevance; the classifier of considered novel or cannot be considered novel or cannot be considered to document is taken alon "Y" document of particular relevance; the classifier of the involve an inventive step combined with one or more other such being obvious to a person skilled in the "&" document member of the same patent for the same patent of	ation but cited to understand invention laimed invention cannot be ered to involve an inventive e laimed invention cannot be powhen the document is a documents, such combination e art
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