

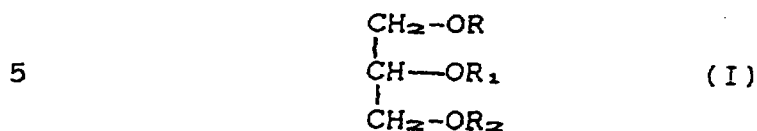
The present invention relates to new derivatives of glycerol, their preparation process, their use as cross-linking agents, the cross-linking or cross-linkable compositions containing them and their use in the textile industry.

Copolymers capable of being made insoluble by cross-linking have been known for a long time. This cross-linking is generally achieved by the introduction into the mixture of monomers to be copolymerised of a monomer containing one or more reactive groups such as the following: carboxyl, vinyl, hydroxyl, oxirane, optionally substituted carbamoyl, optionally etherified carboxyhydroxymethyl, such as, for example, N-methylolacrylamide, acrylamidoglycolic acid, methylene-bisacrylamide, 1,2-diacryloylamino-1,2-dihydroxyethane, tetraallyloxyethane and glycidyl methacrylate.

Certain copolymers can be cross-linked simply by heating, generally in the presence of an acid catalyst or a catalyst capable of liberating an acid. This is the case, for example, with the acrylic, vinyl or acrylvinyl copolymers containing methylol amides of unsaturated organic acids such as acrylic, methacrylic and maleic acid as the cross-linking agent.

However, some of these cross-linking monomers possess the property of liberating either during their polymerisation or at the time of their cross-linking, traces of formaldehyde, the drawbacks of which are known today. Others are either insoluble in water, or only slightly reactive, or are difficult to incorporate in the desired copolymer. The object of the present invention is the provision of new cross-linking agents that remove these drawbacks.

The new cross-linking agents according to the present invention are glycerol derivatives of general formula (I):



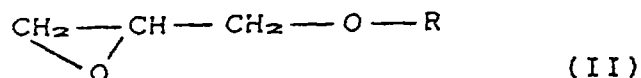
in which R represents an allyl, methylallyl, acryloyl or methacryloyl group and R₁ and R₂ are either identical, representing a glyoxyloyl group, or different, representing a hydrogen atom or a glyoxyloyl group.

The object of the invention is more particularly the glycerol derivatives as defined above, characterised in that in the said formula (I), R represents an allyl, acryloyl or methacryloyl group and R₁ and R₂ keep the meaning given above.

From the latter products, the object of the invention is in particular:

- 3-acryloyloxy-2-glyoxyloyloxy-1-propanol;
- 1-acryloyloxy-3-glyoxyloyloxy-2-propanol;
- 1-acryloyloxy-2,3-diglyoxyloyloxy-propane;
- 3-methacryloyloxy-2-glyoxyloyloxy-1-propanol;
- 1-methacryloyloxy-3-glyoxyloyloxy-2-propanol;
- 1-methacryloyloxy-2,3-diglyoxyloyloxy-propane;
- 3-allyloxy-2-glyoxyloyloxy-1-propanol;
- 1-allyloxy-3-glyoxyloyloxy-2-propanol.

According to the invention, the derivatives of general formula (I) above may be prepared by a process characterised in that glyoxylic acid is reacted with a substituted oxirane of general formula (II):



5 in which R has the meaning previously given, to obtain a product of general formula (I) as defined above:

10 In these preferred conditions for using the process of the invention, the process described above is achieved in the following manner:

The reaction of glyoxylic acid with substituted oxirane of general formula (II) is performed:

- 15 . at a temperature of between 50°C and 120°C, advantageously of roughly 80°C;
- . with an excess of substituted oxirane of general formula (II);
- . with glyoxylic acid in aqueous solution, advantageously with an aqueous solution of glyoxylic acid of 75 ± 10 % by weight;
- 20 . in the presence of a catalyst, which is either a chromium derivative such as chromium acetyl acetate, or preferably a basic catalyst, such as a tertiary amine such as triethylamine or dimethyl laurylamine;
- 25 . possibly in the presence of a solvent such as an aliphatic or aromatic hydrocarbon, such as ...;
- . by eliminating, at the end of the reaction, the excess of substituted oxirane used by washing the reaction medium diluted with water with a compatible organic solvent, non-miscible with water, preferably diethyl oxide.
- 30

35 The product of general formula (I) may be identified thanks to the preparation of a derivative characteristic of its

aldehyde function(s) such as oxime, O-methyl oxime, phenylhydrazone, dinitrophenylhydrazone, according to the standard methods for the preparation of these derivatives.

5 For example, the desired product of general formula (I) may be identified by the isolation of its O-methyl oxime or oximes obtained by reacting in an aqueous medium an excess of methoxyamine hydrochloride on the crude reaction mixture, the non-transformed initial oxirane of which was eliminated
10 beforehand. The O-methyl oxime(s) obtained in this way can be purified by means known per se, such as distillation, chromatography, etc.

The object of the present application is also the use of
15 derivatives of general formula (I) as defined above as cross-linking agents.

As cross-linking agents, the derivatives of formula (I) according to the invention may advantageously be present in
20 a cross-linking and/or cross-linkable composition, containing at least one glycerol derivative as defined above which can be copolymerised with at least one monomer copolymerisable with this derivative.

25 It is thus that the presence in this derivative of the glycerol having an ethylene bond allows its polymerisation or its copolymerisation with other monomers whilst conserving its cross-linking activity. It is likely that the glyoxyloyl group(s) present in this glycerol derivative
30 react(s) on the hydroxyl groups of the polymers or of the copolymers formed to constitute acetal bridges and cross-link the macromolecules in this way, for, as will be shown later, the composition according to the invention behaves differently to a simple mixture.

The monomers which can be copolymerised with a derivative of formula (I) according to the invention to give copolymers, which themselves can be involved in a cross-linking reaction, advantageously contain the acrylic or methacrylic monomers such as C_1 - C_{18} alkyl acrylates and methacrylates, vinyl ethers and esters such as vinyl acetate, vinyl propionate, vinyl chloride, (meth)acrylic acid, and its alkali metal or ammonium salts, acrylonitrile, styrene or substituted olefins such as vinylsulphonic acid, preferably salified in the form of sodium salt. Mixtures of these monomers may equally be used.

This copolymerisation of the glycerol derivative of general formula (I) with other unsaturated monomers may be carried out in dispersion, in emulsion, in solution either by a batch process, or by semi-continuous or continuous processes, according to known methods, in the presence of one or more polymerisation initiators such as a Redox system, an azo-compound, a peroxide and/or a hydroperoxide. The proportion of the cross-linking agent introduced into the copolymer may vary largely from 0.1 to 15 % by weight, preferably from 0.5 to 5 % by weight relative to the total weight of the monomers used.

The cross-linking and/or cross-linkable copolymers are obtained by copolymerising the glycerol derivative used as cross-linking agent prepared earlier. The choice of monomers involved in the copolymerisation enables the modification of certain physical properties of the substances obtained after cross-linking, such as the flexibility, the hardness and the colouration. The introduction into the copolymer of reactive groups such as hydroxyl, carboxyl, carbamoyl or other groups, can usefully enhance the cross-linking properties. The cross-linking effect can also be enhanced by the addition of known catalysts such as acids, ammonium salts or

salts of mineral or organic acids of metals having several valencies, such as, for example, chlorides, nitrates of magnesium, zinc, calcium, aluminium and zirconium.

- 5 To show the cross-linking capability of cross-linking and/or cross-linkable compositions according to the invention, the property of these compositions of giving, by the simple heating of films resistant to organic solvents, is brought to the fore. The heating produces cross-linking even within
10 the macromolecules of the copolymer or between the macromolecules of the copolymer.

The properties of cross-linking and/or cross-linkable compositions of the invention make them more particularly
15 advantageous in the textile industry or in the paper industry. These compositions may in effect be used for producing mats of fibres or of non-woven fabrics or to improve the effects of treatments to make the fabrics crease-resistant. In particular they allow woven or unwoven
20 fabrics, that have good resistance to organic solvents, particularly organic solvents used in dry cleaning operations, to be obtained and the abrasion resistance and the crease-resistance and also durability during washing of the treatments intended to impart crease-resistance to the
25 fabrics to be increased; they therefore enable crease-resistant materials to be obtained because of the treatment of a fabric containing cellulose threads or fibres by means of such a composition.

- 30 The following examples are given as illustrations and in no way limit the invention. In these examples, the physical-chemical inspections are achieved as follows:

- the dry extract, expressed in percentage by weight, is determined by drying 1 g of dispersion for 3 hours at 105°C;
 - 5 - the Brookfield viscosity is determined at 20-22°C with an RVT Brookfield viscometer equipped with the 1 axis at a speed of 50 rpm;
 - the swelling ratio, SR, is determined at ambient
10 temperature by immersion in trichloroethylene of a flat circular test piece having a diameter of 50 mm cut from a dry film, of approximately 0.5 mm thick, of the dispersion to be tested. The SR is measured simultaneously on a non-heat-treated film and on a film
15 treated for 10 minutes at 150°C. The SR is calculated by the relationship
- $$SR = \frac{100 (df - di)}{df}$$
- 20 in which di is the initial diameter of the test piece and df is the final diameter;
 - the NMR spectra are determined on a Brucker AC 200 apparatus (50 MHz ¹³C and 200 MHz ¹H). The chemical
25 displacements are expressed in ppm relative to the tetramethylsilane.

Example 1

- 30 Preparation of 1-methacryloyloxy-3-glyoxyloyloxy-2-propanol and 3-methacryloyloxy-2-glyoxyloyloxy-1-propanol.

The following are heated for 3 hours to 80°C with agitation:

- 300 g (2.11 moles) of glycidyl methacrylate;
- 48.8 g (0.53 moles) of monohydrated glyoxylic acid;
- 5.36 g (53 moles) of triethylamine;
- 0.15 g of paramethoxyphenol,

5

then the reaction medium is cooled down to ambient temperature. In this way an oily solution designated Ac is obtained and used as it is. In order to characterise the products present in this solution Ac, it is poured into a
10 mixture of 355 g water and 355 g of diethyl oxide. After decanting, the aqueous phase is washed twice with 355 g of diethyl oxide and the ether phase is washed twice with 355 g of water. After the elimination of the diethyl oxide, 156 g (1.1 mole) of non-transformed glycidyl methacrylate is
15 isolated from the reunited ether phases. The reunited aqueous phases are concentrated under vacuum to a total weight of 1140 g, designated hereinafter solution A. 19 g (0.23 mole) of methoxyamine hydrochloride is introduced into 100 g of this solution A, then the solution obtained is left
20 for 2 hours at ambient temperature.

In this way a milky suspension is obtained, which is washed twice with 136 g of dichloromethane, then the chloromethylenic phases are reunited, dried over anhydrous
25 magnesium sulphate and finally concentrated under vacuum. In this way 7.5 g of a yellow oil is isolated, which is purified by preparative chromatography on a column (500X25) filled with silica of a size grading of 10 micrometers, eluting with a hexane-ethyl acetate mixture 8/2 by volume,
30 which allows the isolation on the one hand of 5 g (20.4 mmols) of 1-methacryloyloxy-3-methoxyiminoacetoxymethoxy-2-propanol and on the other hand of 2 g (8.15 mmols) of 3-methacryloyloxy-2-methoxyiminoacetoxymethoxy-1-propanol characterised by their NMR¹H spectra recorded in the
35 deuterized chloroform.

1-methacryloyloxy-3-methoxyiminoacetox-2-propanol (50/50 diastereoisomer mixture).

	7.49 ppm, s, 1H, CH = N-
5	6.13 ppm, m, 1H, CH ₂ = C
	5.60 ppm, m, 1H, CH ₂ = C
	4.39-4.16 ppm, m, 5H -CH ₂ - CH - CH ₂ -
	4.04 ppm, s, 3H, OCH ₃
	2.7 ppm, s, 1H, OH
10	1.93 ppm, m, 3H, CH ₃ - C=

3-methacryloyloxy-2-methoxyiminoacetox-1-propanol (mixture of isomers)

15		isomers	
		majority	minority
	-CH = N, s, 1H	7.46 ppm	7.49 ppm
	CH ₂ = C, m, 1H	6.11 ppm	6.09 ppm
20	CH ₂ = C, m, 1H	5.58 ppm	5.58 ppm
	-CH-O-CO-, quintuplet, 1H, J = 4.9 Hz	5.23 ppm	5.30 ppm
	-CH ₂ -O-CO-, m, 2H	4.48 ppm	4.42 - 4.3 ppm
	-OCH ₃ , s, 3H	4.02 ppm	4.02 ppm
25	-CH ₂ OH, d, 2H, J = 4.9 Hz	3.78 ppm	3.80 ppm
	-OH, s, 1H	2.60 ppm	2.50 ppm
	CH ₃ -C=, m, 3H	1.91 ppm	1.91 ppm

Consequently, solution A contains at least 50.28 g (0.23 mole) of 1-methacryloyloxy-3-glyoxyloxy-2-propanol and 20.1 g (93 moles) of 3-methacryloyloxy-2-glyoxyloxy-1-propanol, i.e. a yield of 61 % of the theoretical value calculated relative to the glyoxylic acid used.

Example 2

Operating as in Example 1, starting with 270.2 g (2.11
 5 moles) of glycidyl acrylate, 48.8 g (0.53 moles) of
 monohydrated glyoxylic acid, 5.36 g (53 mmoles) of
 triethylamine and 0.15 g of paramethoxyphenol, there is
 obtained a mixture of 1-acryloyloxy-3-glyoxyloxy-2-
 propanol and 3-acryloyloxy-2-glyoxyloxy-1-propanol with
 10 a yield of greater than 65% of the theoretical value
 calculated relative to the glyoxylic acid used.

These products have been characterised by the isolation of
 their O-methyl oxime by using the process described in
 15 Example 1.

1-acryloyloxy-3-methoxyiminoacetox-2-propanol

Microanalysis		C%	H%	N%
20	C ₉ H ₁₃ NO ₆ calculated	46.75	5.7	6.05
	Mol. Wt. = 231.2 found	46.5	5.8	6.2

Physical analysis: NMR¹H (CDCl₃)

7.51 ppm, s, 1H, CH = N

6.44 ppm, dd, 1H, J=1.8 Hz and J=17 Hz, CH₂ = C

25 6.13 ppm, dd, 1H, J=17 Hz and J=10.3 Hz, CH - CO

5.87 ppm, dd, 1H, J=1.8 Hz and J=10.3 Hz, CH₂=C

4.29-4.20 ppm, m, 5H, -CH₂ - $\underset{\text{O}}{\text{CH}}$ -CH₂-

4.05 ppm, s, 3H, -OCH₃

30 2.7 ppm, s, 1H, -OH

3-acryloyloxy-2-methoxyiminoacetox-1-propanol

Physical analysis -NMR¹H (CDCl₃)

		isomers	
		majority	minority
5	-CH=N, s, 1H	7.49	7.51
	CH ₂ =C, dd, 1H, J=1.8 Hz		
	and J= 17 Hz	6.44	6.43
	=CH-CO, dd, 1H, J=17 Hz and		
	J=10.3 Hz	5.87	5.865
10	CH-OCO, quintuplet, 1H, J=4.9 Hz	5.23	5.30
	COOCH ₂ , m, 2H	4.53 - 4.43	4.46 - 4.40
	OCH ₃ , s, 3H	4.06	4.06
	OH, d, 2H, J=4.9 Hz	3.83	3.83

15 Example 3

Operating as in Example 1, starting with 300 g (2.63 moles) of allyl and glycidyl oxide, 60.5 g (0.6575 mole) of monohydrated glyoxylic acid, 6.6 g (66 mmols) of triethylamine and 150 mg of paramethoxyphenol, there is obtained a mixture of 1-allyloxy-3-glyoxyloxy-2-propanol and 3-allyloxy-2-glyoxyloxy-1-propanol with a yield greater than 70 % of the theoretical value calculated relative to the glyoxylic acid used.

25

These products have been identified by the isolation of their O-methyl oxime according to the process described in Example 1. The physical characteristics of these oximes are given hereafter.

30

1-allyloxy-3-methoxyiminoacetox-2-propanol

Physical analysis NMR_H (CDCl₃)

7.47 ppm, s, 1H, CH=N

5.90 ppm, m, 1H, =CH-C

35 5.22 ppm, m, 2H, CH₂ =

- 4.29 ppm, part AB of a system ABX, 2H, $J_{AB} = 11.5$ Hz
 $J_{AX} = 4.9$ Hz, $J_{BX} = 6$ Hz, O-CH₂
 4.05 ppm, m, 1H, CH-O
 4.02 ppm, s, 3H, OCH₃
 5 3.98 ppm, m, 2H, allyl CH₂
 3.48 ppm, part AB of a system ABX, 2H, $J_{AB} = 9.8$ Hz
 $J_{AX} = 4.5$ Hz, $J_{BX} = 5.8$ Hz, O-CH₂
 2.8 ppm, s, 1H, OH
- 10 3-allyloxy-2-methoxyiminoacetoxy-1-propanol
 Physical analysis NMR¹H (CDCl₃)
 7.46 ppm, s, 1H, -CH=N
 5.78 ppm, m, 1H, =CH-
 5.17 ppm, m, 3H, CH₂= and CHOCO
 15 4.0 ppm, s, 3H, OCH₃
 3.95 ppm, m, 2H, =C-CH₂ - O
 3.79 ppm, d, 2H, -CH₂-OH
 3.62 ppm, d, 2H, O- CH₂ -CH-
 2.95 ppm, s, 1H, OH

20

Example 4

A solution, designated S₁₄, is prepared by dissolving the following, with agitation, in 199.6 g of distilled water at
 25 ambient temperature:

- 16.1 g of an aqueous solution at 28 % by weight of the sodium salt ethoxylated lauryl ether sulphate with 3 to 4 moles of ethylene oxide;
- 30 - 33.8 g of an aqueous solution at 20% by weight of oleocetyl alcohol with 25 moles of ethylene oxide;
- 1 g of sodium hydrogen carbonate;
- 1.2 g of potassium peroxodisulphate;
- 2.61 g of methacrylamide.

35

Simultaneously a solution, designated S_{24} , is prepared by mixing the following, with agitation, at ambient temperature:

- 192.7 g of n-butyl acrylate;
- 5 - 245.85 g of methyl methacrylate;
- 2.25 g of acrylic acid;
- 21.10 g of solution Ac prepared in Example 1.

250 g of distilled water is heated to 83°C in a
10 polymerisation reactor, then with agitation, at this
 temperature, the solution obtained by mixing
 extemporaneously the two preceding solutions is introduced
 over a period of 4 hours, then when the introduction is
 complete, the reaction medium is maintained at 83 ± 1 °C,
15 with agitation, for one hour and then it is cooled to
 ambient temperature.

After filtration through a sieve having a mesh size of 0.16
mm, an aqueous fluid dispersion is obtained, having a milky
20 appearance, a pH of 3.95, a dry extract of 47.76 %, a
 Brookfield viscosity of 50 mPa.s, a particle size (average
 of the order $\bar{z}$) of 172 nm, a swelling ratio, SR, of 122 %
 and a swelling ratio of 110 % after heat treatment.

25 Example 5

A solution, designated S_{15} , is prepared by dissolving the
following in 273.6 g of distilled water, with agitation, at
ambient temperature:

30

- 3.6 g of an aqueous solution at 50 % by weight of a
sodium salt of ether sulphate of ethoxylated
tributylphenol with 7 moles of ethylene oxide;
- 4.5 g of an aqueous solution at 20 % by weight of
35 ethoxylated nonylphenol with 30 moles of ethylene oxide;

- 0.9 g of ethoxylated nonylphenol with 6 moles of ethylene oxide;
- 1 g of sodium hydrogen carbonate;
- 2.61 g of methacrylamide;
- 5 - 1.35 g of potassium peroxodisulphate.

Simultaneously, a solution, designated S_{25} , is prepared by mixing the following with agitation at ambient temperature:

- 232.9 g of styrene;
- 10 - 205.7 g of n-butyl acrylate;
- 2.25 g of acrylic acid;
- 21.10 g of a solution Ac prepared in Example 1.

The following are heated to 82°C, with agitation, in a
15 polymerisation reactor:

- 250 g of distilled water;
- 0.45 g of an aqueous solution at 50 % by weight of a sodium salt of ether sulphate of ethoxylated tributylphenol with 7 moles of ethylene oxide,
- 20 then the solution obtained by mixing extemporaneously solutions S_{15} and S_{25} is introduced over a period of 4 hours, with agitation, whilst maintaining the temperature at $84 \pm 1^\circ\text{C}$. When the introduction is complete, the reaction medium is maintained for one hour at 80°C with agitation, then it
- 25 is cooled down to ambient temperature and finally it is filtered through a sieve having a mesh size of 0.16 mm. In this way is obtained a fluid dispersion with a milky appearance, having a pH of 3.35, a dry extract of 44.5 %, a Brookfield viscosity of 38 mPa.s, a particle size (average
- 30 of the order $\bar{z}$) of 230 nm, a swelling ratio of 114 % and a swelling ratio of 110 % after heat treatment.

Example 6

A solution, designated S_{16} , is prepared by dissolving the following, with agitation, at ambient temperature in 209.7 g of distilled water:

- 27 g of an aqueous solution at 25% by weight of linear C_{14} - C_{18} sodium alkanesulphonate;
- 11.25 g of an aqueous solution at 20% by weight of ethoxylated nonylphenol with 30 moles of ethylene oxide;
- 11.25 g of an aqueous solution at 20% by weight of ethoxylated oleocetylic alcohol with 25 moles of ethylene oxide;
- 0.68 g of sodium acetate;
- 0.90 g of potassium peroxodisulphate;
- 4.5 g of an aqueous solution at 29.7% by weight of sodium vinylsulphonate;
- 2.61 g of methacrylamide.

Simultaneously, a solution, designated S_{26} , is prepared by mixing the following, with agitation, at ambient temperature:

- 137.9 g of vinyl acetate;
- 301.5 g of n-butyl acrylate;
- 21.1 g of solution Ac prepared in example 1.

250 g of distilled water is heated in a polymerisation reactor to 80°C, then at this temperature, with agitation, the following are successively introduced, in a single operation: an aqueous solution containing 0.45 g of potassium peroxodisulphate in 10 g of water, then one minute later, an aqueous solution containing 0.5 g of sodium metabisulphite in 10 g of water and finally the solution obtained by mixing extemporaneously the preceding solutions

S_{16} and S_{26} is introduced over a period of 4 hours, with agitation, whilst maintaining the temperature at 84°C. At the end of the introduction, the reaction medium is kept at 84°C for one hour with agitation, then it is cooled to ambient temperature and finally it is filtered through a sieve having a mesh size of 0.16 mm. In this way a fluid dispersion is obtained having a milky appearance, a pH of 3.2, a Brookfield viscosity of 34 mPa.s, a particle size (average of the order of z) of 264 nm, a swelling ratio of 130% and a swelling ratio after heat treatment of 110%.

Example 7 for comparison

A solution, designated S_{17} , is prepared by dissolving the following, with agitation, at ambient temperature in 209.7 g of distilled water:

- 27 g of an aqueous solution at 25% by weight of linear C_{14} - C_{18} sodium alkanesulphonate;
- 11.25 g of an aqueous solution at 20% by weight of ethoxylated nonylphenol with 30 moles of ethylene oxide;
- 11.25 g of an aqueous solution at 20% by weight of ethoxylated oleocetylic alcohol with 25 moles of ethylene oxide;
- 0.68 g of sodium acetate;
- 0.90 g of potassium peroxosulphate;
- 4.5 g of an aqueous solution at 29.7% by weight of sodium vinylsulphonate;
- 2.61 g of methacrylamide.

30

Simultaneously a solution, designated S_{27} , is prepared by mixing the following with agitation at ambient temperature:

- 137.9 g of vinyl acetate;
- 301.5 g of n-butyl acrylate;
- 4.4 g (31 moles) of glycidyl methacrylate.

35

250 g of distilled water is heated to 80°C in a polymerisation reactor, then at this temperature, with agitation, the following are introduced successively, in a single operation: an aqueous solution containing 0.45 g of potassium peroxodisulphate in 10 g of water, then one minute later an aqueous solution containing 0.5 g of sodium metabisulphite in 10 g of water and finally over a period of 4 hours the aqueous solution obtained by mixing extemporaneously the aforementioned solutions S₁ and S₂ is introduced, with agitation, maintaining the temperature at 84°C. At the end of the introduction, the reaction medium is maintained, with agitation, at 84°C for one hour. Then the following is introduced with agitation:

- 2.295 g (31 moles) of monohydrated glyoxylic acid, then the reaction medium is maintained, with agitation, at 83 ± 1°C for one hour before being cooled down to ambient temperature and finally it is cooled to ambient temperature and filtered through a sieve with a mesh size of 0.16 mm. In this way a fluid dispersion having a milky appearance is obtained, giving a film soluble in trichloroethylene, which shows the absence of cross-linking. Neither does this film display thermo-cross-linking when heated to 150°C.

Example 8 for comparison

Example 7 for comparison is reproduced by replacing the glycidyl methacrylate by an equivalent quantity of 2,3-dihydroxypropyl methacrylate, i.e. 4.96 g (31 moles).

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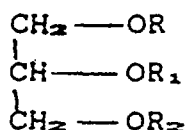
At the end of the reaction, a fluid dispersion having a milky appearance is obtained, giving a film soluble in trichloroethylene, which shows the absence of cross-linking. Neither does this film display thermo-cross-linking when heated to 150°C.

35

C L A I M S

1. Glycerol derivatives of general formula (I):

5



10

in which R represents an allyl, methylallyl, acryloyl or methacryloyl group, and R_1 and R_2 are either identical, representing a glyoxyloyl group, or different, representing a hydrogen atom or a glyoxyloyl group.

15

2. Glycerol derivatives according to Claim 1, characterised in that in formula (I) R represents an allyl, acryloyl or methacryloyl group.

20

3. 3-acryloyloxy-2-glyoxyloyloxy-1-propanol.

4. 1-acryloyloxy-3-glyoxyloyloxy-2-propanol.

5. 3-methacryloyloxy-2-glyoxyloyloxy-1-propanol.

25

6. 1-methacryloyloxy-3-glyoxyloyloxy-2-propanol.

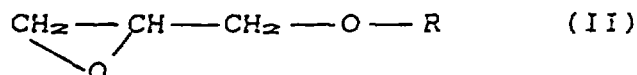
7. 3-allyloxy-2-glyoxyloyloxy-1-propanol.

8. 1-allyloxy-3-glyoxyloyloxy-2-propanol.

30

9. A preparation process for products of general formula (I) as defined in Claim 1, characterised in that glyoxylic acid is reacted with a substituted oxirane of general formula (II):

35



in which R has the significance given in Claim 1.



10. A process according to Claim 9,
characterised in that glyoxylic acid is reacted with
5 a substituted oxirane of general formula (II) in the
presence of a basic catalyst.
11. The use of derivatives of general formula (I) as
defined in Claim 1 as cross-linking agents.
12. A cross-linking and/or cross-linkable composition,
characterised in that it contains at least one
glycerol derivative according to Claim 1
15 copolymerised with at least one monomer
copolymerisable with this derivative.
13. A composition according to Claim 12,
characterised in that the copolymerisable monomer is
chosen from the group of acrylic or methacrylic
20 monomers, vinyl ethers and esters, acrylic acid and
methacrylic acid, acrylonitrile, styrene, olefins
and mixtures thereof.
14. A non-woven material,
25 characterised in that it is obtained from natural or
synthetic fibres or a mixture thereof by means of a
composition according to any one of Claims 12 or 13.
15. A crease-resistant material,
30 characterised in that it is obtained by treating a
fabric containing cellulose threads or fibres by
means of a composition according to any one of
Claims 12 or 13.

