COMMONWEALTH of AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

~~I~~/We L'OREAL
of 14 rue Royale
75008 PARIS - France.

602333

hereby apply for the grant of a Standard Patent for an invention entitled:

"NEW POLYMERS CAPABLE OF ABSORBING ULTRAVIOLET RADIATION, PREPARATION THEREOF AND APPLICATION THEREOF, ESPECIALLY IN COSMETICOLOGY"

which is described in the accompanying ~~provisional~~ complete specification.

Details of basic application(s):—

Number	Convention Country	Date
86 04544	FRANCE	28th March 1986

LODGED AT SUB-OFFICE
27 MAR 1987
Melbourne

APPLICATION ACCEPTED AND AMENDMENTS ALLOWED 31-7-90

The address for service is care of DAVIES & COLLISON, Patent Attorneys, of 1 Little Collins Street, Melbourne, in the State of Victoria, Commonwealth of Australia.

Dated this 26th day of March 1987

To: THE COMMISSIONER OF PATENTS

K. M. Rimington
.....
(a member of the firm of DAVIES & COLLISON for and on behalf of the Applicant).

Davies & Collison, Melbourne and Canberra.

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952–1973

DECLARATION IN SUPPORT OF CONVENTION OR NON–CONVENTION APPLICATION FOR A PATENT OR PATENT OF ADDITION

In support of the Application made for a patent ~~patent of addition~~ for an invention

Insert title of invention.

entitled: "NEW POLYMERS CAPABLE OF ABSORBING ULTRAVIOLET RADIATION, PREPARATION THEREOF AND APPLICATION THEREOF, ESPECIALLY IN COSMETICOLOGY"

Insert full name(s) and address(es) of declarant(s) being the applicant(s) or person(s) authorized to sign on behalf of an applicant company.

I/~~We~~ ANDRE VIOUT
of L'OREAL,
of 14 rue Royale,
75008 PARIS - France.

do solemnly and sincerely declare as follows :–

Cross out whichever of paragraphs 1(a) or 1(b) does not apply

1(a) relates to application made by individual(s)
1(b) relates to application made by company; insert name of applicant company.

1. (a) ~~I am~~/~~We are~~ ~~XXXXXXXXXXXXXXXX~~ the applicant ~~XXXXXXXXXXXXXXXX~~ for the ~~patent of addition~~

or (b) I am authorized by

L'OREAL

the applicant..... for the patent ~~patent of addition~~ to make this declaration on its ~~their~~ behalf.

Cross out whichever of paragraphs 2(a) or 2(b) does not apply

2(a) relates to application made by inventor(s)
2(b) relates to application made by company(s) or person(s) who are not inventor(s); insert full name(s) and address(es) of inventors.

2. (a) I am/We are the actual inventor..... of the invention

or (b)

Serge FORESTIER,
of 16 allee Ferdinand Buisson
77410 CLAYE-SOUILLY - France.

Claude MAHIEU,
of 90 avenue de Villiers,
75017 PARIS - France.

~~is~~/~~are~~ the actual inventor.s..... of the invention and the facts upon which the applicant.....

State manner in which applicant(s) derive title from inventor(s)

~~is~~/~~are~~ entitled to make the application are as follows :–

The applicant would, if a patent were granted on an application made by the said actual inventors, be entitled to have the patent assigned to it.

Cross out paragraphs 3 and 4 for non-convention applications. For convention applications, insert basic country(s) followed by date(s) and basic applicant(s).

3. The basic application..... as defined by Section 141 of the Act ~~was~~/~~were~~ made

in ....FRANCE..... on the ....28th March 1986.....
by....L'OREAL.....
in ..... on the .....
by.....
in ..... on the .....
by.....

4. The basic application..... referred to in paragraph 3 of this Declaration ~~was~~/~~were~~ the first application..... made in a Convention country in respect of the invention the subject of the application.

Insert place and date of signature.

Declared at PARIS this 13th day of March 1987

L'OREAL 14, Rue Royale, PARIS-8e

André VIOUT
Directeur du Département Brevets

Signature of declarant(s) (no attestation required)

.....

Note: Initial all alterations.

DAVIES & COLLISON, MELBOURNE and CANBERRA.

(12) PATENT ABRIDGMENT (11) Document No. AU-B-70721/87
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 602333

(54) Title
BENZYLIDENEBORNANONE POLYMERS

International Patent Classification(s)
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(71) Applicant(s)
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(72) Inventor(s)
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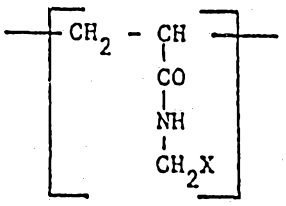
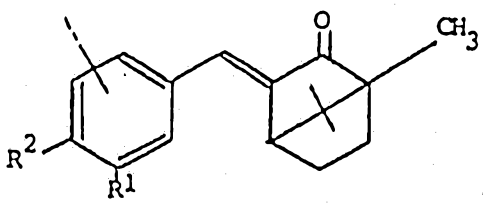
(57) Claim

1. Ultraviolet radiation-absorbing polymers, characterized in that they contain units of formula I:



(I)

in which X is a group derived from benzylidenebornanone of formula II:



(II)

in which R^1 represents a hydrogen atom or a C_1-C_{12} alkoxy group and R^2 represents a C_4-C_{12} alkoxy group.

COMMONWEALTH OF AUSTRALIA

PATENT ACT 1952

COMPLETE SPECIFICATION

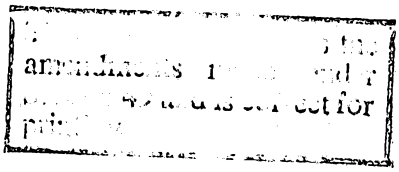
(Original)

FOR OFFICE USE 602333

Class Int. Class

Application Number:
Lodged:

Complete Specification Lodged:
Accepted:
Published:



Priority:

Related Art:

Name of Applicant: L'OREAL

Address of Applicant: 14 rue Royale
75008 PARIS - France.

Actual Inventor(s): Serge FORESTIER
Claude MAHIEU

Address for Service: DAVIES & COLLISON, Patent Attorneys,
1 Little Collins Street, Melbourne, 3000.

Complete Specification for the invention entitled:

"NEW POLYMERS CAPABLE OF ABSORBING ULTRAVIOLET RADIATION, PREPARATION THEREOF AND APPLICATION THEREOF, ESPECIALLY IN COSMETICOLOGY"

The following statement is a full description of this invention, including the best method of performing it known to us :-

New polymers capable of absorbing ultraviolet radiation, preparation thereof and application thereof, especially in cosmeticology.

The present invention relates to new polymers which are capable of absorbing ultraviolet radiation, to their preparation and to their application, especially in cosmeticology.

It is known that exposure of the human body to ultraviolet radiation, and in particular to solar radiation, causes an erythema of the skin which may, in some cases, go as far as burns of relatively high intensity. It is also known that the ultraviolet rays responsible for these effects are those with wavelengths within the range between approximately 280 and 315 nm.

Therefore, substances capable of absorbing ultraviolet radiation within the wavelength range 280-315 nm while allowing the tanning of the skin, since these compounds do not absorb ultraviolet rays responsible for tanning, i.e. those with wavelengths within the range of 315 to 400 nm, are generally used in cosmetic compositions intended for protecting the skin against solar erythema.

However, it has been observed, in some subjects with sensitive skin, that ultraviolet radiations with wavelengths between approximately 315 and 340 nm will promote the triggering of the reaction causing erythema or amplify this reaction.

Moreover, it is known that, in order to avoid

especially the penetration of ultraviolet radiation-absorbing substances into the organism through the skin, the production of polymers capable of absorbing ultraviolet radiation by binding these substances to macromolecular chains has been proposed.

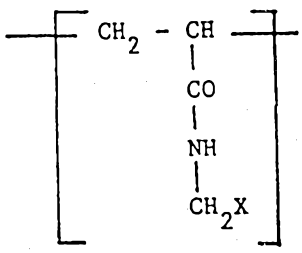
New polymers which absorb ultraviolet radiation, the absorption maximum of which is located within the wavelength range 315-340 nm, and which are compatible with the formulation of cosmetic compositions which can be applied to the skin, have now been discovered. These new polymers may thus be included in the formulation of highly protective cosmetic compositions which can be used by sensitive subjects, and also by normal subjects, in the case of an intense exposure to solar radiation.

Sunscreen cosmetic compositions containing methylated acrylamide polymers with side chains containing unsubstituted benzylidene-camphor groups have been described in French Patent Application No. 2,430,938. These polymers must be at a relatively high concentration in order to achieve a high protection factor. However, in this case, the compositions had disadvantages, in particular an unpleasant sticky touch at the time of application and an uncomfortable feeling after application. In order to avoid these disadvantages, the polymer had to be prepared under special conditions so as to avoid the formation of, or to remove, high molecular weight polymer fractions.

It has been discovered surprisingly that polymers

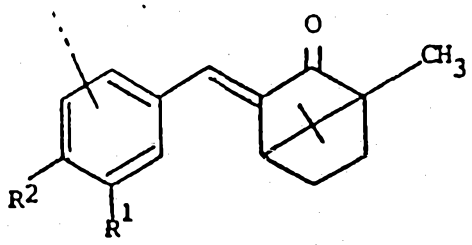
derived from substituted benzylidene-camphor of the present invention do not have these disadvantages. It is possible to retain high molecular mass fractions without any very serious effects on the ease of formulating the composition or on the comfort of application to the skin. Additionally, the polymers of the present invention have not revealed any toxicity on application to the skin, and even when taken orally, whereas the corresponding alkoxybenzylidene-camphor precursors have a certain toxicity when taken orally.

The new polymers of the invention are characterized in that they contain units of formula I:



(I)

in which X is a group derived from benzylidenebornanone of formula II:



(II)

in which R^1 represents a hydrogen atom or a C_1-C_{12} alkoxy group and R^2 represents a C_4-C_{12} alkoxy group.

Among the polymers of the invention, there will be mentioned, in particular:

those which contain units of formula I in which R^1 represents a hydrogen atom or a methoxy or butoxy group; and

those in which R^2 represents a butoxy, hexyloxy, octyloxy or dodecyloxy group.

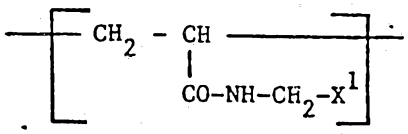
The group X is attached to the side chain of unit I in position 2' or 3'.

The polymers of the invention have an average molecular weight generally between one thousand and one million, and preferably between 1,500 and 100,000.

The polymers of the invention may be either homopolymers or copolymers, the said copolymers being, on the one hand, those which contain exclusively units of formula I, but which contain at least two different types of units of formula I (i.e. having different values for X) and, on the other hand, copolymers which contain both units of formula I and other similar units such as those of formula I' as defined below, which are capable of absorbing ultraviolet radiations.

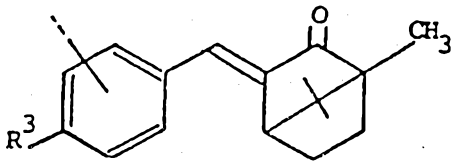
The polymers of the invention contain at least 5 mol%, and preferably at least 10%, of units of formula I.

Among the copolymers of the invention which contain units other than those of formula I, which are capable of absorbing ultraviolet radiation, there will be mentioned, in particular, those which contain units of formula I':



(I')

in which X^1 represents a group derived from bornanone of formula II':



in which R^3 represents a hydrogen atom or a C_1-C_4 alkyl group.

The respective proportions of units of formulae I and I' may vary, for example, from 5:95 to 95:5 (in moles).

The introduction of units of formula I' especially enables the wavelength range of UV radiations absorbed by the polymer to be extended towards UVB.

The invention also relates to a process for the preparation of the polymers defined above.

This process is mainly characterized in that a "sunscreen-monomer" is prepared, of formula IV:

$$CH_2 = CH - CO - NH - CH_2 - X \qquad (IV)$$

in which X is defined as above, and in that the said

sunscreen-monomer is subjected to a homopolymerization or a copolymerization with at least one other ethylenically unsaturated comonomer which is capable of absorbing ultraviolet radiation.

The polymerization reaction may be carried out according to conventional polymerization methods, i.e. in bulk, in solution, in suspension or in emulsion, using a polymerization initiator. It is preferably carried out in solution or in suspension.

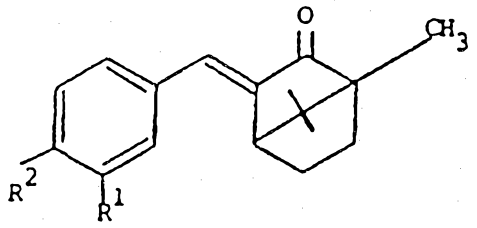
The polymerization initiators are in general conventional radical polymerization initiators. Their choice depends mainly on the different monomers used and on the reaction medium.

Among the different initiators which can be used, there may be mentioned, in particular, peroxides such as benzoyl peroxide, lauroyl peroxide, acetyl peroxide, tert-butylhydroperoxide, benzoylhydroperoxide, hydrogen peroxide, initiators such as azobisisobutyronitrile, redox initiation systems such as sodium persulphate coupled with sodium bisulphite, or the redox system consisting of the hydrogen peroxide-ascorbic acid pair. The concentration of the initiator is generally between 0.2 and 35% and preferably between 0.5 and 20% by weight relative to the total weight of monomers.

The molar mass of the polymers may be adjusted by all known methods, for example by polymerization in dilute solution, by polymerization in the presence of large amounts

of initiator, by the introduction of so-called chain-regulating agents and the like.

In order to prepare the sunscreen monomers of formula IV, N-hydroxymethylacrylamide is reacted with a benzylidenebornanone derivative of formula V:



(V)

in which R^1 and R^2 are as defined above.

This reaction is carried out under the usual conditions of the Friedel-Crafts alkylation reaction, in the presence of an acid catalyst such as sulphuric acid.

The position of the substituent introduced depends on the nature of the substituent R^1. When R^1 represents a hydrogen atom, the acrylamidomethyl substituent is introduced in position 3'. When R^1 represents a C_1-C_{12} alkoxy group, the acrylamidomethyl substituent is introduced in position 2'.

The monomers of formula IV'

$$CH_2=CH-CO-NH-CH_2-X^1 \qquad (IV')$$

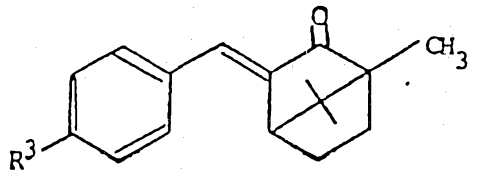
in which X^1 is defined as above with the proviso that R^3 in X^1 does not represent hydrogen, are prepared in a way similar to that described for monomers of formula IV.

The invention also relates to the derivatives of formula IV and IV', as means for implementing the process of the invention.

The benzylidenebornanone derivatives of formula V

used as starting products in the process of the present application may be obtained, for example, according to the process described in French Patent Application No. 78/20,801 (publication no. 2,430,938).

The bornanone derivatives of formula V':



(V')

may be prepared, for example, in a way similar to that described in French Patent 2,111,757.

As mentioned above, polymers containing units of formula I may be used as protective agents against ultraviolet radiations, and, in particular, in the preparation of cosmetic compositions intended for protecting the skin against sunburns. In addition to a valuable protective effect, these polymers are well suited for the preparation of cosmetic formulations which are suitable for protecting the skin against the effects of exposure to sunlight. They have, in particular, good solubility in oily excipients such as, for example, higher fatty alcohol benzoates (especially C_{12}-C_{15} fatty alcohol benzoates).

These polymers absorb ultraviolet radiation within wavelength ranges which may be between 280 and 370 nm. This absorption depends especially on the nature of the substituent R^1.

Thus, when R^1 represents a hydrogen atom, the

polymer based on the unit of formula I absorbs ultraviolet radiation within a wavelength range between 280 and 350 nm, with an absorption maximum of approximately 315 nm.

When R^1 represents an alkoxy group, the polymer absorbs ultraviolet radiation within the wavelength range of approximately 280 to 370 nm, with an absorption maximum of approximately 335 nm.

The invention also relates to cosmetic compositions for protection against ultraviolet radiations, characterized in that they contain as active ingredient at least one polymer, as defined above, containing units of formula I.

These compositions may be present in the form of aqueous or aqueous-alcohol solutions, oily solutions or emulsions, or in the form of sticks. Additionally, they may be incorporated, in combination with a propellant, in suitable containers in the form of pressurized compositions for aerosols.

The cosmetic compositions of the invention may contain, in addition to the ultraviolet radiation-absorbing polymers, various adjuvants usually present in cosmetic compositions of this type, for example moisturizers, emollients or thickeners, surfactants, preservatives, perfumes, pigments and the like.

In the compositions of the invention, the polymers containing units of formula I are generally present in a proportion which may range from 0.2 to 20% by weight

relative to the total weight of the composition.

The absorbing power of the sunscreen was previously expressed using the Ksp (specific K) value, which is a function of the amount of sunscreen substances contained in the sample, the optical density measured and a constant which depends on the apparatus.

The definition of Ksp is given in the book "Introduction to Electronic Absorption Spectroscopy in Organic Chemistry" by Gillian and Stern., Publ. Arnold, London 1954, page 10.

$$Ksp = \frac{k}{c}$$

with $$K = \frac{d}{l}$$

d = optical density measured

c = solution concentration (g/ml)

l = cell thickness in cm

The absorbing power is now defined by the term "specific absorbance, a_s", defined by French Standard T.01,030 (January 1972) which is linked to Ksp by the relationship:

$$\frac{Ksp}{a_s} = 1000$$

In the present application, the absorbing power is expressed in terms of specific absorbence.

The following examples illustrate the invention without, however, limiting it.

EXAMPLE 1

Preparation of 2'-acrylamidomethyl-4'-butoxy-5'methoxy-3-benzylidenecamphor:

a) Preparation of 4'-butoxy-3-methoxy-3-benzylidenecamphor

182.68 g of camphor and 71.29 g of sodium methylate in one litre of toluene are heated for one hour at 80°C. 249.9 g of 4-butoxy-3-methoxybenzaldehyde are added and the reaction mixture is heated under reflux for 2.5 hours.

After cooling, the reaction mixture is poured into 1.5 litres of water. The organic phase is decanted off, washed with water, and then dried over sodium sulphate. After evaporating off the toluene under reduced pressure, the oily residue is recrystallized in a 25:75 mixture of water:isopropanol. 164 g of the product expected are obtained in the form of fine crystals with the following characteristics:

Melting point: 62°C

Elemental analysis:

	C	H
Calculated:	77.19	8.17
Found:	77.22	8.75

UV spectrum (methanol)

λ Max.: 330 nm

ε : 20,900

b) Preparation of 2'-acrylamidomethyl-4'-butoxy-5'-methoxy-3-benzylidenecamphor:

500 cm^3 of concentrated sulphuric acid and 500 cm^3 of acetic acid are mixed at 0°C. 335 g of 4'-butoxy-3'-methoxy-3-benzylidenecamphor are slowly introduced, with stirring, maintaining the temperature at approximately 0°C. When the product is dissolved, 0.1 g of sodium nitrite and 102 g of N-hydroxymethylacrylamide is added.

The mixture is stirred for 2 hours at 0°C and the reaction mixture is slowly poured into iced water.

The gummy precipitate formed hardens gradually.

The suspension is filtered, washed several times with water and dried under vacuum. 410 g of the product expected are obtained in the form of a whitish powder with the following characteristics:

Melting point: 55°C

Elemental analysis:

	C	H	N	O
Calculated ($2H_2O$):	67.68	8.46	3.04	20.82
Found ($2H_2O$):	67.48	8.48	3.00	20.67

UV spectrum (chloroform)

λ Max.: 331 nm

a_s = 30

^1H NMR spectrum ($CDCl_3$/TMS): in agreement with the structure.

EXAMPLE 2

Preparation of poly(2'-acrylamidomethyl-4'-butoxy-5'-methoxy-3-benzylidenecamphor)

a) Polymerization initiated by hydrogen peroxide-ascorbic

acid system

100 g of 2'-acrylamidomethyl-4'-butoxy-5'-methoxy-3-benzylidenecamphor obtained in Example 1 b) is dissolved in 200 g of isopropanol and 15 g of 30% hydrogen peroxide at 80°C. A solution of 10 g of ascorbic acid in 200 g of water is added in the course of 2 h 40 min, at 80°C, and the mixture is heated under reflux for a further period of 30 min. The mixture is cooled to ambient temperature and the isopropanol is decanted off. The polymer is washed with methanol, dried under vacuum and ground. 67 g of a product are obtained in the form of a yellowish powder with the following characteristics:

Elemental analysis:

	C	H	N	O
Calculated ($0.75H_2O$):	71.15	8.32	3.19	17.33
Found ($0.75H_2O$):	71.05	8.29	3.10	16.97

UV spectrum (chloroform)

λ Max.: 334 nm

a_s = 27

No free monomer is detected by silica gel chromatography using $CHCl_3$ as the solvent and 30:70 hexane: ether as the eluent.

b) Polymerization initiated by azobisisobutyronitrile:

100 g of 2'-acrylamidomethyl-4'-butoxy-5'-methoxy-3-benzylidenecamphor and 10 g of azobisisobutyronitrile in 750 cm^3 of toluene are heated under reflux for 4 hours. The solvent is distilled off under reduced pressure and

the residue is redissolved in a minimum of anhydrous acetone. The polymer expected is obtained by precipitating in hexane. 90 g of a yellow powder are obtained, with the following characteristics:

UV spectrum (chloroform)

λ Max.: 332 nm

a_s = 28

EXAMPLES 3 TO 6

a) The different 3'-acrylamidomethyl-4'-alkoxy-3-benzylidenecamphor of formula $CH_2=CO-NH-CH_2-X$ in which X represents a group of formula II attached in position 3' to the acrylamidomethyl group, with R^2 representing $-O-C_4H_9$, $-O-C_6H_{13}$, $-O-C_8H_{17}$ or $-O-C_{12}H_{25}$ and R^1 representing -H, were prepared according to a procedure similar to that of Example 1b).

The characteristics of these compounds are given in Table 1 below.

TABLE 1

Ex	R_2	UV Spectrum (CH_2Cl_2)		ELEMENTAL ANALYSIS							
				Calculated %				Found %			
		max (nm)	specific absorbance	C	H	N	O	C	H	N	O
				$C_{25}H_{33}NO_3$							
3a	$-OC_4H_9$	312	47	75.95	8.35	3.54	12.15	76.01	8.32	3.50	12.16
				$C_{27}H_{37}NO_3$							
4a	$-OC_6H_{13}$	313	46	76.55	8.80	3.30	11.73	76.66	8.97	3.36	11.01
				$C_{29}H_{41}NO_3 \cdot 0.5\ H_2O$							
5a	$-OC_8H_{17}$	315	51	75.59	9.22	3.06	12.14	75.65	9.13	3.04	12.17
				$C_{33}H_{49}NO_3$							
6a	$-OC_{12}H_{25}$	314	42	78.11	9.66	2.76	9.47	78.21	9.55	2.81	9.41

b) The different poly(3'-acrylamidomethyl-4'-alkoxy-3-benzylidenecamphor) homopolymers consisting of units of general formula I in which R^2 represents $-O-C_4H_9$, $-O-C_6H_{13}$, $-O-C_8H_{17}$ or $-O-C_{12}H_{25}$, and R^1 represents -H were prepared according to a procedure similar to that described in

Example 2a.

The characteristics of these polymers are given in Table 2 below:

TABLE 2

Ex	R_2	UV Spectrum (CH_2Cl_2)		ELEMENTAL ANALYSIS							
				Calculated %				Found %			
		max (nm)	specific absorbance	C	H	N	O	C	H	N	O
3	$-OC_4H_9$	315	43	$C_{25}H_{33}NO_3 \cdot 0.5\ H_2O$							
				74.26	8.42	3.47	13.86	74.24	8.37	3.43	13.96
4	$-OC_6H_{13}$	316	47	$C_{27}H_{37}NO_3 \cdot 0.25\ H_2O$							
				75.79	8.71	3.27	12.16	75.92	8.86	3.20	12.31
5	$-OC_8H_{17}$	315	47	$C_{29}H_{41}NO_3 \cdot 0.25\ H_2O$							
				76.40	9.11	3.07	11.42	76.18	9.10	3.12	11.66
6	$-OC_{12}H_{25}$	315	35	$C_{33}H_{49}NO_3 \cdot 0.25\ H_2O$							
				77.42	9.68	2.74	10.17	77.43	9.75	2.49	10.54

EXAMPLE 7

Preparation of an acrylamidomethyl-3-benzylidenecamphor/3'-acrylamidomethyl-4'-hexyloxy-3-benzylidenecamphor copolymer:

A mixture of 21.6 g of acrylamidomethyl-3-benzylidenecamphor, 28.3 g of 3'-acrylamidomethyl-4'-hexyloxy-3-benzylidenecamphor and 7.5 g of 30% hydrogen peroxide in 100 g of isopropanol is heated under reflux. A solution of 5 g of ascorbic acid in 50 g of water is added dropwise in the course of 3 hours. When the introduction is complete, the mixture is stirred for a further period of 30 minutes under reflux. The reaction mixture is allowed to cool and the polymer formed is decanted off. After washing with methanol, filtering and drying, 43 g of copolymer are obtained with the following characteristics:

Elemental analysis: $(C_{48}H_{62}N_2O_5 \cdot H_2O)_n$

	C	H	N	O
Calculated	75.01	8.49	3.60	12.89
Found	75.39	8.38	3.66	12.57

UV spectrum

λ Max.: 302 nm

Specific absorbance: 45

EXAMPLES OF FORMULATION

EXAMPLE I

A milk (oil-in-water emulsion) was prepared, with the following composition (by weight):

Polymer of Example 7 ..... 1.5

Polymer of Example 2a	1.5
Cetyl stearyl alcohol	1.6
Cetyl stearyl alcohol with 33 moles of ethylene oxide	6.4
Mixture of glycerol monostearate and distearate sold under the name GELEOL by GATTEFOSSE	3.5
C_{12}-C_{15} alcohol benzoate sold under the name FINSOLV TN by FINETEX	15
Vaseline oil	3.5
Propylene glycol	12
2-ethylhexyl para-aminobenzoate	3
Preservative	0.2
Perfume	0.3
Demineralized water q.s.	100 g

The emulsion is prepared following the procedure below:

Phase A consisting of the polymers of Examples 8 and 2a, cetyl stearyl alcohol, cetyl stearyl alcohol with 33 moles of ethylene oxide, glycerol monostearate and distearate, C_{12}-C_{15} alcohol benzoate, vaseline oil and 2-ethylhexyl para-aminobenzoate is heated to 85°C on a water bath.

Phase B consisting of propylene glycol and water is heated to 85°C on a water bath.

Phase A is poured into phase B over a period of 10 minutes, with vigorous stirring. The stirring is then

slowed down, and the preservative followed by the perfume are then added at a temperature of 40°C. The mixture is allowed to cool to ambient temperature, with moderate stirring.

EXAMPLE II

A milk is prepared in a similar way, with the following composition:

Polymer of Example 2b	3
Polymer of Example 2a	2
Oleyl cetyl alcohol with 30 moles of ethylene oxide	6
Stearyl alcohol	4
FINSOLV TN	15
Oleyl alcohol	4
70% sorbitol	16
Preservative	0.2
Perfume	0.3
Demineralized water q.s.	100 g

EXAMPLE III

Composition in the form of a thick oil:

Polymer of Example 4	3
2-ethylhexyl para-methoxycinnamate	3
FINSOLV TN	26
Silica sold under the name AEROSIL R 972 by DEGUSSA	7
Cyclotetradimethylsiloxane	10
Isopropyl myristate q.s.	100 g

EXAMPLE IV

Cream (water-in-oil):

Polymer of Example 4	5
Magnesium stearate	3.5
Octyl dodecanol	10
Hydrogenated lanolin sold under the name HYDROLAN H by ONYX	1.5
Clear lanolin	4
Beeswax	4.5
Sorbitan sesquioleate	4.5
FINSOLV TN	15
Vaseline oil	10
Preservative	0.2
Demineralized water q.s.	100 g

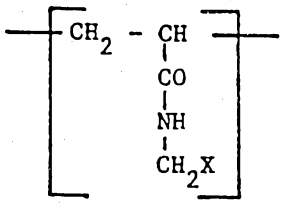
EXAMPLE V

Composition in the form of an oil:

Polymer of Example 7	3.8
2-ethylhexyl glyceryl ether palmitate	30
Cyclotetradimethylsiloxane	20
Perfume	0.2
FINSOLV TN q.s.	100 g

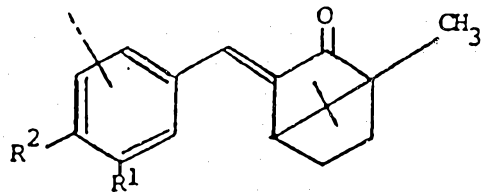
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS :

1. Ultraviolet radiation-absorbing polymers, characterized in that they contain units of formula I:



(I)

in which X is a group derived from benzylidenebornanone of formula II:



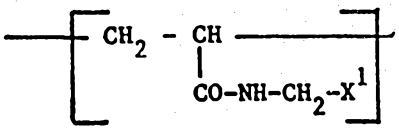
(II)

in which R^1 represents a hydrogen atom or a C_1-C_{12} alkoxy group and R^2 represents a C_4-C_{12} alkoxy group.

2. Polymers according to claim 1, characterized in that R^1 represents a hydrogen atom or a methoxy or butoxy group.

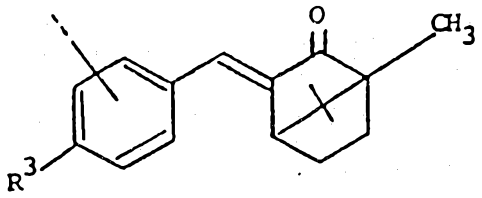
3. Polymers according to either one of the preceding claims, characterized in that R^2 represents a butoxy, hexyloxy, octyloxy or dodecyloxy group.

4. Polymers according to any one of the preceding claims, characterized in that they contain, in addition, units of formula I':



(I')

in which X^1 represents a group derived from bornanone of formula II':



(II')

in which R^3 represents a hydrogen atom or a C_1-C_4 alkyl group.

5. Polymers according to any one of the preceding claims, characterized in that they contain at least 5 mol% of units of formula I.

6. Polymers according to claim 4, characterized in that they contain units I and I' in proportions which may range from 5:95 to 95:5 in moles.

7. Polymers according to any one of the preceding claims, characterized in that they have a molar mass from one thousand to one million.

8. Polymers according to claim 7, characterized in that they have a molar mass from 1500 to 100,000.

9. Process for the preparation of the polymers as defined in any one of the preceding claims, characterized in that a "sunscreen monomer" of formula IV:

$$CH_2 = CH - CO - NH - CH_2 - X \qquad (IV)$$

in which X is defined as above, is prepared and in that the said sunscreen monomer is subjected to a homopolymerization or to a copolymerization with at least one other ethylenically unsaturated comonomer which is capable of absorbing

ultraviolet radiation.

10. As means for the preparation of the polymers of any one of claims 1 to 8, monomers of formula IV or IV':

$$CH_2 = CH - CO - NH - CH_2 - X \qquad (IV)$$

$$CH_2 = CH - CO - NH - CH_2 - X^1 \qquad (IV')$$

in which X and X^1 are defined as in claims 1 and 4 respectively with the proviso that R^3 in X^1 does not represent hydrogen.

11. Cosmetic compositions for protection against ultraviolet radiations, characterized in that they contain, as active ingredient, at least one polymer as defined in any one of claims 1 to 8.

12. Compositions according to claim 11, characterized in that they contain from 0.2 to 20% by weight of the said polymers.

13. Use of the polymers as defined in any one of claims 1 to 8, in the preparation of cosmetic compositions intended for protecting the skin against sunburn.

14. Polymers according to Claim 1, cosmetic compositions comprising a said polymer, or processes for the preparation or use thereof, substantially as hereinbefore described with reference to the Examples.

DATED this 5th day of July, 1990

L'OREAL

By Its Patent Attorneys

DAVIES & COLLISON