COMMONWEALTH of AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

We L'OREAL,
of 14, rue Royale,
75008,
PARIS

597022

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

"COSMETIC PREPARATIONS INTENDED TO PROTECT THE SKIN AGAINST THE UNDESIRABLE EFFECTS OF ULTRAVIOLET RADIATION"

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

Details of basic application(s):—

Number	Convention Country	Date
86 00274	FRANCE	10th January 1986

APPLICATION ACCEPTED AND AMENDMENTS ALLOWED 8.3.90

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 12th day of January 19 87

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

Insert title of invention.

In support of the Application made for a patent ~~patent of addition~~ for an invention entitled : "COSMETIC PREPARATIONS INTENDED TO PROTECT THE SKIN AGAINST THE UNDESIRABLE EFFECTS OF ULTRAVIOLET RADIATION"

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 the applicant for the patent of addition~~

or (b) I am authorized by

L'OREAL

the applicant..... for the ~~patent of addition~~ patent to make this declaration on ~~their~~ its 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 the actual inventor of the invention~~

or (b) ~~We are~~

Claude MAHIEU, of 90 avenue de Villiers, 75017 Paris, FRANCE; Christos PAPANTONIOU, of 17, rue des Basserons, 95160 Montmorency, FRANCE; Bernard JACQUET, of 50 rue Prosper Legoute, 92160 Antony, FRANCE

~~I~~ are the actual inventor..... of the invention and the facts upon which the applicant..... is ~~are~~ entitled to make the application are as follows :–

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

The applicant would if a patent were granted on an application made by the 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 ..... 10th January 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 ..... this 31st day of December 1986

Signature of declarant(s) (no attestation required)

Directeur du Département BREVETS

André VIOUT

Note: Initial all alterations.

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

DAVIES & COLLISON, MELBOURNE and CANBERRA.

(12) PATENT ABRIDGMENT (11) Document No. AU-B-67484/87
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 597022

(54) Title
U.V. FILTER COMPOSITION WITH ACRYLAMIDE UNIT COVALENTLY BONDED DIRECTLY TO BASE POLYMER

International Patent Classification(s)
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(71) Applicant(s)
L'OREAL

(72) Inventor(s)
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(74) Attorney or Agent
DAVIES & COLLISON, MELBOURNE

(56) Prior Art Documents
GB 1579697

(57) The object of the present invention is new cosmetic preparations intended to protect the skin against the undesirable effects of ultraviolet radiation, and in particular against the undesirable effects of exposure to the sun (burning and possibly browning of the skin).

CLAIM

1. Cosmetic preparations intended to protect the skin against the undesirable effects of ultraviolet radiation, containing as active ingredient filtering the ultraviolet radiation at least one polymer composition containing a polymer with acrylamide structural units bonded covalently to a compound absorbing ultraviolet radiation, characterized in that the polymer of said polymer composition have a molecular weight distribution such that at least 80% of the polymer molecules have a molecular weight less thar 20,000, the molecular weights being measured by the method of exclusion chromatography, in comparison with standard samples of polystyrene.

COMMONWEALTH OF AUSTRALIA

PATENT ACT 1952

COMPLETE SPECIFICATION

(Original)

597022

FOR OFFICE USE

Class Int. Class

Application Number: 67484/89
Lodged:

Complete Specification Lodged:
Accepted:
Published:

Priority:

Related Art:

This document contains the amendments made under Section 49 and is correct for printing.

Name of Applicant: L'OREAL,

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FRANCE

Actual Inventor(s): Claude MAHIEU
Christos PAPANTONIOU
Bernard JACQUET

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

Complete Specification for the invention entitled:

"COSMETIC PREPARATIONS INTENDED TO PROTECT THE SKIN AGAINST THE UNDESIRABLE EFFECTS OF ULTRAVIOLET RADIATION"

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

The object of the present invention is new cosmetic preparations intended to protect the skin against the undesirable effects of ultraviolet radiation, and in particular against the undesirable effects of exposure to the sun (burning and possibly browning of the skin).

It is known that ultraviolet radiation having a wavelength in the range from 280 to about 350 nm is responsible for the inflammation or erythema of the skin observed when the human body is exposed without protection to the sun's rays. This wavelength range is sometimes known as the "erythematous zone".

It is also known that the ultraviolet radiation responsible for bronzing the skin has a wavelength of from 315 to about 400 nm.

Preparations are known which have the property of absorbing the ultraviolet in the erythematous zone, while allowing the radiation responsible for bronzing to pass, and the use of such compounds as "solar filters" in cosmetic preparations promoting the bronzing of the skin and preventing burning and irritation of the skin has already been proposed.

In addition, some users wish to avoid browning and the use has therefore been proposed in these cosmetic preparations of "filters" forming a screen of greater or lesser proportions against ultraviolet radiation in the wavelength range 315-400 nm, possibly in association with compounds filtering UV radiation in the erythematous zone, so as to avoid both browning and burning of the skin.

The use of solar filters bonded covalently to polymers has been recommended, notably in French patents 73.23254 and 76.23174. Presentation in the form of polymers has the advantage of reducing or suppressing the penetration of the filter compound into the organism by passing through the epidermis, which makes it possible to avoid any risk of toxic side-effects.

However, continued study of such "anti-solar polymers" showed that the use of them had certain disadvantages.

To obtain preparations having a high filtering power it is necessary to use considerable concentrations of anti-solar polymer, and this raises difficulties both at the stage of the manufacture of cosmetic preparations and at the stage of applying these preparations to the skin.

Indeed, when it is wished to produce high concentrations, considerable difficulties are experienced in bringing the polymers into solution, which represents a disadvantage at the formulation level. This disadvantage is even more pronounced when an attempt is made, in order to produce a high filtering efficiency, polymers of the homopolymer type, practically every group of which is replaced by a filter substance.

In addition, anti-solar cosmetic preparations obtained with such high concentrations of anti-solar polymers are not satisfactory for the user, since they have a sticky and greasy feel which is unpleasant.

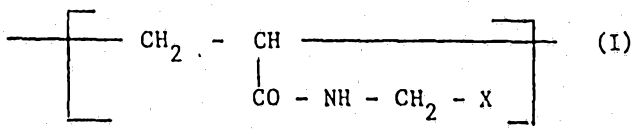
It has now been discovered that if appropriate measures are taken on the preparation of the anti-solar polymers, it is possible to obtain new compositions which have a high proportion of polymer molecules of low molecular weight, by means of which the disadvantages mentioned above may be eliminated.

The present invention has as its object new cosmetic preparations intended to protect the skin against the undesirable effects of ultraviolet radiation which contain as an active ingredient filtering the ultraviolet radiation at least one polymer composition containing polymers with acrylamide groups covalently bonded to a compound absorbing the ultraviolet, possibly in association with groups derived from hydrophilic comonomers, characterized in that the polymers of said

polymer composition have a molecular weight distribution such that at least 80% of the polymer molecules have a molecular weight less than 20,000, the molecular weights being measured by the method of size exclusion chromatography, in comparison with standard samples of polystyrene.

The polymer compounds used according to the invention preferably have a molecular weight distribution such that fewer than 10% of the molecules have, under the same conditions as those given above, a molecular weight greater than 40,000.

The invention has in particular as its object cosmetic preparations such as those described previously, characterized in that said polymers contain groups of formula I



(I)

in which X represents an aromatic group imparting to the polymers an ultraviolet absorption in the wavelength zone possibly ranging from 280 to 400 nm, possibly in association with groups derived from hydrophilic ethylen-unsaturated comonomers, it being understood that the groups of formula I represent at least 10% by weight of the polymer.

When groups derived from hydrophilic comonomers are present, the groups of formula I may represent, for example, 10 to 99% by weight of the polymer.

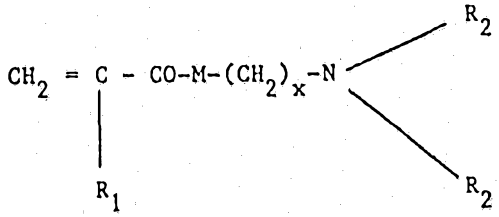
The polymers present in the polymer compound used according to the invention are therefore notably polymers containing solely groups of formula I, it being understood that several different groups, corresponding to different X groups, may be present in the same polymer molecule.

It is known that solar filters are present in cosmetic preparations either in the form of oily solutions, in the form of aqueous or hydroalcoholic solutions, or else in the form of aqueous and/or oily solutions in compounds in the form of emulsions.

The polymer compounds as described above which contain only groups of formula I are sufficently soluble in oils and the production, with these compounds, of oil-based cosmetic preparations does not present any particular difficulties.

On the other hand, if it is required to obtain a water-soluble polymer compound, it is necessary to polymerize the "filter monomers" corresponding to the groups of formula I with hydrophilic comonomers.

The hydrophilic comonomers are chosen in particular from N-vinylpryyolidone, N,N-dimethylacrylamide, acrylic acid, methacrylic acid and monomers of the general formula:



(II)

where M represents -O- or -NH-,

x is a number equal to 2 or 3,

R_1 represents -H or $-CH_3$ and

R_2 represents $-CH_3$ or $-C_2H_5$,

it being understood that the amine groups present may be quaternized or salified before or after polymerization.

Among the comonomers of general formula II it is possible to mention by way of example N,N-2-dimethylamino ethyl, N,N-3-diethylaminopropyl methacrylamide, etc.

The amine groups may be salified with a mineral acid, for example hydrochloric acid, or an organic acid such as lactic acid. They may also be quaternized by a conventional quaternization agent such as dimethyl sulphate, methyl chloride, chloroacetic acid, etc.

To prepare the polymer compounds as decribed above, monomers of formula III

$$CH_2 = CH\text{-}CO\text{-}NH\text{-}CH_2\text{-}X \qquad (III)$$

where X is defined as previously, are polymerized in solution, possibly in the presence of ethylene-unsaturated hydrophilic comonomers, in the presence of a polymerization initiator, using known methods to promote the formation of polymer molecules of low molecular weight.

Generally speaking, the initial filter monomers of formula III may be prepared by known methods described, for example, in French patents 73.23254 and 76.23174.

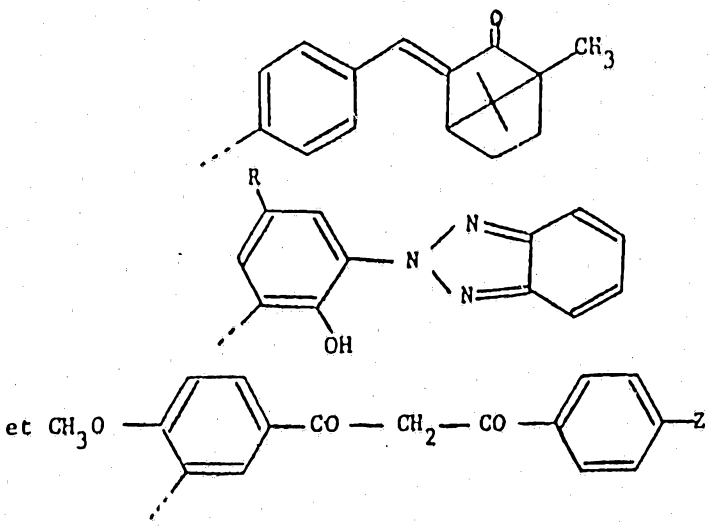
The process for preparing said polymer compounds may also have the following characteristics, taken individually or in combination.

- The polymerization initiator is a redox pair, for example the pair ascorbic acid - hydrogen peroxide;

- to obtain polymer compounds having low molecular weights it is possible to use various known processes, taken individually or in combination. Among these processes can be mentioned the use of a large quantity of initiator, the use of so-called chain-transfer agents (for example halogenated compounds, aldehydes, thiols, etc.), or else the use of a large quantity of

solvent during polymerization.

Among the radicals of the filter substances symbolized by X in formulae I and III particular mention will be made, by way of example, of the radicals represented by the following formulae:

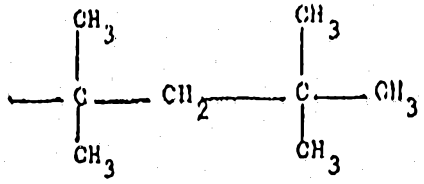


in which R represents a methyl or tertiary octyl group and Z represents a t-butyl group, i.e. the radicals of 3-benzylidene d1 camphor, [2-(2'-hydroxy-5'-tert-octyl phenyl)] 2H benzotriazole, [2-2'-hydroxy-5'-methyl phenyl)] 2H benzotriazole and 4-tert-butyl-4'methoxy dibenzoylmethane respectively.

The present invention therefore has as its object cosmetic preparations intended to protect the skin against the undesirable effects of ultraviolet radiation which contain as an active ingredient filtering the ultraviolet radiation at least one polymer compound as described previously.

These preparations are prefer ably presented in the form

in which R represents a methyl or tertiary octyl group of formula



and Z represents a t-butyl group, i.e. the radicals of 3-benzylidene dl camphor, [2-(2'-hydroxy-5'-tert-octyl phenyl)] 2H benzotriazole, [2-2'-hydroxy-5'-methyl phenyl)] 2H benzotriazole and 4-tert-butyl-4'methoxy dibenzoylmethane respectively.

The present invention therefore has as its object cosmetic preparations intended to protect the skin against the undesirable effects of ultraviolet radiation which contain as an active ingredient filtering the ultraviolet radiation at least one polymer compound as described previously.

These preparations are preferably presented in the form

of aqueous, hydroalcoholic or oil solutions, aqueous emulsions, lotions, creams, milks, gels, sticks or in the form of aerosol compositions.

These cosmetic preparations contain, in addition to the polymers having groups of formula I, the usual adjuvants generally present in such preparations and possibly other substances capable of absorbing ultraviolet radiation.

In the cosmetic preparations of the invention the concentration of polymer containing groups of formula I is variable, since it depends on the degree of protection which it is required to obtain. Generally speaking, the polymer concentration may vary from 1 to 20% by weight in relation to the total weight of the preparation.

A further object of the invention is the use of polymers containing acrylamide groups bonded covalently to a compound absorbing ultraviolet radiation in the production of anti-solar cosmetic preparations, characterized in that at least 80% of the polymer molecules have a molecular weight less than 20,000, the molecular weights being measured by size exclusion chromatography, in comparison with standard samples of polystyrene.

The absorbent power of the filter was previously expressed by means of the Ksp value (specific K), which is a function of the quantity of filtering substances contained in the sample, the measured optical density and a constantdepending on the apparatus.

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

$$Ksp = \frac{K}{\quad}$$

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

d = measured optical density
c = concentration of the solution (g/ml)
l = thickness of the cell in cm.

At present the absorbent power is defined by the term "specific absorbance a_s", define by French standard T.01030 (January 1972), linked to Ksp by the relationship

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

In the present application the absorben power is expressed by means of the specific absorbance.

The following examples illustrate the invention, wihtout, however, limiting it in any way.

Examples of the preparation of polymers

EXAMPLE 1 Preparation of a polymer derived from 3-benzylidene camphor from purified monomer.

Stage 1: Preparation of the monomer [3-(4-acylamidomehtyl benzylidene)] dl camphor.

500 g pure sulphuric acid
241 g 3-benzylidene-dl-camphor
1 g sodium nitrite

are introduced ito a reactor.

After obtaining a solution, the reactor is cooled to 0°C by means of a water bath and ice. 110 g of hydroxymethylacyl-amide in powdered form is then added and the mixture is allowed slowly to return to ambient temperature and stirring is maintained for 48 hours.

The reaction mixture obtained is poured slowly into five litres of a mixture of water and ice while being stirred; the

light beige, paste-like precipitate formed is collected and washed with water, then dissolved in two litres of ethyl acetate; the organic solution is washed with water until a neutral pH is obtained, dried over anhydrous sodium sulphate, filtered an concentrated at a temperature below 50°C under reduced pressure (20 mm Hg, i.e. about 260 Pa) until the weight is constant.

An oily, light brown residue is obtained which crystallizes coarsely on cooling.

ANALYSES

a) Thin-layer chromatography on silica gel with fluorescence indicator, eluent ethyl acetate - development with UV and iodine vapour.

2 main products Rf = 0.7 and 0.8
2 secondary products Rf = 0.33 and 0.55
presence of 3-benzylidene camphor, 5%.

b) UV spectrum

λ_{max} ($CHCl_3$) = 295 nm

Stage 2: Purification of the monomer.

50 g of untreated monomer obtained as above is mixed with 375 ml diethyl ether. The suspension is stirred vigorously for 30 minutes until a fine, white-beige precipitate is obtained. The precipitate is collected on sintered glass, then washed with 150 ml diethyl ether and dried at 25°C for 16 hours under reduced pressure.

25 g of a beige crystalline compound is collected.

ANALYSES

a) Thin-layer chromatography (TLC), silica gel support with fluorescence indicator, eluent ethyl acetate, devleopment with UV and iodine vapour.

One main product Rf = 0.75
One secondary product Rf = 0.35
Absence of 3-benzylidene camphor

b) UV spectrum

λ_{max} ($CHCL_3$) = 295 nm a_s = 71

Stage 3: Recrystallization

Recrystallization is effected in a water-alcohol mixture in the proportions: 40 cm^3 H_2O + 60 cm^3 ethyl alcohol

3 g of the compound obtained as above is dissolved at 60°C in 12 ml of the water-ethanol solution.

After cooling theproduct is obtained in the form of white crystals. After filtration and drying, 1.9 g of the required compound isobtained.

ANALYSES:

a) Thin-layer chromatography, silica gel support, with fluorescence indicator, eluent: ethyl acetate, development with UV and iodine vapour.

A single product Rf = 0.75

b) NMR spectrum ($CDCl_3$ + TMS)

The spectrum is compatible with the presence of the acrylamidomethyl function fixed in the para position of the aromatic cycle.

c) UV spectrum

λ_{max} $CHCl_3$ = 297 nm a_s = 80

Stage 4: Preparation of the homopolymer

100 g of the monomer,obtained as in the preceding stage, in solution in 200 g isopropanol and 15 g of a 30% solution of hydrogen peroxide are mixed. The mixture is heated, with stirring, to 80°C; when this temperature is reached, a solution

of 10 g ascorbic acid in 200 g water is introduced regularly within 3 hours. Stirring is maintained for half an hour. The polymer formed, which is insoluble in the reaction medium, is in suspension in the form of oily droplets. When the reaction is completed and the stirring is discontinued the polymer is decanted. The supernatant phase, composed of isopropyl alcohol, water, monomer and initiator residue, is removed. The polymer is dissolved in 200 g methylene chloride. Methanol is added to this solution until the appearance of an incipient opalescence, which is obtained by the addition of 200 g methanol. This solution in concentrated at 50°C under normal pressure in order progressively to remove the methylene chloride and to promote a slow precipitation of the polymer. During the concentration 200 g methanol is again introduced and the removal of the methylene chloride is continued.

At the end of this operation the oily product precipitated is collected, dried and pulverized. 70 g of pure polymer in the form of a light yellow powder is obtained.

ANALYSES:

a) TLC silica gel support, with fluorescence indicator, eluent ethyle acetate, development by UV

Polymer: Rf = 0

Absence of monomer (Rf = 0.75)

Absence of 3-benzylidene camphor (Rf = 0.95)

b) UV spectrum

$\lambda_{max}(CHCl_3)$ = 295 nm a_s = 68

EXAMPLE 2

Preparation of a polymer derived from 3-benzylidene camphor from untreated monomer.

As in example 1, stage 4, the monomer obtained ized as in example 1, stage 1.

ANALYSES:

a) TLC: identical to example 1, stage 4.

b) UV spectrum: $\lambda_{max}(CHCl_3)$ = 295 nm a_s = 58

c) Determination of the molecular weight distribution.

The polymer obtained is characterized in solution in tetrahydrofurane (THF) by size exclusion chromatography in a set of columns of porosity 60, 500, 3×10^3, 3×10^4 Å; standards: polystyrene.

Molecular weight distribution:

$\bar{M} < 4000$	43%
$4,000 < \bar{M} < 17,000$	46%
$17,000 < \bar{M} < 40,000$	3%
$40,000 < \bar{M} < 68,000$	2%
$68,000 < \bar{M}$	6%

EXAMPLE 3:

Preparation of a polymer derived from 2H[2-(2'-hydroxy-t-octyl-5'-phenyl)] benzotriazole.

Stage 1

Preparation of the monomer 2H[2-(2'hydroxy-3'-acrylamidomethyl-t-octyl-5'-phenyl)] benzotriazole.

600 g sulphuric

163 g 2H[2-(2'-hydroxy-t-octyl-5'phenyl)]-benzotirazole are introduced into a reactor.

This bringing into solution is exothermal and the temperature of the mixture reaches 35°C. After complete dissolving the reaction mixture is cooled to 0°C60.6 g hydroxymethyl acrylamide is introduced in portions within 30 minutes and cooling is then stopped. The temperature reaches and remains at 30°C throughout the duration of the reaction.

After 24 hours of reaction the mixture is diluted with

500 ml ethanol and then poured slowly into 5 litres of a mixture of water and ice with vigorous stirring; the white powder obtained is filtered, then washed with water until a pH of 5 is obtained; after filtration the untreated product is dissolved in 3 litres of chloroform. The residual water is removed by decantation; after drying over sodium sulphate the organic phase is conventrated to 250 g and the oily residue is dissolved in 2 litres of cyclohexane with reflux. The solution is filtered, then cooled: after crystallization the required product is filtered and dried.

153 g of the required product is obtained, i.e. a yield of 75%.

ANALYSES

F° = 156°C

TLC: LS 254 silica gel support
solvent chloroform
eluent:
- ethyl acetate 90
- chloroform 10

UV development Rf = 0.66 (initial product Rf = 0.96)

UV spectrum with 1 mg/100 ml in chloroform

$\lambda_{max.1}$ = 305 nm; a_{s1} = 40.8
$\lambda_{max.2}$ = 340 nm; a_{s2} = 37.9

STAGE 2: PREPARATION OF THE HOMOPOLYMER

- 35 g 2H[2-(2'-hydroxy-3'-acrylamidomethyl-t-octyl-5'-phenyl)]-benzotriazole
- 70 g isopropanol
- 5.25 g of a 30% solution of H_2O_2

are introduced into a reactor.

The mixture is heated to 80°C and then a solution of 3.5 g ascorbic acid in 70 ml water is added at a constant rate

in 3 hours, and stirring is then continued for a further 30 minutes.

The mixture is then cooled to 0°C. The raw polymer deposited at the bottom of the reactor is recovered by filtration.

Quantity obtained: 35 g

ANALYSES:

a) TLC on silica gel; UV development;
solvent $CHCl_3$; eluent ethyl ether.
Polymer: Rf = 0
Absence of monomer (Rf = 0.95)

b) UV spectrum (solvent: $CHCl_3$)
max.1 = 304 nm a_{s1} = 37.5
max.2 = 340 nm a_{s2} = 33.5

c) Determination of the molecular weight distribution under conditions identical to those in example 2.

$\bar{M} <$ 4,000	44%
4,000 $< \bar{M} <$ 17,000	47%
17,000 $< \bar{M} <$ 40,000	8%
40,000 $< \bar{M}$ 68,000	4%
68,000 $< \bar{M}$	1%

EXAMPLE 4: Preparation of a polymer derived from 4-t-butyl-4'-methoxy-3'-methyl dibenzoylmethane.

STAGE 1: Preparation of the monomer 4-t-butyl-3'-acrylamidomethyl-4'-methoxy dibenzoylmethane

- 600 g sulphuric acid
- 93 g 4-t-butyl-4'-methoxy dibenzoylmethane

are introduced into a reactor.

This mixture is stirred for 15 minutes in order to dissolve the solid; after complete dissolving the reaction mixture

is cooled to 0°C, and then, within 30 minutes, 30.3 g hydroxymethylacrylamide is introduced in portions and cooling is stopped. The colour has changed from orange to red.

After 24 hours' reaction the mixture is poured slowly into 4 litres of a mixture of water and ice with vigorous stirring. The precipitate is washed with water and filtered, then dissolved in 500 ml dichloroethane. The organic phase is washed with water until neutral, then concentred dry. The residue is recrystallized in 1 litre of toluene in the presence of animal black.

100 g of the product required is obtained (yield = 85%). This is a new product which forms part of the invention.

ANALYSES

F° = 164°C

- TLC
  - support: LS 254 silica gel
  - solvent: chloroform
  - eluent: ethyl ether
  - UV development: main product Rf = 0.33
    secondary product Rf = 0.08
    initial product: Rf = 0.86
- UV spectrum at 1 mg/100 ml in chloroform

$\lambda_{max.}$ = 357 nm a_s = 86

STAGE 2: PREPARATION OF THE HOMOPOLYMER

- 100 g 4-t-butyl-3'acrylamidomethyl-4'methoxydibenzouylmethane
- 200 g isopropanol
- 15 g of a 30% solution of H_2O_2

are introduced into a reactor.

The mixture is heated to 80°C with stirring.

A solution of 10 g ascorbic acid in 200 ml water is added at a constant rate in 3 hours and the stirring is continued

for a further 30 minutes.

The reaction mixture is cooled to 0°C and the stirring is halted.

The solid polymer deposited is collected by filtration, dissolved in 200 g methylene chloride and methanol is added until the beginning of opalescence (which takes about 200 g methanol). The solution is concentrated at ambient pressure by heating to 50°C in order to remove the methylene chloride. The polymer, which is insoluble in methanol, is precipitated, whereas the residual monomer remains in solution. 50 g pure polymer is obtained after drying.

Analyses: TLC on silica gel; UV development; solvent $CHCl_3$; eluent ethyle ether.
Polymer: Rf = 0
Absence of monomer (Rf = 0.5)
- UV spectrum: λ_{max} ($CHCl_3$) = 356 nm a_s = 69.2

- Determination of the molecular weight distribution under conditions identical to those in example 2.

$\bar{M}$ < 4,000	35%
4,000 < $\bar{M}$ <17,000	63%
17,000 < $\bar{M}$ <40,000	2%
40,000 < $\bar{M}$	not detectable.

EXAMPLE 5

Copolymer composed of d1[3-(4'-acrylamidomethyl-benzyidene)] camphor and [2-(2'-hydroxy-3'-acrylamidomethyl-5'-t'octyl phenyl)] 2H-benzotriazole.

50 g of monomer prepared as in example 1, stage 1, 50g of monomer prepared as in example 3, stage 1, 200 g isopropanol and 20 g ascorbic in solution in 100 g water are introduced into a reactor. The reaction mixture is brought to reflux and

then 75 g of a 30% hydrogen peroxide solution diluted with 30 g water is introduced. During the reaction the polymer formed is separated from the solvent. On ceasing stirring after a reaction time of 4 hours the polymer is deposited at the bottom of the reactor. The supernatant phase, composed of isopropyl alcohol, water, monomers and iniator residues, is removed. The polymer is dissolved in 200 g methylene chloride and isopropyl ether is then added until there is a beginning of opalescence. The solution is concentrated under normal pressure at 50°C until the methylene chloride is removed, which brings about the precipitation of the polymer in the form of an oil. It is collected, dried and pulverized. 80 g of light yellow powder is obtained.

ANALYSES:

- TLC: support: silica gel with fluorescence indicator;
  eluent: ethyl acetate or diethyl ether.

  Results: absence of residual monomers; polymer Rf = 0

- UV spectrum at 1 mg/100 ml in $CHCl_3$

  $\lambda_{max.1}$ = 298 nm a_s = 42

  $\lambda_{max.2}$ = 340 nm a_s = 18

Molecular weight distribution: more than 80% of the polymer having a molecular weight less than 20,000.

EXAMPLE 6

Homopolymer ofd1[3-(acrylamidomethyl-4'benzylidene)] camphor.

15 g of the monomer of example 1, stage 1, 30 g isopropanol, 2.25 g of a 30% solution of hydrogen peroxide and 0.375 g dodecy mercaptan are mixed. The reaction mixture is brought to the solvent reflux, and then a solution of 1.5 g ascorbic

acid in 30 ml water is added. The completion of polymerization and the purification of the polymer are effected as in example 1, stage 4.

The polymer is characterized by its UV spectrum in solution in chloroform

λ_{max} = 296 nm a_s = 59

Distribution of molecular weights: more than 80% polymer having a molecular weight less than 20,000.

EXAMPLE 7

Copolymer composed of [3-(4'-acrylamidomethyl-benzylidene)] di-camphor and trimethyl ammoniopropyl methacrylamide chloride (or MAPTAC).

60 g of the monomer of example 1, stage 1, 80 g of an aqueous 50% solution of MAPTAC, 120 g isopropanol and 20 g acetic acid are mixed. This mixture is brought, under nitrogen to solvent reflux and then a solution of 75 of 30% hydrogen peroxide, diluted with 30 g water, is added regularly in 35 minutes.

At the end of this addition the reaction is continued for 2½ hours, and them the reaction mixture, concentrated to 270 g, is diluted with 55 g acetone. The opalescent solution of raw polymer is poured slowly into 5.5 litres of acetone with vigorous stirring and the polymer presipitated is collected and dried. 66 g of pure polymer which is soluble in water is obtained.

- TLC
  - support: silica gel;
  - solvent: methanol;
  - eluent: ethyl acetate.

Absence of residual filter monomer.

- UV spectrum in water:

λ_{max} = 295 nm a_s = 20

NMR 1_H: indicates a composition of 40% filter monomer structural units and 60% MAPTAC structural units.

Molecular weight distribution: more than 80% polymer having a molecular weight less than 20,000.

EXAMPLE 8.

Copolymer composed of 2H-[2-(2'-hydroxy-3'-acryliamido-methyl-5'-tert.-octyl phenyl)]-benzotriazole and MAPTAC.

45 g of the monomer prepared as in example 3, stage 1, 110 g of a 50% MAPTAC solution, 5 g dodecyl mercaptan, 200 g isopropanol and 2.5 g azobis-isobutyronitrile are mixed together. This mixture, under notrogen, is brought to solvent reflux and held there for 6 hours. The polymer formed, which is insoluble in the reaction medium, is recovered and dissolved in a 50/50 mixture of methylene chloride and methanol, then precipitated with 6 litres diethyl ether. After drying, 79 g of water-soluble polymer is obtained.

- TLC.
  Support: silica gel;
  solvent: methanol;
  eluent: diethyl ether.

Absence of residual filter monomer.

- UV spectrum in water

$\lambda_{max\ 1}$ = 300 nm a_s = 12.0

$\lambda_{max\ 2}$ = 335 nm a_s = 10.7

Molecular weight distribution: more than 80% polymer having a molecular weight less than 20,000.

EXAMPLE 9

Copolymer composed of [3-(4'-acrylamidomethyl-benzylidene)] dl-camphor and 2-acrylamido-2-methylpropane sulphonic acid (AMPS).

95 g of polymer prepared as in example 1, stage 1, 5 g AMPS, 200 g isopropanol and 20 g ascorbic acid in solution in 100 g water are mixed together. This mixture is brought to the solvent reflux and 75 g of a 30% hydrogen peroxide solution diluted with 30 g water is added regularly within 30 minutes. The polymerization reaction is continued for 2½ hours. The precipitated polymer is dissolved in 200 ml tetrahydrofurane and precipitated in 4 litres acetonitrile. After drying 76 g of pure polymer is obtained.

- TLC
  Support: silica gel;
  solvent: chloroform;
  eluant: ethyl acetate.

Absence of free filter monomer.

- UV spectrum in chloroform

λ_n = 296 nm a_s = 52

Microanalysis:	C	H	N	S
Found:	72.9	7.8	4.1	0.6

Molecular weight distribution: more than 80% polymer having a molecular weight less than 20,000.

EXAMPLE 10

Copolymer composed of [3-(4'-acrylamidomethyl-benzylidene] dl-camphor and AMPS.

60 g monomer prepared as in example 1, stage 1, 40 g AMPS, 200 g isopropanol and 20 g ascorbic acid in solution in 100 g water are mixed together.

This mixture is brought to solvent reflux and then 75 g of a 30% hydrogen peroxide solution diluted with 30 g water is

added within 30 minutes. The polymerization reaction is continued for 2½hours. The heterogeneous reaction mixture is homogenized with 50 g methanol, brought to neutrality by the addition of a 5N sodium hydroxide solution and then precipitated in 4 litres acetonitrile.

63 g of water-soluble ploymer is obtained.

- TLC
  Support: silica gel;
  solvent: methanol;
  eluent: diethyl ether
  Absence of free filter monomer.

- UV spectrum in water:
  λ_{max} = 298 nm a_s = 12.5

Microanalysis:	C	H	N	S
Found:	46.29	5.77	3.70	5.10

Molecular weight distribution: more than 80% polymer having a molecular weight less than 20,000.

EXAMPLE 11

Copolymer composed of [3-(4'-acrylamidomethyl-benzylidene)] dl-camphor and acrylic acid.

10 g monomer prepared as in example 1, stage 1, 40 g acrylic acid, 100 g isopropanol and 7.5 g of a 30% hydrogen peroxide solution are mixed together. The reaction mixture is brought to reflux. A solution of 5 g ascorbic acid in 100 g water is added regularly within 3 hours. The polymerization reaction is maintained for 4 hours.

The final reaction medium is concentrated, then diluted with acetonitrile until opalescence appears, then finally precipitated in 2 litres acetonitrile.

29 g of dry product is obtained which, after neutraliz-

ation with sodium hydroxide, is completely soluble in water.

- TLC:
  Support: silica gel;
  solvent: methanol;
  eluent: diethyl ether

Absence of residual filter monomer.

UV specturm (before neutralization) in methanol:

λ_{max} = 296 nm a_s = 11.9

Acid number: 470

Microanalysis: (before neutralization)	C	H	N	O
Found:	53.9	6.5	1.6	35.5

Molecular weight distribution: more than 80% polymer having a molecular weight less than 20,000.

EXAMPLE 12

Copolymer composed of [3-(4'-acrylamidomethyl-benzylidene] dl-camphor and N,N-dimethylacrylamide.

4g monomer prepared as in example 1, stage 3, 16 g N,N-dimethylacrylamide, 40 g isopropanol a 3 g 30% hydrogen peroxide solution are mixed, the reaction mixture is reflux heated and a solution of 2 g ascorbic acid in 40 g water is added regularly within 3 hours. The polymerization reaction is maintained for 4 hours. The reaction mixture is concentrated, the residue is dissolved in 100 g acetone and precipitated in 1 litre ethyl acetate. 13 g of product soluble in water, propylene carbonate and sorbitol is obtained.

- TLC:
  Support: silica gel;
  solvent: methanol;
  eluent: ethyl acetate.

Absence of residual filter monomer.

- UV spectrum in ethanol:

λ_{max} = 294 nm a_s = 8

Microanalysis:	C	H	N	O
Found:	56.3	8.4	10.3	23.6

Molecular weight distribution: more than 80% polymer having a molecular weight less than 20,000.

COMPARATIVE EXAMPLE

The polymer prepared as in example 2 is compared with the homopolymer prepared as in example 6 of French patent 73.23254, which is characterized under conditions identical to those previously described. The results are as follows.

a) Molecular weight distribution:

$\bar{M} < 4000$	13%
$4,000 < \bar{M} < 17,000$	33%
$17,000 < \bar{M} < 40,000$	20%
$40,000 < \bar{M} < 68,000$	15%
$68,000 < \bar{M}$	19%

b) Ease of application.

The polymer prepared as in example 2 of the present patent application is more readily formulable than the polymer as in example 6 of French patent 73.23254. It is, in fact, more rapidly soluble than the latter in the oily phases of the emulsions and at lower temperature. These differences are illustrated by a comparison of the following formulae.

Mixture of glycerol mono- and distearate, marketed by Gattefosse under the name GELEOL	2 g
Mixture of C_{12}-C_{18} aliphatic alcohols	7 g
Cetyl alcohol	1.5 g
Vaseline oil	5 g
Benzoate of alcohols with 12 to 15 carbon atoms marketed by FINETEX under the name FINSOLV-TN	15 g
Polymer *	5 g
Total	35.5 g

* Polymer as in example 2, or comparison polymer.

It is found that the polymer prepared as in example 2 is dissolved in 10 minutes at 95°C, whereas the polymer prepared as in example 6 of French patent 73.23254 is dissolved in 20 minutes at the same temperature.

c) Cosmetic properties.

Two creams were prepared in the form of oil-in-water emulsions, the fat phases of which were composed of the oil solutions prepared above and 0.5 g polydimethylsiloxane, marketed by Dow Corning under the name Fluid 200.

The aqueous phase is composed of:
glycerine . . . . . 20 g
KATHON-CG (preservative; Rohm and Haas), q.s
Perfume, q.s.
Water, qsp . . . . . 44.5 g

It was found that the cream containing the polymer prepared as in example 2 is more lubricating, is less adhesive and has, on application, a less greasy appearance and feel than the cream containing the polymer perpared as in example 6 of French patent 73.23254.

Examples of cosmetic preparations

Example A

Using the procedure described in the comparative example above, an anti-solar cream was prepared (oil-in-water emulsion) replacing the polymer of example 2 by the polymer of example 1.

Example B

In a similar manner a cream (water-in-oil emulsion) was prepared which had the following formulation:

- Polymer of example 2 . . . . . 5 g
- Magnesium stearate . . . . . 4 g
- Octyl dodecanol . . . . . 10 g
- Hydrogenated lanolin marketed by ONYX under the name HYDROLAN H . . . . . 1 g

- Clear lanolin . . . . . 4 g
- Beeswax . . . . . 6 g
- Sorbitol sesquioleate . . . . . 4.5 g
- Glycerol monostearate . . . . . 1 g
- Oleic alcohol . . . . . 5 g
- 2-ethylhexyl palmitic glyceryl ether palmitic ester . . . . . 2 g
- Vaseline oil . . . . . 20 g
- Preservative. . . . . 0.2 g
- Demineralized waster, qsp . . . . . 100 g

It is possible to replace the polymer of example 2 by one of the polymers prepared as in examples 5 or 6 in this example.

Example C

A composition was prepared in the form of a solar oil having the following formulation:

- Polymer of example 4 . . . . . 0.5 g
- Oleic alcohol . . . . . 40 g
- Pentaerythritol tetracaprylate/ caprate marketed under the name CRODAMOL PTC by CRODA . . . . . 10 g
- Ditertiobutyl paracresol 0.05g
- Benzoate of C_{12}-C_{15} alcohols marketed by FINETEX under the name FINSOLV TN 49.45 g

Example D

A composition in the form of a milk was prepared having the following formulation:

- Polymer of example 2 . . . . . 5 g
- Oleocetylic alcohol with 30 moles ethylene oxide . . . . . 8 g
- Stearylic acid . . . . . 5 g
- Oleic alcohol. . . . . 6 g
- Palmitic ester of 2-ethylhexylglyceryl ether . . . . . 4 g
- Vaseline oil . . . . . 10 g

- Polydimethyl silane . . . . . 1 g
- Sorbitol, 70% . . . . . 5 g
- Preservative (KATHON CG) . . . . . 0.2 g
- Perfume . . . . . 0.6 g
- Demineralized water, qsp. . . . . .100 g

A similar composition was prepared by replacing in the preceding formulation the polymer of example 2 by the polymer of example 3.

Example E

A composition was prepared in the form of a thickened oil having the following formulation:

- -Polymer of example 3 . . . . . 1 g
- 2-thylhexyl paramethoxy cinnamate . 2 g
- Myristic alcohol with 3 moles propylene oxide marketed by WITCO under the name WITCONOL APM . . 5 g
- 2-thylhexyl palmitate . . . . . 10 g
- Ditertiobutyl paracresol. 0.05g
- Silica marketed by DEGUSSA under the name AEROSIL R972 . . . . . 6 g
- Perfume . . . . . 0.5 g
- Isostearyl benzoate, qsp. . . . . 100 g

A similar compound was prepared by replacing, in this example, the polymer of example 3 by the polymer of example 4.

Example F

A composition was prepared in the form of an oi-in-water emulsion having the following formulation:

- Polymer of example 2 . . . . . 5 g
- Mixture 80/20 of cetyl/stearylic alcohol with 33 moles ethylene oxide marketed by HENKEL under the name SINNOWAX AO . . . . . 7 g
- Mixture of glycerol mono- and distearate marketed by GATTEFOSSE under the name GELEOL. . . . . 2 g

- Cetyl alcohol . . . . . 1.5 g
- Vaseline oil . . . . . 5 g
- Benzoate of C_{12}-C_{15} alcohols marketed by FINETEX under the name FINSOLV TN 15 g
- Glycerine . . . . . 20 g
- Preservative. . . . . 0.2 g
- Perfume . . . . . 0.6 g
- Demineralized water, qsp. . . . . 100 g

Example G

A composition was prepared in the form of a stick having the following formulation:

- Polymer of example 4 . . . . . 1 g
- Glyceryl tribehenate. . . . . 6 g
- Glyceric ester of C_{18}-C_{36} fatty acids marketed by CRODA under the name SYNCROWAX HGL-C . . . . . 8 g
- Glycol distearate marketed by CRODA under the name SYNCROWAX ERLC . . 6 g
- Ricinoleic acid triglycerides . . 10 g
- Oleic alcohol . . . . . 10 g
- Benzoate of C_{12}-C_{15} alcohols marketed byFINETEX under the name FINSOLV TN 58.9 g
- Ditertiobutyl paracresol . . . . 0.1 g

Example H

A composition was prepared in the form of a solar oil having the following formulation:

- Polymer of example 2 . . . . . 3.5 g
- 2-ethylhexyl para-amino benzoate. 2.9 g
- 2-ethylhexyl paramethoxy cinnamate 4 g
- Oleic alcohol . . . . . 15 g
- Isopropyl myristate . . . . . 20 g
- Palmitic ester of 2-ethylhexyl glyceryl ether 6 g
- Cyclopentadimethyl siloxane . . . 5 g
- Octamethylcyclotetra siloxane . . 5 g
- Cyclotetradimethyl siloxane, qsp 100 g

Example I

A composition was prepared in the form of a milk having the following formulation:

- Polymer of example 3 . . . . . 7 g
- Oleocerylic alcohol with 30 moles ethylene oxide . . . . . 6 g
- Stearylic alcohol. . . . . 4 g
- Polydimethyl siloxane. . . . . 1 g
- Benzoate of C_{12}-C_{15} alcohols marketed byFINETEX under the name FINSOLV TN 15 g
- Oleic alcohol . . . . . 4 g
- Sorbitol, 70% . . . . . 15 g
- Preservative (KATHON CG) . . . . . 0.2 g
- Perfume . . . . . 0.2 g
- Demineralized water, qsp . . . . . 100 g

A similar composition was prepared by replacing in this formulation the polymer of example 3 by that of example 4.

Example J

A composition was prepared in the form of an oil-in-water emulsion having the following formulation:

- Polymer of example 2 . . . . . 3 g
- 2-ethylhexyl paramethoxycinnamate. . 3 g
- Glycerine . . . . . 5 g
- Sorbitol, 70%. . . . . 4 g
- Soya lecithine, 40%, in surfactant solution marketed by AMERICAN LECITHIN under the name ALCOLEC 4135. . . . . 5.5 g
- Shea butter . . . . . 4 g
- Beeswax . . . . . 4 g
- Sunflower oil. . . . . 6 g
- Isostearyl benzoate. . . . . 10 g
- Preservative . . . . . 0.03 g
- Perfume . . . . . 0.05 g
- Cetyl alcohol . . . . . 6 g
- Stearyl alcohol . . . . . 2 g
- Demineralized water . . . . . qs 100 g

Example K

SOLAR GEL

- Polymer prepared as in example 7 . . 2.5 g
- Cellosize PCG 10 (hydroxyethyl cellulose) . . . . . 1 g
- Ethyl alcohol . . . . . 12 g
- Propylene glycol . . . . . 8 g
- Preservative . . . . . qs
- Perfume . . . . . qs
- Water . . . . . qsp 100 g

Example I

SOLAR CREAM (oil-in-water emulsion)

- Polymer prepared as in example 12 4 g
- Stearic acid . . . . . 2.5 g
- Triethanolamine . . . . . 0.2 g
- Liquid lanolin . . . . . 6 g
- Mixture of glycerol monostearate and polyethylene glycol stearate (100 OE) . . . . . 5 g
- Triglycerides of myristic/palmitic/ stearic acids . . . . . 6 g
- Stearyl alcohol . . . . . 2.5 g
- Vaseline oil . . . . . 10 g
- Propylene glycol . . . . . 5 g
- Preservative . . . . . qs
- Perfume . . . . . qs
- Water . . . . . qsp 100 g

Example M

SOLAR LOTION

- Polymer prepared as in example 10 . . 1.5 g
- Polymer prepared as in example 9 . . 1.5 g
- Mixture of glycerol monostearate and polyethylene glycol stearate (100 OE) 50/50 . . . . . 2.5 g
- Stearyl alcohol . . . . . 4 g
- Vaseline oil . . . . . 10 g
- Isopropyl myristate . . . . . 5 g

- Cellosize PCG (hydroxyethyl cellulose 0.5 g
- Preservative . . . . . qs
- Perfume . . . . . qs
- Water . . . . . qsp 100.0 g

Example N

SOLAR CREAM (oil-in-water emulsion)

- Polymer prepared as in example 8 . . 5.0 g
- Mixture of cetyl/stearyl alcohol and cetyl/oxyehtylenated stearyl alcohol (33 OE) (80/20) . . . . . 7.0 g
- Glycerol mono- and distearate. . . . 2.0 g
- Cetyl alcohol . . . . . 1.5 g
- C_{12}-C_{15} alcohol benzoate marketed under the name FINSOLV TN (WITCO). . 15.0 g
- Glycerine . . . . . 5.0 g
- Preservative . . . . . qs
- Perfume . . . . . qs
- Water . . . . . qsp 100.0 g

Example O

SOLAR CREAM (water-in-oil emulsion)

- Polymer prepared as in example 11 2.0 g
- Esters of glycerine/sorbitol and fatty acid marketed by ATLAS under the name ARLACEL 481 . . . . . 4.0 g
- Hydrogenated polyoxyethylenated castor oil with 7 moles ethylene oxide marketed by ATLAS under the name ARLACEL 989 . . . . . 8.0 g
- -hydroxyoctacosanyl-12-hydroxy-stearate marketed by AZKO under the name ELFACOS C 26 . . . . . 5.0 g
- Vaseline oil . . . . . 15.0 g
- Isopropyl myristate . . . . . 4.0 g
- NaOH . . . . . qs pH=8.0
- Water . . . . . qsp100.0 g

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

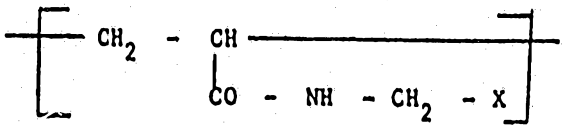
1. Cosmetic preparations intended to protect the skin against the undesirable effects of ultraviolet radiation, containing as active ingredient filtering the ultraviolet radiation at least one polymer composition containing a polymer with acrylamide structural units bonded covalently to a compound absorbing ultraviolet radiation, characterized in that the polymer of said polymer composition have a molecular weight distribution such that at least 80% of the polymer molecules have a molecular weight less than 20,000, the molecular weights being measured by the method of exclusion chromatography, in comparison with standard samples of polystyrene.

2. Preparations as in claim 1, wherein said polymer additionally has structural units derived from a hydrophilic comonomer.

3. Preparations as in claim 2, wherein the hydrophilic comonomer is ethylenically unsaturated.

4. Preparations as in any preceding claim, characterized in that fewer than 10% of the polymer molecules have a molecular weight greater than 40,000.

5. Preparations as in any preceding claims, characterized in that said polymer contains structural units of formula I



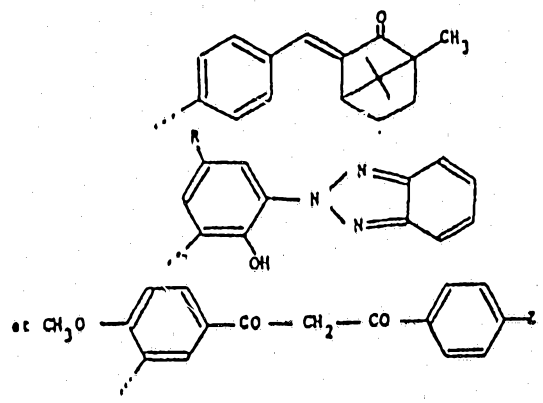
(I)

in which X represents an aromatic group imparting to the polymers an absorption of ultraviolet radiation in the

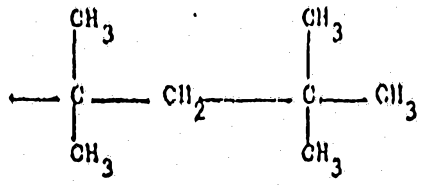
wavelength zone ranging from 280 to 400 nm, provided that the structural units of formula I represent at least 10% by weight of the polymer.

6. Preparations as in claim 5, characterized in that the structural units of formula I represent from 10 to 99% by weight of the polymer.

7. Preparations as in claim 5 or claim 6, characterized in that X is selected from the groups of formulae:



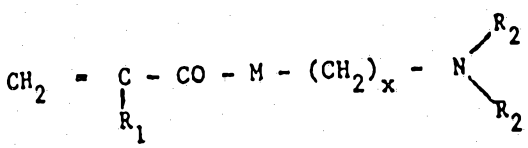
in which R represents a methyl or tertiary-octyl group of formula



and Z represents a t-butyl group.

8. Preparations as in any one of claims 5 to 7, characterized in that said hydrophilic comonomers are selected from N-vinylpyrrolidone, N,N-dimethylacrylamide,

acrylic acid, methacrylic acid and monomers of the general formula:



(II)

in which M represents -O- or -NH-,
x is a number equal to 2 or 3,
R_1 represents -H or $-CH_3$ and
R_2 represents $-CH_3$ or $-C_2H_5$,
provided that the amine groups present can be quaternized or salified before or after polymerization.

9. Cosmetic preparations as in any one of the preceding claims, characterized in that the concentration of said polymer is from 1 to 20% by weight in relation to the total weight of the preparation.

10. Cosmetic preparations as in any one of the preceding claims, characterized in that they occur in the form of aqueous, hydroalcoholic or oil solutions, aqueous emulsions, lotions, creams, milks, gels, sticks or in the form of preparations for aerosols.

11. Cosmetic preparations in accordance with claim 1 and substantially as hereinbefore described with reference to the Examples excluding the Comparative Example.

DATED THIS 5th March, 1990
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Attorneys of Australia.
Patent Attorneys for the Applicant