FORM 1

604812

SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

L Givaudan & Cie, incorporated in Switzerland, of 1214 Vernier, Geneve, SWITZERLAND, hereby apply for the grant of a standard patent for an invention entitled:

"UV-Absorbing Higher Alkyl Quaternary Ammonium Salts of Cinnamate Esters".

which is described in the accompanying complete specification.

Details of basic application(s):-

Basic Applic. No:	Country:	Application Date:
945914	UNITED STATES OF AMERICA	23 December 1986

The address for service is:-

Spruson & Ferguson
Patent Attorneys
Level 33 St Martins Tower
31 Market Street
Sydney New South Wales Australia

DATED this SIXTEENTH day of DECEMBER 1987

L Givaudan & Cie

By: M.J. Anderson

Registered Patent Attorney

LODGED AT SUB-OFFICE 22 DEC 1987 Sydney

AUSTRALIAN PATENT OFFICE LS

TO: THE COMMISSIONER OF PATENTS
OUR REF: 45995
S&F CODE: 54700

FEE STAMP TO VALUE OF $ 210 ATTACHED
MAIL OFFICER

APPLICATION ACCEPTED AND AMENDMENTS
5845/2
5.10.90

AUSTRALIA
CONVENTION
STANDARD
& PETTY PATENT
DECLARATION

COMMONWEALTH OF AUSTRALIA

THE PATENTS ACT 1952

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

~~Ref. 6550/24~~

In support of the Convention Application made for a patent for an invention entitled:

Title of Invention: Light screen agent

Full name(s) and address(es) of Declarant(s)

I Roland Borer

of 10 Stockackerstrasse, CH-4153 Reinach, Switzerland

do solemnly and sincerely declare as follows:–

Full name(s) of Applicant(s)

1. I am authorised by

L.GIVAUDAN & CIE Société Anonyme
CH-1214 Vernier, Geneva, Switzerland

the applicant(~~s~~) for the patent to make this declaration on its/~~their~~ behalf.

2. The basic application(~~s~~) as defined by Section 141 of the Act was/~~were~~ made

Basic Country(ies): in the United States of America

Priority Date(s): on December 23, 1986

Basic Applicant(s): by [ ]

[X] the inventor(~~s~~) cited in paragraph 3.

3. Full name(s) and address(es) of inventor(s)

Isaac David Cohen
1885 East 13th Street
Brooklyn, N.Y. 11229, United States of America

LODGED AT SUB-OFFICE
22 DEC 1987
Sydney

respectively is/~~are~~ the actual inventor(~~s~~) of the invention and the facts upon which the applicant(~~s~~) is/~~are~~ entitled to make the application are as follows:

Set out how Applicant(s) derive title from actual inventor(s) e.g. The Applicant(s) is/are the assignee(s) of the invention from the inventor(s)

(X) the inventor(~~s~~) have assigned the invention to Givaudan Corp., Clifton, U.S.A. who have re-assigned all their rights for Australia to the Applicant.

( ) the Applicant is the assignee of the invention from the inventor(s).

4. The basic application(~~s~~) referred to in paragraph 2 of this Declaration was/~~were~~ the first application(~~s~~) made in a Convention country in respect of the invention (~~s~~) the subject of the application.

Declared at Basle this 1st day of December 19 87

To:

The Commissioner of Patents,
COMMONWEALTH OF AUSTRALIA

Roland Borer
.....
Signature of Declarant(s)

(12) PATENT ABRIDGMENT (11) Document No. AU-B-82921/87
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 604812

(54) Title
U.V.- ABSORBING QUATERNARY SALTS OF CINNAMATE ESTERS

International Patent Classification(s)
(51)[4] **C07C 093/20 A61K 007/44**

(21) Application No. : **82921/87** (22) Application Date : **22.12.87**

(30) Priority Data

(31) Number	(32) Date	(33) Country
945914	**23.12.86**	**US UNITED STATES OF AMERICA**

(43) Publication Date : **23.06.88**

(44) Publication Date of Accepted Application : **03.01.91**

(71) Applicant(s)
L. GIVAUDAN & CIE

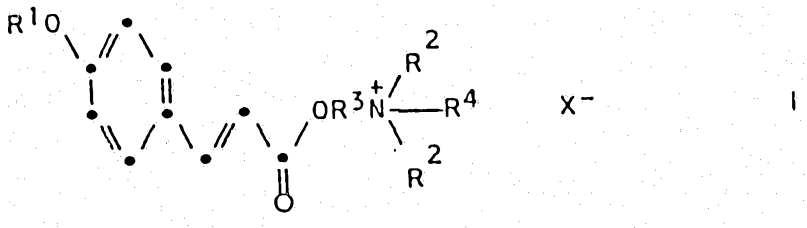
(72) Inventor(s)
ISAAC DAVID COHEN

(74) Attorney or Agent
SPRUSON & FERGUSON, GPO Box 3898, SYDNEY NSW 2001

(56) Prior Art Documents
DE 957162
FR 2504330
EP 165710

(57) Claim

1. A compound of the formula

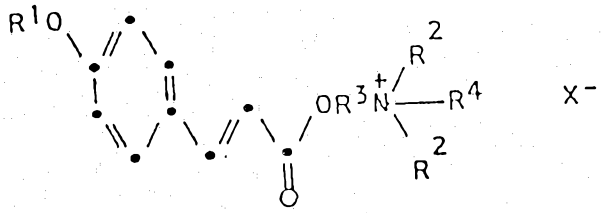


I

wherein R^1 is an alkyl group containing from one to four carbon atoms; R^2 is an alkyl group containing from one to six carbon atoms; R^3 is an alkylene group containing from two to six carbon atoms; R^4 is an alkyl group containing from sixteen to twenty-two carbon atoms; and X^- is a halogen anion.

.../2

8. A method for protecting skin, hair or fabric from the effects of ultraviolet radiation, which comprises applying to said skin, hair or fabric an effective ultraviolet absorbing amount of a compound of the formula



I

wherein R^1 is an alkyl group containing from one to four carbon atoms; R^2 is an alkyl group containing from one to six carbon atoms; R^3 is an alkylene group containing from two to six carbon atoms; R^4 is an alkyl group containing from sixteen to twenty-two carbon atoms; and X^- is a halogen anion,

in a carrier suitable for application to said skin, hair or fabric.

604812

S & F Ref: 45995

FORM 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE:

Class Int Class

Complete Specification Lodged:
Accepted:
Published:

Priority:

Related Art:

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

Name and Address of Applicant: L Givaudan & Cie
1214 Vernier
Geneve
SWITZERLAND

Address for Service: Spruson & Ferguson, Patent Attorneys
Level 33 St Martins Tower, 31 Market Street
Sydney, New South Wales, 2000, Australia

Complete Specification for the invention entitled:

"UV-Absorbing Higher Alkyl Quaternary Ammonium Salts of Cinnamate Esters".

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

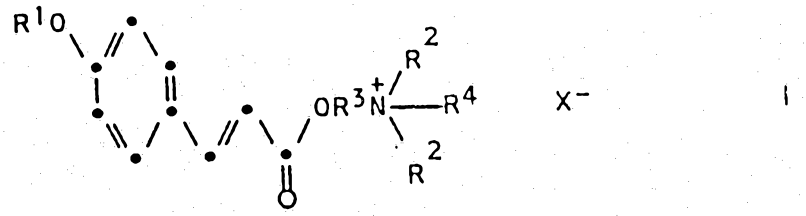
AUSTRALIAN PATENT OFFICE LS

5845/3

Ref. 6550/24

ABSTRACT

Higher alkyl quaternary halide salts of cinnamate esters of the general formula I



I

wherein R^1 is an alkyl group containing from one to four carbon atoms; R^2 is an alkyl group containing from one to six carbon atoms; R^3 is alkylene containing from two to six carbon atoms; R^4 is an alkyl group containing from sixteen to twenty-two carbon atoms; and X^- is a halogen anion

are useful as sunscreen agents. Sunscreen compositions containing same and methods of using are provided.

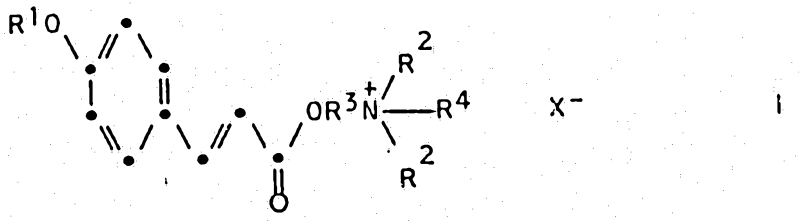
A 1978 FDA monograph on over-the-counter sunscreens [Federal Register, Vol. 43, No. 166, August 25, 1978] indicates that risk factors of chronic exposure to the sun may include the development of keratoses, skin cancers, and premature aging of the skin. More recently, a review on the use of sunscreens in hair-care products [J.P. Pavlichko, Drug and Cosmetic Industry, 137 (6), 35 (1985)] states that "hair damage from exposure to sunlight can produce color fading, texture changes, reduction of water uptake, loss of elasticity, and keratin structure changes". These and other publications highlight an increasing awareness about the detrimental effects that extended exposure to the sun has on living and non-living tissue, as well as to commercial and industrial materials. It is generally accepted that these detrimental effects can be prevented or mitigated by the use of sunscreen agents which efficiently absorb ultraviolet radiation.

A successful sunscreen agent must not only be able to efficiently absorb the ultraviolet light which can cause damage to skin, hair, fabric, etc. but must also have other properties that make it compatible with the system in which it is being used. For example, skin care preparations such as astringents, hydroalcoholic suntan lotions and hydroalcoholic gels are generally formulated without any oily components. For such products, it is required that the UV absorber possess significant aqueous, alcoholic and/or hydroalcoholic solubility, and be, at the same time, resistant towards removal from the skin surface by washing, perspiration, etc. The ability of the UV absorber to adhere to and be retained by the skin during swimming and during

activities causing perspiration, i.e., substantivity, is a highly desirable property in a cosmetic sunscreen. Similarly, it is also a highly desirable property for sunscreens used in hair conditioners and fabric softeners, where it is also required that the sunscreen be capable of being incorporated into aqueous-based systems while at the same time be highly substantive to the hair or fabric to be protected.

For products such as hair conditioners, fabric softeners and skin care preparations there is a need for the development of new and unique UV absorbing molecules which have solubility characteristics that allow for formulation into alcoholic, hydroalcoholic and/or aqueous systems while at the same time providing high substantivity to the surface to be protected.

In accordance with the present invention there are provided halide salts of cationic cinnamate esters of the general formula



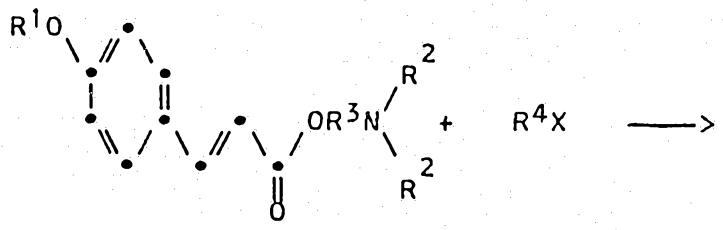
I

wherein R^1 is an alkyl group containing from one to four carbon atoms; R^2 is an alkyl group containing from one to six carbon atoms; R^3 is an alkylene group containing from two to six carbon atoms; R^4 is an alkyl group containing from sixteen to twenty-two carbon atoms; and X^- is a halogen anion, e.g. fluoride, chloride, bromide or iodide.

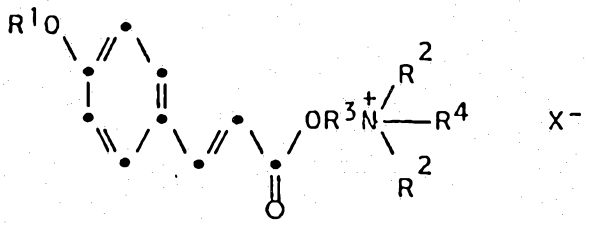
It has now been found that these novel salts, which have a long chain alkyl group bonded to a quaternary nitrogen, are effective ultraviolet absorbers which possess an unexpectedly high degree of substantivity. p-Methoxy cinnamate esters containing quaternary ammonium groups in which the quaternary centers are substituted with lower alkyl groups have been reported. [See A. Berg et al., German Patent Specification 957,162, and L. Jung et al., French Patent Publication 2,504,530.] Nothing reported in the prior art however, teaches nor suggests that the novel salts of this invention would have the unique combination of properties which allow them to be formulated effectively into alcoholic, hydroalcoholic, and/or aqueous compositions to provide sunscreen products which have superior substantivity.

The cationic cinnamate esters of this invention may be conveniently prepared via quaternization of suitably substituted tertiary amines II with alkylating agents III as shown below in Scheme I,

SCHEME I



II III



I

wherein R^1, R^2, R^3, R^4, and X^- are as defined above.

In the preferrred procedure, the tertiary amine and the alkylating agent are brought together to react in approximately a 1:1 molar ratio. The reaction may be carried out in the presence or absence of solvent and at ambient or elevated temperature. The use of a polar solvent at reflux to effect the alkylation is generally preferred. Especially preferred polar solvents are alcoholic solvents

such as methanol, ethanol, isopropanol and the like. If desired, the crude products may be further purified by recrystallization from appropriate solvents.

Compounds of formula II may be readily prepared by any of a number of processes known to those skilled in the art, i.e., condensation of activated cinnamic acid derivatives with dialkylamino alcohols. [See for example Jung et al., supra.]

The novel salts of this invention, i.e., those salts of formula I wherein R^4 is an alkyl group of from sixteen to twenty-two carbon atoms, all possess superior substantivity properties. For economic reasons such as availability of starting materials, it is preferred, however, to use a novel salt wherein R^1 is a methyl group, R^2 is a methyl or ethyl group, R^3 is ethylene, propylene or butylene and the halogen anion is either bromide or chloride. Although substantivity appears to increase markedly as length of the R^4 substituent increases (all other substituents being held constant) those salts wherein R^4 is hexadecyl or octadecyl are also preferred for economic reasons with the octadecyl being particularly preferred because of its superior substantivity. It is especially preferred to use an octadecyl salt wherein R^2 is methyl and R^3 is ethylene, as these salts appear to offer superior substantivity properties to those salts in which R^2 is ethyl and/or R^3 is propylene or butylene.

The novel salts of formula I may be used as sunscreen agents, e.g. in compositions for the protection of hair, fabric and skin from the deleterious effects of the sun. They may be effectively incorporated in concentrations of from about 0.1 to about 10.0% by weight into aqueous, alcoholic or hydroalcoholic solutions, suspensions or gels, as well as into emulsified lotions, creams, milks, aerosols, gels and the like by methods well known in the art. When

used in topical preparations for protection of the skin such as sunscreen lotions, lip balms, sticks and gels, it is preferred to use a salt of formula I in a range from about 2% to about 10% by weight. In skin care preparations such as hand and body creams, facial creams, facial makeup, after shaves, colognes and astringents, it is preferred to use from about 0.1% to about 5% by weight. In compositions for the protection of hair such as shampoos, conditioners, styling mousses, styling gels and glazes, it is also preferred to use from about 0.1% to about 5% by weight. Fabric treatment formulations such as liquid and solid fabric softeners and detergents may contain from about 0.1% to about 1.0% of a compound of formula I.

A number of examples are provided herein to illustrate the preferred embodiments of this invention. Included are examples directed to the synthesis of the novel compounds of this invention and examples directed to the utility of these compounds. The examples provided herein are included for the sole purpose of illustrating the preferred embodiments and should not be construed as limiting. They are intended to embrace any equivalents or obvious extensions which are known or should be known to a person skilled in the art.

EXAMPLE 1: PREPARATION OF QUATERNARY SALTS

A) 2-(N,N-Dimethyl-N-n-hexadecylamino)ethyl 3-(4-methoxyphenyl)-2-propenoate bromide

A mixture of 2-(N,N-dimethylamino)ethyl 3-(4-methoxyphenyl)-2-propenoate (50.0g; 0.20 mole) and 1-bromohexadecane (61.1g; 0.20 mole) was heated to 100°C for 0.5h. The resultant mass was finely pulverized, triturated with diethylether and dried. The product (93.1g; 84.0%) was obtained as an off-white solid: m.p. 112-123°C. Spectral data (^{1}H NMR, IR and UV) were consistent with the assigned

structure.

B) 2-(N,N-Dimethyl-N-n-octadecylamino)ethyl 3-(4-methoxyphenyl)-2-propenoate bromide

A mixture of 2-(N,N-dimethylamino)ethyl 3-(4-methoxyphenyl)-2-propenoate (24.9g; 0.10 mole), isopropanol (50ml), and 1-bromooctadecane (33.3g; 0.10 mole) was allowed to reflux under a dry atmosphere for 5h. The hot reaction mixture was diluted with toluene (125ml) and cooled to 0°C. The product (38.8g; 66.7%) was filtered and dried. A white solid was obtained: m.p. 162-164°C. Spectral data (^{1}H NMR, IR, and UV) were consistent with the assigned structure.

The wavelengths of maximum absorption (λ max) in ethanol, and the intensity of the absorption calculated as molar extinction coefficient (ε max) for the above salts can be found below in Table 1 of Example 2. Table 1 also gives data for other, similarly prepared salts of this invention.

EXAMPLE 2: SUBSTANTIVITY TO HAIR

The substantivity of the novel salts of formula I to hair was tested in the following manner. A 0.01% w/v solution (0.01g of sunscreen per 100ml of solution) of each sunscreen to be evaluated was prepared in 50% aqueous ethanol. A swatch of virgin, brunette hair weighing 0.10g was immersed into 10ml of the sunscreen solution and allowed to stand undisturbed at room temperature for 30 min. The solution was decanted away from the hair, and the hair shaken free of excess liquid and transferred to a clean, dry beaker, where it was allowed to air-dry overnight. Following this, the hair was allowed to stand undisturbed in 10ml of distilled water for 30 min. at room temperature, then was transferred to a clean beaker and redried

overnight. Finally, the swatch was soaked in 10ml of absolute ethanol for 30 min.; an analysis of this ethanol wash by UV spectrophotometry indicated the extent to which the sunscreen remained bound onto the hair following the aqueous soak. A blank control using 50% aqueous ethanol in place of the initial sunscreen solution confirmed that no inherent UV-absorbing material was leached from the hair by the ethanol wash and that all the UV absorption was due to the absorber which had adhered to the hair as a result of this experiment. The substantivity of the sunscreen can be calculated as follows:

Sunscreen Concentration (mg/ml) in ethanol wash =

$$\frac{\text{(mol. wt. sunscreen)(absorbance of solution)}}{(\varepsilon \text{ max[ethanol] of sunscreen})}$$

Thus, total mg sunscreen per g hair =

$$\frac{\text{(total ml sol.)(mol.wt. sunscreen)(absorbance of solution)}}{(\varepsilon \text{ max[ethanol] of sunscreen})(\text{total wt. hair, g})}$$

$$\text{absorbance} = \text{extinction} = \log \frac{I_o}{I} = \varepsilon \cdot c \cdot d.$$

Table 1 gives the results found for the novel salts of formula I prepared as illustrated in Example 1.

TABLE 1

COMPOUND	λ MAX	ε MAX	mg SUNSCREEN/ g HAIR
2-(N,N-Dimethyl-N-n-hexadecyl-amino)ethyl 3-(4-methoxyphenyl)-2-propenoate bromide (a)	316	24,500	0.794
2-(N,N-Dimethyl-N-n-octadecyl-amino)ethyl 3-(4-methoxyphenyl)-2-propenoate bromide (b)	316	25,700	1.076
2-(N,N-Dimethyl-N-n-hexadecyl-amino)ethyl 3-(4-methoxyphenyl)-2-propenoate chloride (c)	314	25,600	0.495
2-(N,N-Diethyl-N-n-octadecyl-amino)ethyl 3-(4-methoxyphenyl)-2-propenoate bromide (c)	314	29,100	0.507
3-(N,N-Diethyl-N-n-eicosylamino)-1-propyl 3-(4-methoxyphenyl)-2-propenoate bromide (c)	312	21,200	1.457
2-(N,N-Dimethyl-N-n-docosylamino)-ethyl 3-(4-methoxyphenyl)-2-propenoate bromide (c)	316	22,200	2.396

(a) Example 1A.

(b) Example 1B.

(c) Novel compounds of formula I prepared in a manner similar to Example 1.

Table 1 demonstrates that the novel salts of this invention are highly substantive to hair.

The superior substantivity properties of those salts wherein R^4 is an alkyl group of from sixteen to twenty-two carbon atoms is graphically illustrated in figure I. In figure I, the substantivities (mg sunscreen/g hair) have been plotted against the number of carbon atoms in the R^4 alkyl group for a series of novel compounds of formula I wherein all the substituents are held constant (R^1 and R^2 are methyl, R^3 is ethyl and X^- is bromide) except R^4, which varies from propyl (three carbons) to docosyl (twenty two carbons).

EXAMPLE 3: SUBSTANTIVITY TO COTTON

The substantivity of the novel salts of formula I to cotton was tested in the following manner. A 4.0% w/v solution of the salt prepared in Example 1B was prepared in 50% aqueous isopropanol at room temperature. Approximately 0.2ml of the sunscreen solution was pipetted onto commercial 100% cotton toweling, which had been previously laundered and treated with brightening agents. The solution, which saturated a 1 inch diameter circle of fabric, was dried in a stream of hot air for several minutes. The presence of sunscreen on the fabric was readily confirmed by an examination of the fabric under short-wave UV light, viz., the sunscreen appeared dark blue or blue-black against a bright blue fluorescent background. The towel sample was allowed to stand undisturbed in a bath of distilled water at 50-55^{o}C for 8 min., then was removed and redried in a hot air stream. A reexamination of the fabric under UV light revealed essentially complete retention of the sunscreen by the fabric material. Similar results were found for the other salts of formula I listed in Table 1.

EXAMPLE 4: APPLICATIONS

The following examples illustrate the use of the novel salts in aqueous and hydroalcoholic systems as well as in oil/water emulsions.

A) Rinse Out Conditioner - oil/water emulsion

Part I	% by weight
Water	q.s. to 100
Standamol Conc. 1002™ (Henkel) (Cetearyl alcohol (mixture of fatty alcohols, predominantly cetyl/ stearyl alcohols)/PEG-40 hydrogenated castor oil (polyethylene glycol derivatives of hydrogenated castor oil with an average of 40 moles of ethylene oxide)) Stearalkonium chloride (benzyl dimethyl stearyl ammonium chloride)	3.00
Ceteth-2 (polyoxyethylene (2) cetyl ether having the formula $CH_3(CH_2)_{14}CH_2(OCH_2CH_2)_nOH$, $\bar{n} = 2$)	2.00
Propylene glycol	1.00
Stearalkonium chloride	3.00
Methyl paraben (4-hydroxy benzoic acid methyl ester)	0.10
2-(N,N-Dimethyl-N-n-docosylamino)-ethyl 3-(4-methoxyphenyl)-2-propenoate bromide	0.50

Part II	
Panthenol	0.50
Kathon CG™ (Rohm and Haas) (2-Methyl-5-chloroisothiazolinone/ 2-methylisothiazolinone)	0.03
Citric acid	0.02
Water	10.00

Part III

Fragrance	q.s.

The ingredients of Part I are blended at 70°C until uniform. The ingredients of Part II are blended at room temperature until all solids have been dissolved. Part II is then added to Part I with mixing until homogeneous. The product is cooled with mixing and perfumed at 40°C.

B) Styling Mousse - hydroalcoholic aerosol

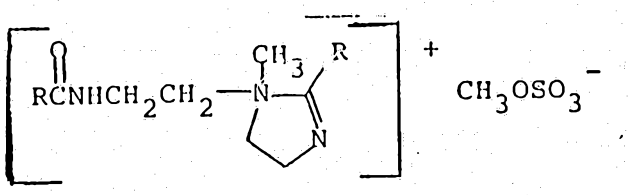
Part I	% by weight
Polyquaternium-4 (2% in water) (a copolymer of hydroxyethylcellulose and diallyldimethylammonium chloride)	50.00
Quaternium-26 (minkamidopropyl dimethyl 2-hydroxyethyl ammonium chloride having the formula $[RCONH(CH_2)_3N(CH_3)_2CH_2CH_2OH]\ Cl^-$, where R represents the fatty acid groups derived from mink oil)	3.50
Glycerin	7.00
Water	q.s. to 100
2-(N,N-Dimethyl-N-n-octadecyl-amino)ethyl 3-(4-methoxyphenyl)-2 propenoate bromide	1.00

Part II

Alcohol	20.00
PVP/VA copolymer (a copolymer of vinyl acetate and vinylpyrrolidone monomer having the formula $(C_6H_9NO \cdot C_4H_6O_2)_x$	2.00
PPG-12 PEG-50 lanolin (polyoxypropylene (50) polyoxyethylene (12) lanolin having the formula $R(OCH(CH_3(CH_2)_x(OCH_2CH_2)_yOH$; R = lanolin radical, $\bar{x}$ = 12, $\bar{y}$ = 50)	0.50
Fragrance	q.s.

The ingredients of Parts I and II are mixed separately in the order listed. Part I is then added to Part II with thorough mixing. The resultant mixture is filled into an appropriate aerosol container and diluted to 94.00% with propellant A-46.

C) Fabric Softener - an aqueous system

Component	% by weight
Water	q.s. to 100
Quaternium-27 (an imidazole methosulfate derivative of tallow acid amide having the formula  where R is derived from the tallow acid radical)	6.00
Fragrance	0.20
2-(N,N-Dimethyl-N-n-hexadecylamino)ethyl 3-(4-methoxyphenyl)-2-propenoate bromide	1.00

The quaternium-27 and water are each heated to 50°C, and combined with mixing. The quaternary bromide is added and the mixture is allowed to cool. The product is perfumed at 40°C.

D) Daily Use Cream - an oil/water emulsion

Part I	% by weight
Water	q.s. to 100
Propylene glycol	5.00
Methyl paraben	0.20
2-N,N-Dimethyl-N-n hexadecyl-amino)ethyl 3-(4-methoxyphenyl)-2-propenoate chloride	3.00

Part II	
Mineral oil	10.00
Arlacel 165™ (ICI Americas) (glyceryl stearate having the formula: $CH_3(CH_2)_{16}COOCH_2CH(OH)CH_2OH$/ PEG-100 stearate (polyoxyethylene (100) monostearate of the formula: $CH_3(CH_2)_{16}COOCH_2CH)_nOH$, $\overline{n}$ = 100))	8.00
Cetyl alcohol	4.00
Stearic acid	3.00
Stearyl alcohol	1.00
Jojoba oil	0.50
Propyl paraben	0.10

Part III

Fragrance	q.s.

Parts I and II are heated separately to 80°C. When both phases are clear and uniform, Part II is added to Part I with continuous mixing. The product is cooled with mixing and perfumed at 40°C.

E) Sunscreen Lotion - an oil/water emulsion

Part I	% by weight
Water	q.s. to 100
Glycerin	10.00
Methyl paraben	0.25
Citric acid	0.17
2-(N,N-Dimethyl-N-n-octadecyl-amino)ethyl 3-(4-methoxyphenyl)-2-propenoate bromide	2.00

Part II	
Caprylic/capric triglyceride	3.00
Isopropyl palmitate	2.00
Mineral oil	1.00
Emulgade 1000 Ni™ (Henkel) (Cetearyl alcohol/ceteareth-20 [polyoxyethylene (20) cetyl/stearyl ether: $R(OCH_2CH_2)_nOH$, R = cetyl/stearyl blend, $\bar{n}$ = 20)]	2.00

Part II Con't

Tocopheryl acetate	0.50
Glyceryl stearate	2.00
Stearamidopropyl dimethylamine	1.00
Dimethicone (a mixture of fully methylated linear siloxane polymers end-blocked with trimethylsiloxy units: $(CH_3)_3SiO[Si(CH_3)_2-O]_nSi(CH_3)_3$)	0.20
Propyl paraben (4-hydroxy benzoic acid propyl ester)	0.10

Part III

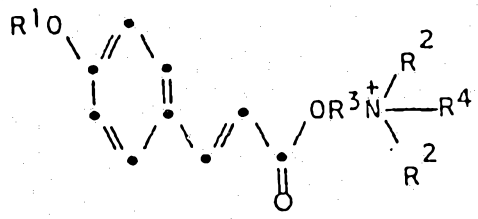
Fragrance	q.s.

Parts I and II are heated separately to 80°C. When both phases are clear and uniform, Part II is added to Part I with continuous mixing. The product is cooled with mixing and perfumed at 40°C.

~~Claims~~

The claims defining the invention are as follows:

1. A compound of the formula



I

wherein R^1 is an alkyl group containing from one to four carbon atoms; R^2 is an alkyl group containing from one to six carbon atoms; R^3 is an alkylene group containing from two to six carbon atoms; R^4 is an alkyl group containing from sixteen to twenty-two carbon atoms; and X^- is a halogen anion.

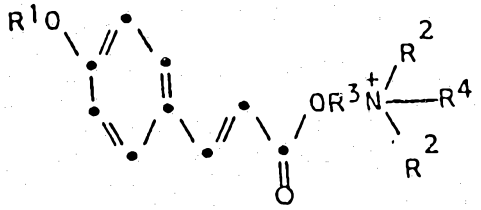
2. A compound according to claim 1 wherein R^1 is a methyl group; R^2 is a methyl or ethyl group; R^3 is ethylene, propylene or butylene; and X^- is bromide or chloride.

3. A compound according to claim 1 or 2 wherein R^4 is an alkyl group containing sixteen, eighteen, twenty or twenty-two carbon atoms.

4. The compound according to claim 1, 2 or 3 wherein R^2 methyl; R^3 ethylene; and R^4 is an alkyl group containing sixteen or eighteen carbon atoms.

5. The compound according to claim 1, 2, 3 or 4 wherein R^4 is n-octadecyl; and X^- is bromide.

6. An ultraviolet light absorbing composition comprising a compound of the formula

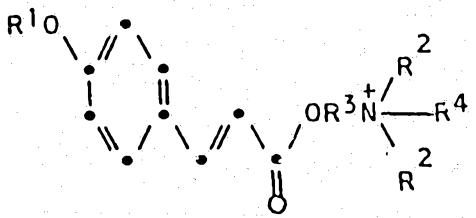


I

wherein R^1 is an alkyl group containing from one to four carbon atoms; R^2 is an alkyl group containing from one to six carbon atoms; R^3 is an alkylene group containing from two to six carbon atoms; R^4 is an alkyl group containing from sixteen to twenty-two carbon atoms; and X^- is a halogen anion,

in a suitable carrier, said compound being present in an effective ultraviolet absorbing amount.

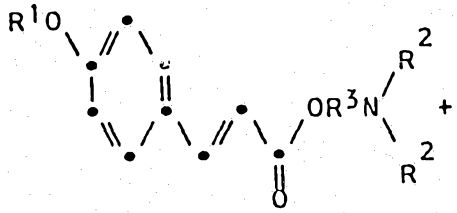
7. Process for the manufacture of compounds of formula



I

wherein R^1 is an alkyl group containing from one to four carbon atoms; R^2 is an alkyl group containing from one to six carbon atoms; R^3 is an alkylene group containing from two to six carbon atoms; R^4 is an alkyl group containing from sixteen to twenty-two carbon atoms; and X^- is a halogen anion,

comprising reacting an amine of formula



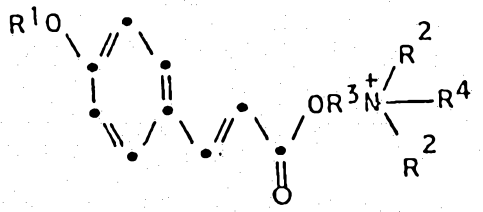
II

with the alkylating agent

$$R^4X \qquad \text{III}$$

wherein R^1 to R^4 and X are as above.

8. A method for protecting skin, hair or fabric from the effects of ultraviolet radiation, which comprises applying to said skin, hair or fabric an effective ultraviolet absorbing amount of a compound of the formula

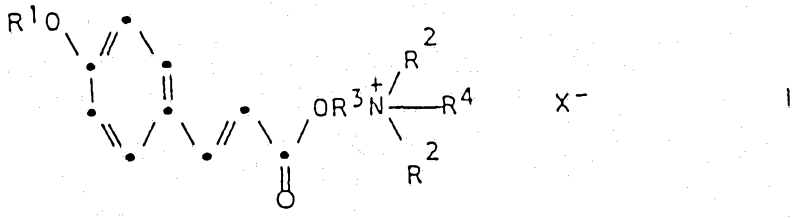


I

wherein R^1 is an alkyl group containing from one to four carbon atoms; R^2 is an alkyl group containing from one to six carbon atoms; R^3 is an alkylene group containing from two to six carbon atoms; R^4 is an alkyl group containing from sixteen to twenty-two carbon atoms; and X^- is a halogen anion,

in a carrier suitable for application to said skin, hair or fabric.

9. Use of the compounds of the formula



I

wherein R^1 is an alkyl group containing from one to four carbon atoms; R^2 is an alkyl group containing from one to six carbon atoms; R^3 is an alkylene group containing from two to six carbon atoms; R^4 is an alkyl group containing from sixteen to twenty-two carbon atoms; and X^- is a halogen anion, as ultravoilet absorbing agents.

10. Higher alkyl quaternary ammonium halide salts of cationic cinnamate esters substantially as hereinbefore described with reference to any one of the Examples.

11. An ultraviolet light absorbing composition comprising higher alkyl quaternary ammonium halide salts of cationic cinnamate esters, which composition is substantially as hereinbefore described with reference to any one of the Examples.

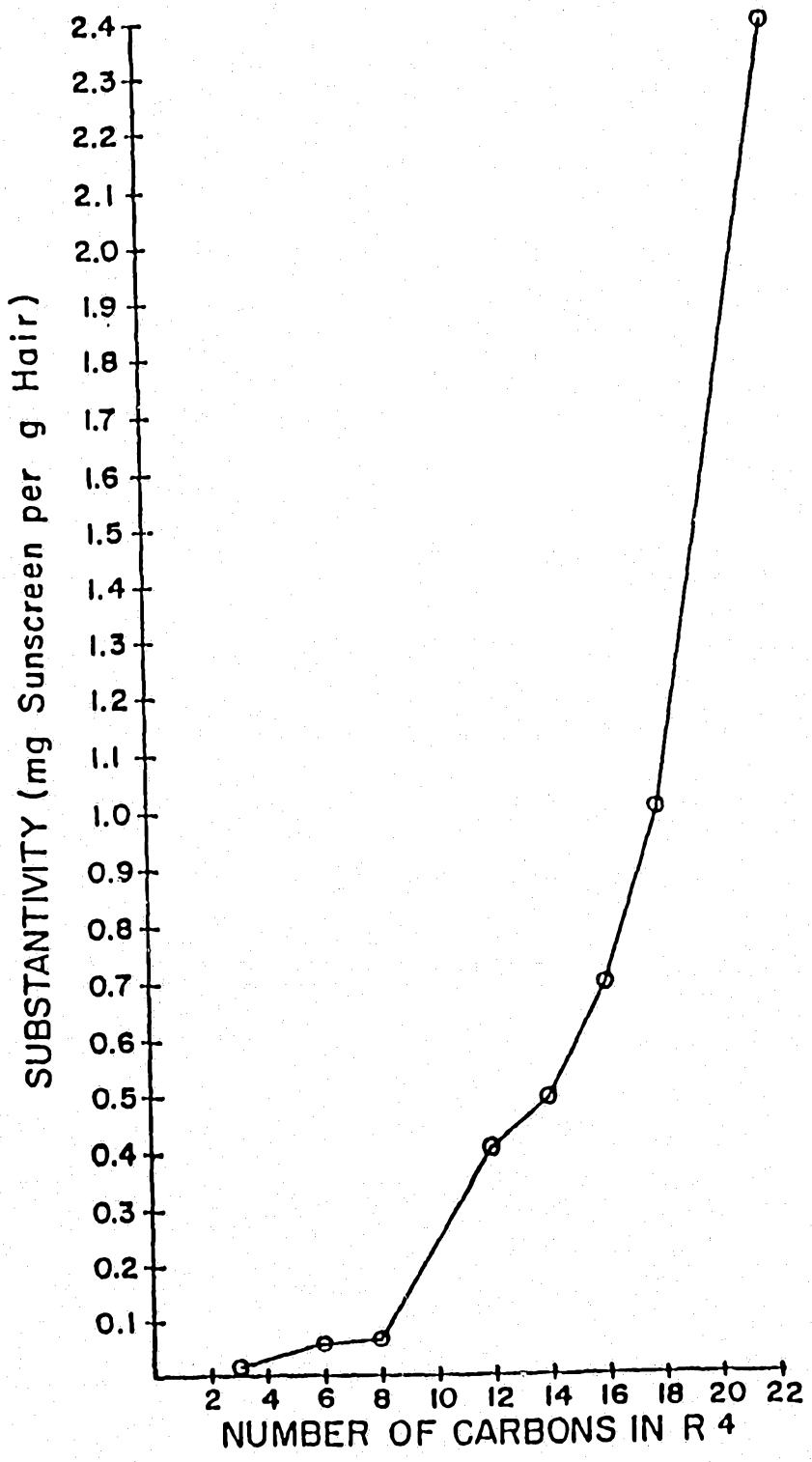
12. Process for the manufacture of higher alkyl quaternary ammonium halide salts of cationic cinnamate esters substantially as hereinbefore described with reference to any one of the Examples.

DATED this TENTH day of September 1990
L Givaudan & Cie

Patent Attorneys for the Applicant
SPRUSON & FERGUSON

IAD/248Z

FIGURE 1


SUBSTANTIVITY (mg Sunscreen per g Hair)
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
2 4 6 8 10 12 14 16 18 20 22
NUMBER OF CARBONS IN R 4