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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
División de Nuevas Creaciones
E. S. D.

Ref: EXPDIENTE No 00-000313
Solicitud de patente a nombre de
INDUSTRIA E COMERCIO DE COSMETICOS NATURA LTDA

Como el extracto de la solicitud de patente indicada en la referencia se publicó en la Gaceta de Propiedad Industrial No 514 del 22 de marzo último, pido que de conformidad con el artículo 44 de la Decisión 486, se rinda el examen la patentabilidad de la invención.

Adjunto el recibo No 02-61171 por concepto de las tasas oficiales.

Atentamente,


MARCELA CASTILLO TORRES
T.P. 80331 C.S. Judicatura
C.C. 39.784.109 Bogotá

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Industria y Comercio
SUPERINTENDENCIA

SUPERINDUSTRIA Y COMERCIO
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FECHA : SEPTIEMBRE 12 DE 2002

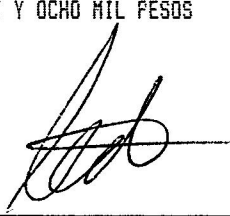
***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Vr. PAGO
CASTILLO PINEDA	CONSIGNACION	BANCO POPULAR	050-00110-6	4797150	12/09/2002	2,978,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01	SOLICITUDES	
		85 EXAMEN DE PATENTABILIDAD DE INVEN	318,000.00
		TOTAL :	\$ 318,000.00

SON: TRESCIENTOS DIEZ Y OCHO MIL PESOS

RESP. LE : 

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

Carrera 13 No. 27-00 Pisos 5, 7 y 10
Conmutador 382 0840
Fax 350 5220
E-mail: info@sic.gov.co
www.sic.gov.co
Bogotá, D.C., Colombia

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375.
2005/02/17

**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES**

2020/
Bogotá, D.C.,

Doctora
Marcela Castillo Torres
Apoderada

Oficio N°
12118

REFERENCIA	Radicación	00 00313
	Trámite	002
	Evento	001
	Actuación	430
	Folios	014

Como resultado del examen de patentabilidad de la solicitud de patente de invención N° 00 00313, realizado según el artículo 45 de la decisión 486 de la comisión de la Comunidad Andina, se notifica:

Documentos estudiados:

- . Descripción: folios 66-73
- . Ejemplos: folios 73-76
- . Capítulo reivindicatorio estudiado: folios 77-79
- . Se reivindica prioridad presentada en Brasil, el 08.01.99, bajo el número PI9900085.7

Objeto de la invención

Según las reivindicaciones 1 a 10 de la presente solicitud, se refiere composiciones para la protección de la piel de los rayos del sol en forma de emulsión agua en aceite, que contienen como ingredientes activos óxido de titanio y óxido de zinc, se describe también el proceso para su preparación.

Clasificación internacional de patentes A 61 K 7/42

Claridad de la solicitud

El artículo 30 de la decisión 486 de la comisión de la comunidad andina establece que:
"Las reivindicaciones definirán la materia que se desea proteger mediante la patente.
Deben ser claras y concisas y estar enteramente sustentadas por la descripción"

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Teniendo en cuenta lo anterior, el contenido de la reivindicación 10 no es claro, debido a que define un proceso de acuerdo con las reivindicaciones 5-9, cuando lo que se pretende proteger es una emulsión de acuerdo con dichas reivindicaciones.

Favor hacer las aclaraciones y correcciones del caso.

Determinación del estado de la técnica:

Consultadas las fuentes de información con que cuenta este despacho, se encontraron los siguientes documentos, anteriores a la fecha de prioridad de la presente solicitud - 08.01.99-, relacionados con la materia de la presente solicitud:

Nº	Documento	Título	Fecha de publicación
1	US 5340567	"Composiciones protectoras solares"	23.08.94
2	US 5032390	"Composiciones cosméticas anti quemaduras solares"	16.07.91

Evaluación de los requisitos de patentabilidad:

El artículo 14 de la decisión 486 de la comisión de la comunidad andina establece que: *"Los países miembros otorgarán patentes para las invenciones, sean de producto o de procedimiento, en todos los campos de la tecnología, siempre que sean nuevas, tengan nivel inventivo y sean susceptibles de aplicación industrial"*

En cumplimiento del artículo 14 de la decisión 486 de la comisión de la comunidad andina, se procedió a evaluar los requisitos de novedad, nivel inventivo y aplicación industrial con el fin de establecer la patentabilidad de la invención reivindicada en la solicitud en estudio.

Evaluación del NIVEL INVENTIVO

El art. 18 de la Decisión 486 contempla *"Se considerará que una invención tiene nivel inventivo, si para una persona del oficio normalmente versada en la materia técnica correspondiente, esa invención no hubiese resultado obvia ni se hubiese derivado de manera evidente del estado de la técnica"*

La patente US 5340567 se relaciona con composiciones solares que contienen dióxido de titanio y óxido de zinc que protegen la piel de los rayos del sol en proporciones que van desde 2-25%. Finalmente se revelan composiciones que contienen derivados de PEG

La patente US 5032390 publica composiciones anti solares que contienen óxido de zinc y óxido de titanio en cantidades de 1-25% y emulsionantes que contienen aceites de silicona.

Teniendo en cuenta el objeto de la solicitud, el cual es proporcionar composiciones para el cuidado de la piel de los rayos del sol que contienen óxido de zinc y óxido de titanio, es una derivación evidente del estado de la técnica ya que los documentos citados enseñan composiciones similares que tienen el mismo propósito.

Una persona versada en la materia utilizaría las enseñanzas de los documentos citados y fabricaría las composiciones que se pretenden proteger.

Finalmente, no se presentan ventajas de las composiciones que se pretenden proteger en relación con las del estado de la técnica.

En conclusión los requisitos de patentabilidad de la presente solicitud se encuentran afectados así:

Nº	Documento	Reivindicaciones afectadas	Requisito que afecta
1	US 5340567	1-10	Nivel Inventivo
2	US 5032390	1-10	Nivel inventivo

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta días contados a partir de la fecha de la notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo 5 del título primero de la Circular Única N° 10 de 2001

Álix Carmenza Céspedes de Vergel
Jefe de la División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista, de fecha 17 FEB. 2005

CONCEPTO TÉCNICO Número 0177	EXAMINADOR TÉCNICO Código 202024
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US005340567A

United States Patent [19]

Cole et al.

[11] Patent Number: 5,340,567

[45] Date of Patent: Aug. 23, 1994

[54] SUNSCREEN COMPOSITIONS

[75] Inventors: Curtis A. Cole, Langhorne, Pa.;
Martin K. O. Lindemann,
Bridgewater, N.J.; Elvin R.
Lukenbach, Flemington, N.J.; Ralph
C. Stutzman, Ringoes, N.J.

[73] Assignee: Johnson & Johnson Consumer
Products, Inc., Skillman, N.J.

[21] Appl. No.: 827,908

[22] Filed: Jan. 30, 1992

Related U.S. Application Data

[63] Continuation of Ser. No. 452,028, Dec. 15, 1989, abandoned.

[51] Int. Cl.⁵ A61K 7/42; A61K 9/10

[52] U.S. Cl. 424/59; 514/938

[58] Field of Search 424/59

[56] References Cited

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OTHER PUBLICATIONS

Bennett, The Cosmetic Formula, 1937, pp. 79 to 81, 229 & 230.

Chem. Abs., 1986, vol. 105, 102509f, Matsueda et al.

Patent Abstract of Japan 60-231607 (1985), vol. 10, No. 98, p. 164C 339.

Primary Examiner—Dale R. Ore

[57] ABSTRACT

Novel sunscreen compositions containing titanium dioxide having a particle size less than about 35 m μ and zinc oxide having a particle size less than about 50 m μ are described as well as methods of protecting the skin from damaging ultraviolet radiation.

8 Claims, No Drawings

SUNSCREEN COMPOSITIONS

This is a continuation of application Ser. No. 07/452,028, filed Dec. 15, 1989 now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to new and useful ultraviolet radiation sunscreen agents and compositions and to methods of protecting human skin against the potentially harmful effects of sunlight.

Although a tan has long been considered a status symbol indicative of good health and the ability to secure sufficient leisure time to enjoy outdoor activities such as swimming, tennis, golf, skiing and the like, it has become very evident that excessive exposure of the human skin to sunlight is harmful.

It is well documented that human skin is sensitive to sunlight and artificial light containing radiation of wavelengths between about 290 nanometers (nm) and 400 nm. Ultraviolet radiation of wavelengths between about 290 nm and 320 nm (UV-B region) has been known to rapidly produce damaging effects on the skin including reddening or erythema, edema, blistering or other skin eruptions in more severe cases. Prolonged or chronic exposure to radiation in this wavelength range has been associated with serious skin conditions such as actinic keratoses and carcinomas. In recent years, concern has also been expressed regarding ultraviolet radiation of wavelengths above 320 nm (UV-A region) and the adverse effects of such radiation on human skin. The radiation between 320 and 400 nm also contributes to the premature aging of the skin. In addition, recent studies indicate that chronic sun exposure limits the immuno-response of the skin. There is also evidence that a tan will offer some protection against burning but is quite ineffectual against other types of solar damage.

Growing public awareness that the enjoyment of outdoor activities must go hand in hand with adequate sun protection has led to an unprecedented growth in the area of sunscreen products. A desirable sunscreen product should have the following attributes: protection in both the UV-A and UV-B ultraviolet radiation ranges; maintenance of coverage, i.e., waterproof and perspiration proof; application and use convenience, i.e., ease of application, invisibility, non-staining and non-greasy; and freedom from irritation as a result of its ingredients, in particular, its active sunscreen ingredients. Of recent interest in this area have been some concerns over the irritancy and sensitization problems that may occur in some individuals utilizing sunscreen products with high SPF values containing organic sunscreen agents.

The effectiveness of a sunscreen product is indicated by its sun protection factor (SPF). The sun protection factor is the ratio of the amount of exposure (dose) required to produce a minimal erythema reaction in protected skin to the amount required to produce the same reaction in unprotected skin. The absolute dose differs from person to person and is largely dependent on one's genetic predisposition and ethnic origin. If a person would normally require ten minute exposure to sunlight to develop a minimal erythema reaction, this person when using an SPF 15 sunscreen product should be able to tolerate up to 150 minutes of sunlight without an erythema reaction. Recent public awareness of the problems of exposure to sunlight has led to a demand

for sunscreen products with high SPF values, i.e., at or above SPF 8.

Ease of application and cosmetic appeal, on the other hand, rely on subjective evaluations such as visual and tactile impression by the user. Consumer research studies indicate that a sunscreen formulation should rub in easily, leave the skin non-sticky and, above all, should be invisible on the skin after application.

OBJECTS OF THE INVENTION

It is an object of the present invention to provide improved sunscreen agents and compositions.

It is another object of the present invention to provide sunscreen compositions containing sunscreen agents that overcome the disadvantages of heretofore available materials and provide adequate and safe protection for human skin.

It is a further object of this invention to provide methods of protecting human skin against the harmful effects of sunlight.

These and other objects and features of the present invention will become readily apparent to one skilled in the art from the detailed description given hereinafter.

SUMMARY OF THE INVENTION

The foregoing objects and other features and advantages of the present invention are achieved by sunscreen compositions containing inorganic sunscreen agents as the active ingredients. More particularly, the present invention relates to sunscreen compositions containing titanium dioxide and zinc oxide of specific particle size ranges and in specific amounts and ratios as the sunscreen agents. These specific compositions permit the use of lower amounts of the sunscreen active ingredients while still achieving the desired high SPF values for the compositions.

The prior art contains a number of disclosures showing the use of titanium dioxide and zinc oxide as sunscreen materials, in various formulations including the following.

In Japanese Patent Application No. 1981 - 161,881, there is a disclosure of cosmetics containing 0.1-40% of ultrafinely divided titanium oxide with a particle size of 10-30 m μ which has been rendered hydrophobic. It is indicated that when hydrophobically treated titanium oxide with a particle size of 10-30 m μ is blended into cosmetic base materials, it transmits visible light but reflects and scatters the harmful ultraviolet rays. Unfortunately, it has been found that when titanium dioxide of this particle size range is utilized as a sunscreen agent in sunscreen compositions, it may result in the loss of one of the most desired properties of such compositions, i.e., invisibility. Products containing titanium dioxide of the particle size disclosed in this application usually have a white color or cast to them and, therefore, are not invisible. In order to overcome the lack of invisibility or whiteness, specific processing techniques are required.

In a co-pending application Ser. No. 75,713, filed Jul. 20, 1987, sunscreen compositions containing microfine titanium dioxide are disclosed. The particle size of the titanium dioxide is required to be less than 10 m μ . It is also indicated that other sunscreen agents can be utilized with the titanium dioxide.

In German Patent No. 3,642,794 (1987) there is disclosed a cosmetic composition for preventing sunburn which contains 1-25 % zinc oxide of a particle size of 70-300 microns, and it is further indicated that the com-

position may also contain titanium dioxide of a particle size of 30-70 microns. This composition would not be desirable because of its unaesthetic whiteness characteristics at high SPF levels.

In Japanese Patent No. 60,231,607 (1985) there is disclosed a sunscreen cosmetic containing 1-30% zinc oxide powder of particle size from 10-60 m μ . No other sunscreen agents are disclosed.

In Japanese Patent No. 72,042,502 there is disclosed an antisunburn cosmetic containing titanium dioxide having a particle size of 30-40 m μ and it is indicated that a synergistic effect may be achieved by using titanium dioxide with other known UV absorbents but none are disclosed in the abstract.

DETAILED DESCRIPTION OF THE INVENTION

The sunscreen compositions of the present invention contain as active sunscreen agents, microfine titanium dioxide of a specific particle size, i.e., less than about 35 millimicrons (hereinafter designated as "m μ ") and microfine zinc oxide of a specific particle size, i.e., less than about 50 m μ .

The use of the specific titanium dioxide in the above compositions have been found to enhance solar radiation protection without detracting from desirable cosmetic properties such as ease of application and, most importantly, invisibility.

Titanium dioxide is an inorganic substance which is widely used as a pigment in oil and latex paints where a pure white color is desired. It is also employed as an additive in cosmetic products such as bar soaps to enhance the whiteness and opacity of the product. This property of titanium dioxide results from its ability to scatter visible radiation. To obtain maximal scattering and hence whiteness, the particle size of commonly used titanium dioxide is generally between 150 and 350 m μ . Titanium dioxide also absorbs and scatters UV-radiation. As is the case with visible light, optimal scattering is a function of the particle size while absorption of UV-radiation is an inherent property of the titanium dioxide molecule itself.

It is highly desirable that a sunscreen composition after application to the skin should be invisible. Since the scattering of visible light results in an ungainly whitish appearance of the skin, it is essential that the particle size and the processing to prepare the selected titanium dioxide as well as the resulting compositions in which it is utilized maximize UV-B and UV-A absorption and minimize scattering of visible light.

As stated above, the microfine titanium dioxide useful in the present invention is of a particle size of less than about 35 m μ , preferably less than about 10 m μ . The titanium dioxide useful in the present invention can be prepared by well-known commercial methods. One such method is the classic sulfate process discussed in the Kirk-Othmer Encyclopedia, Vol. 23, on page 143 and set forth in a flow diagram on page 146. The essential step in this process is hydrolysis, under carefully controlled conditions, of an acid solution of titanyl sulfate yielding a hydrous precipitate. This precipitate contains adsorbed sulfuric acid (pH~1) and the resulting pigments are unsuitable for cosmetic applications. To render it suitable for such uses, it is neutralized with barium hydroxide to obtain a pH of about 3 to 6 and calcinated to increase the particle size. As a result of this process, the resulting titanium dioxide is usually present in a mixture with barium sulfate. Other processes are

available which do not utilize barium hydroxide as a neutralizing agent. If desired, for stability purposes, these particles can be coated with stearic acid or other suitable materials.

The titanium dioxide useful in the present invention should be present in an amount of from about 2.0 to 25.0% by weight of the total composition, preferably from about 2.0 to 15.0%.

The other sunscreen agent useful in the compositions of the present invention is zinc oxide of a specific particle size. Zinc oxide is an inorganic substance which, conventionally serves as a white pigment in paints, papers, and polymers among other uses. It also has been utilized as a physical sunblock in personal care products. It functions as a pigment by scattering the visible light due to its high index of refraction compared with vehicle components and also due to its particle size range of 200-350 m μ . Zinc oxide also scatters and absorbs ultraviolet radiation. The scattering of visible and ultraviolet radiation is a function of particle size, while absorption of UV radiation is an inherent property of the zinc oxide itself.

It is highly desirable that a sunscreen composition after application to the skin should be invisible. Since the scattering of visible light results in an ungainly whitish appearance of the skin, it is essential that the particle size and the processing to prepare the selected zinc oxide as well as the resulting compositions in which it is utilized maximize UVB and UVA absorption and minimize scattering of visible light.

It has been found that when the zinc oxide of the compositions of the present invention, i.e., particle size less than about 50 m μ , preferably less than about 20 m μ , is utilized, such compositions upon use on the skin are invisible and, therefore, highly desirable.

The zinc oxide useful in the present invention can be prepared by a number of methods well known in the chemistry of zinc. The essential step in such processes is the precipitation under carefully controlled conditions, of an insoluble microfine zinc salt prepared from soluble forms of the zinc ion and precipitating anion. The thus formed insoluble salt must be of such nature that it may be subsequently converted to zinc oxide in a solid state reaction, for example by heat treatment. Specifically, an aqueous solution of zinc sulfate combined with aqueous sodium carbonate results in the precipitation of microfine zinc carbonate, which may be pyrolyzed to zinc oxide by driving off carbon dioxide thereby yielding small particle size zinc oxide.

The zinc oxide useful in the present invention should be present in an amount of from about 2.0 to 25.0% by weight of the total composition, preferably from about 2.0 to 15.0%.

The total amount of the titanium dioxide and zinc oxide by weight of the total composition should be from about 4.0 to 25.0%. If less than about 4.0% by weight of the total composition is utilized, then one will not achieve the desired high SPF values and if greater than 25.0% by weight of the total composition is utilized, processing and economic factors come into consideration.

In connection with the sunscreen compositions of the present invention, it has further been found that when the titanium dioxide and zinc oxide are in a weight ratio of from about 1:25 to 10:1, preferably 1:8 to 3:1, they act as a synergistic combination with respect to SPF values.

The term "synergistic combination" as used herein refers to a combination of sunscreen actives, i.e., tita-

ni-um dioxide of a particular particle size and zinc oxide of a particular particle size which, at a given total concentration, yield higher SPF values than either of the two ingredients individually at the same total concentration. This is such because the SPF values are related to absorbancy of UV light in a non-linear fashion and therefore, synergism cannot be expressed by the mere addition of the SPF values of the two ingredients per se. Alternatively, sunscreen combinations using a lower total concentration exhibiting SPF values equal to or greater than the SPF values of either of the individual sunscreen agents alone also demonstrate synergy.

The sunscreen compositions of the present invention contain titanium dioxide and zinc oxide as the sunscreen agents and an extending medium such as a carrier or vehicle which adapts said agents for application to the skin. Included in these vehicles or carriers can be materials selected from a class known as "filler" materials. It has been observed that when certain of these materials are present, such as clays and talc, the SPF values of the resulting compositions are somewhat enhanced even though these materials when utilized in compositions without sunscreen actives exhibit negligible SPF values. The compositions of the present invention can be in either solid, liquid or aerosol form. The sunscreen agents of the present invention can also be incorporated into various cosmetic and personal care products such as hand and body lotions, oils, ointments, lip balm products, facial cosmetics and the like.

Specific embodiments of the present invention are illustrated by the following examples. It will be understood, however, that the invention is not confined to the specific limitations set forth in the individual examples, but rather to the scope of the appended claims.

EXAMPLE I

An anhydrous sunscreen ointment composition is prepared as follows:

50.0 g. of mineral oil and 5.0 g. of powdered polyethylene are mixed with 35.0 g. of a dispersion of 70 parts titanium dioxide (particle size $< 10 \mu\text{m}$) in 30 parts isostearic acid at a temperature of about 95°C . until a homogeneous melt is obtained. With constant stirring 10.0 g. of microfine zinc oxide (particle size of $18 \mu\text{m}$) are added and uniformly dispersed. Stirring is continued while the mixture is allowed to cool down to ambient temperature.

The resulting composition has the following formulation:

Ingredient	% w/w
mineral oil	50.0
polyethylene	5.0
zinc oxide	10.0
titanium dioxide	24.5
isostearic acid	10.5
	100.0

The in-vitro SPF (Sun Protection Factor) of this composition is measured using the system described by Cole and VanFossen [Cole, C., VanFossen R., (1990) In-vitro model for UVB and UVA protection. In: *Sun-screens: Development, Evaluation and Regulatory Aspects*, N. Shaath and N. Lowe Eds., Marcel Dekker Pub. New York, N.Y. (in press)]. Briefly, this system consists of the measurement of transmission of solar simulated UV radiation through composition (1.2 mg/cm^2) applied to the skin. The excised mouse skin with and without a

sunscreen measurement system consists of an optical sensor that is only sensitive to sunburning radiation and has a sensitivity spectrum similar to the human erythema sensitivity spectrum. The SPF is the ratio of the optical signal through the skin (no sunscreen) divided by the optical signal through the skin with the sunscreen. The system is calibrated against a series of sunscreens of known SPF (4 through 36) determined in-vivo using the FDA monograph method (Federal Register, Aug. 25, 1978, Sunscreen drug products for over-the-counter human drugs. pp 38206-38269.) The resulting SPF of the composition of Example I above is 32 and the composition is aesthetically satisfactory.

EXAMPLE II

An anhydrous sunscreen ointment composition is prepared according to the procedure of Example I by admixing 58.4 g. of mineral oil with 20.8g of a dispersion of 60 parts titanium dioxide (particle size $< 10 \mu\text{m}$) and 40 parts isostearic acid, 12.5 g. zinc oxide (particle size $18 \mu\text{m}$) and 8.3 g. isostearic acid. The resulting composition has the following formulation:

Ingredient	% of w/w
mineral oil	58.4
zinc oxide	12.5
titanium dioxide	12.5
isostearic acid	16.6
	100.0

When this composition is tested according to the in-vitro test procedure of Example I, the SPF is 24. The resulting composition is aesthetically satisfactory.

When the zinc oxide in the above formulation is removed and replaced by an equal weight amount of titanium dioxide (total $\text{TiO}_2 = 25.0\%$) the resulting SPF is 14 and when the titanium dioxide is removed and replaced by an equal weight amount of zinc oxide (total $\text{ZnO} = 25.0\%$) the resulting SPF is 17. The differences in the SPF values are significant and this demonstrates the synergism of the combination of titanium dioxide and zinc oxide in the compositions of the present invention.

EXAMPLE III

A sunscreen lotion composition is prepared as follows:

380.35 g. of deionized water, 18.75 g. of an acrylic/acrylate copolymer (Carboset) and 5.0 g. of a 7.5% (w/v) ammonium hydroxide solution are admixed and stirred vigorously at room temperature until complete dissolution is achieved.

In a separate container, 5.0 g. of polyethylene and 50.0 g. of mineral oil are heated with mixing to 95°C . or until the polyethylene is melted. To this mixture is added 30.0 g. of sorbitan sesquioleate, 30.0 g. of PEG-7 castor wax, 22.5 g. of hydroxylated lanolin, and 130.0 g. of a dispersion of hectorite clay in isopropyl myristate. The mixture is stirred while maintaining a temperature of 60°C .- 65°C . until a uniform melt is achieved. To this mixture is added 90.9 g. of a dispersion of 33% TiO_2 (particle size $20 \mu\text{m}$) in a mixture of mineral oil and triglycerides followed by the slow addition of 107.5 g. of microfine zinc oxide (particle size $18 \mu\text{m}$). After the uniform incorporation of the particulate matter, the temperature is adjusted to 55°C . and 50.0 g. of cyclo-methicone (Silicone Fluid 344-Dow Corning) and

80.0 g. of cyclomethicone (Silicone Fluid 345-Dow Corning) are added. At this point the previously prepared water phase is combined with this mixture under strong agitation. Stirring is continued and the emulsion is allowed to cool slowly.

The resulting composition has the following formulation:

Ingredient	% of w/w
polyethylene	0.50
mineral oil	5.00
Silicone Fluid #344	5.00
Silicone Fluid #345	8.00
hectorite clay/isopropyl myristate dispersion	13.00
sorbitan sesquiolate	3.00
PEG-7 castor oil	3.00
hydroxylated lanolin	2.250
titanium dioxide	3.000
zinc oxide	10.750
mineral oil/triglycerides mixture	6.090
acrylic/acrylate copolymer	1.875
ammonium hydroxide (7½% soln.)	0.500
water	38.035
	100.000

The finished product has a viscosity of about 13,000 cps and an SPF of 25.

This product is subjected to a whiteness test as follows:

0.5 ml of the product is spread over a 3 in. square of black art-construction paper and allowed to "dry" for 1 to 2 hours. Ten whiteness measurements are taken (using a Minolta Chroma Meter) on the L*a*b* color system scale. These measurements are taken in a uniform pattern over the total surface area.

The whiteness value (L*) is an average of the ten values. This L* value correlates well with human observations of product utilized on skin for transparency. The L* values represent shades between 0=black to 100=white with values greater than 50 being deemed aesthetically unacceptable.

When the product of Example III is tested for whiteness according to the above procedure it has an L* value of 37.5 which is very satisfactory.

EXAMPLE IV

A sunscreen cream composition is prepared as follows:

20.0 g. of polysodium methacrylate (Alcosperse 125) is mixed in 499.5 g. of deionized water and then 27.0 g. of propylene glycol, 1.5 g. methylparaben, 1.0 g. of disodium EDTA and 7.00 g. magnesium sulfate are added. The mixture is then heated to 80° C. and 30.0 g. of microfine titanium dioxide (particle size < 10 µm) are dispersed therein with agitation.

In a separate container, 168.0 g. of mineral oil, 10.0 g. of magnesium stearate, 60.0 g. of a mixture of sorbitan oleate, castor wax, beeswax and stearic acid (Arlacel 481), 20.0 g. of PEG-7 castor wax and 50.0 g. of isopropyl myristate are added under constant stirring. The mixture is heated to 80°-85° C. and when a uniform melt is obtained, 100.0 g. of microfine zinc oxide (particle size 18 µm) are slowly stirred into the mixture.

The oil phase is added to the water phase with vigorous stirring and cooled slowly while continuing to mix. At a temperature of 40° C., 6.0 g. of a 33% solution of

Quaternium 15 (Dowicil 200) are added and the mixture is homogenized while warm.

The resulting composition has the following formulation:

Ingredient	% of w/w
mineral oil	16.80
magnesium stearate	1.00
Arlacel 481	6.00
PEG-7 castor oil	2.00
isopropyl myristate	5.00
zinc oxide	10.00
titanium dioxide	3.00
propylene glycol	2.70
methylparaben	0.15
disodium EDTA	0.10
magnesium sulfate	0.70
Dowicil 200 (33%)	0.60
Alcosperse 125	2.00
deionized water	49.95
	100.00

The final product has a viscosity of 108000 cps, an SPF value of 16 and a L* value of 40.

In addition to the preferred embodiments described herein, other embodiments, arrangements and variations within the spirit of the invention and the scope of the appended claims will occur to those skilled in the art.

What is claimed is:

1. A sunscreen composition comprising an extending medium and a synergistic combination of titanium dioxide having a particle size of less than about 35 µm and zinc oxide having a particle size of less than about 50 µm; said titanium dioxide and zinc oxide being present in a weight ratio of from about 1:25 to 10:1 and the total of said titanium dioxide and zinc oxide comprising from about 4.0 to about 25.0% by weight of the total composition.

2. The sunscreen composition of claim 1 where the particle size of the titanium dioxide is less than about 10 µm.

3. The sunscreen composition of claim 1 wherein the particle size of the zinc oxide is about 18 µm.

4. The sunscreen composition of claim 1 containing from about 2.0 to 15.0% by weight of the total composition of titanium dioxide.

5. The sunscreen composition of claim 1 containing from about 2.0 to 15.0% by weight of the total composition of zinc oxide.

6. The sunscreen composition of claim 1 wherein the titanium dioxide and zinc oxide are present in a weight ratio of from about 1:8 to 3:1.

7. A method of protecting human skin from the erythremic effects of ultraviolet radiation which comprises applying to the skin a sunscreen composition containing an extending medium and a synergistic combination of titanium dioxide having a particle size of less than about 35 µm and zinc oxide having a particle size of less than about 50 µm; said titanium dioxide and zinc oxide being present in a weight ratio of from about 1:25 to 10:1 and the total of said titanium dioxide and zinc oxide comprising from about 4.0 to about 25.0% by weight of the total composition.

8. The method of claim 7 wherein the titanium dioxide and zinc oxide are present in a weight ratio of from about 1:8 to 3:1.

* * * * *

United States Patent [19]

Iwaya et al.

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[54] ANTI-SUNTAN COSMETIC COMPOSITION

[75] Inventors: Katsumasa Iwaya, Oyama; Hajime Hotta, Funabashi, both of Japan

[73] Assignee: Kao Corporation, Tokyo, Japan

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[63] Continuation of Ser. No. 941,341, Dec. 15, 1986, abandoned.

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[58] Field of Search 424/59

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Primary Examiner—Dale R. Ore

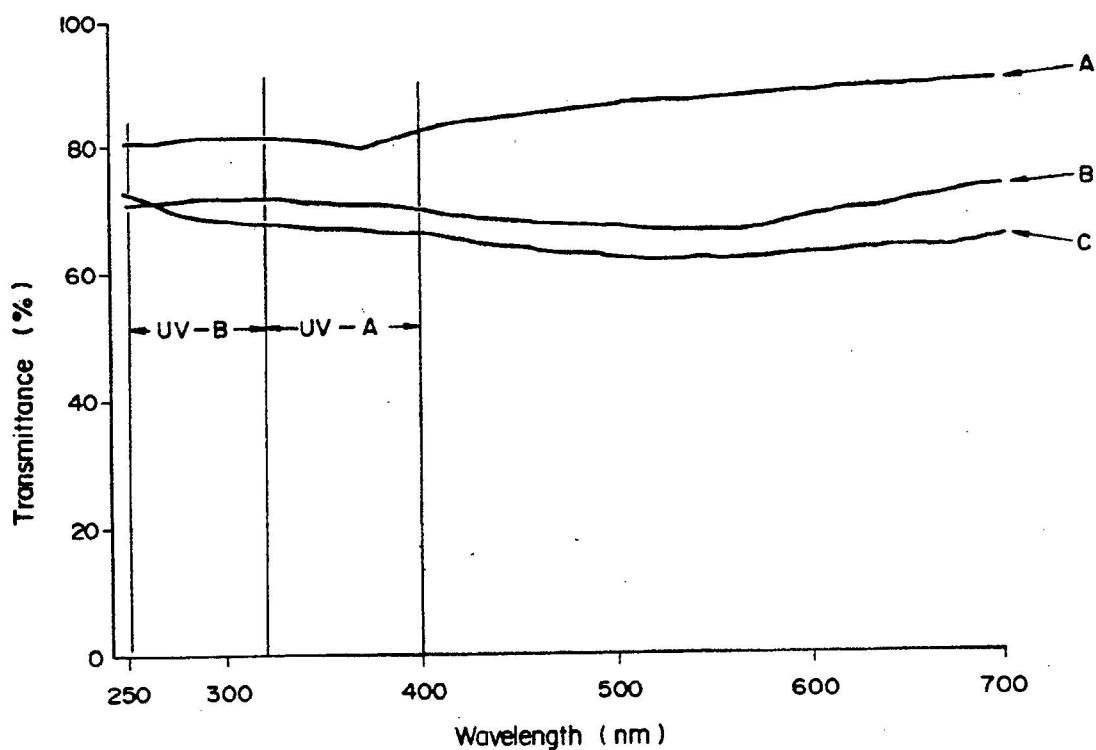
Attorney, Agent, or Firm—Oblon, Spivak, McClelland, Maier & Neustadt

[57] ABSTRACT

A novel anti-suntan cosmetic composition comprises from 1 to 25% by weight of fine particulate zinc oxide having an average particle size of from 70 to 300 m μ , which scatters or absorbs ultraviolet rays, especially those in UV-A region.

The composition prevent human skin from blotches and freckles, and suppress the aging of the skin.

6 Claims, 6 Drawing Sheets



A: Zinc oxide (0.5 μ)

B: Ferric oxide (0.5 μ)

C: Titanium oxide (0.4 μ)

ANTI-SUNTAN COSMETIC COMPOSITION

This is a continuation of application Ser. No. 06/941,341, filed on Dec. 15, 1986, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to an anti-suntan cosmetic composition and, more particularly, to an anti-suntan cosmetic composition comprising a specific zinc oxide which scatters or absorbs ultraviolet rays, especially those in UV-A region, harmful to the skin. The skin can be protected from suntan by the anti-suntan cosmetic composition, so that the skin would not be blotched or freckled and also be prevented from aging.

2. Description of the Prior Art

As an anti-suntan cosmetic composition, ultraviolet absorbers or titanium oxide having specific particle size have been conventionally used. Such anti-suntan cosmetic compositions absorb or scatter ultraviolet rays of wavelength in a high energy region near 250-350 nm, by which the skin would be inflamed.

As a result of the recent progress for the study on harmfulness of ultra-violet rays, it has been found that ultraviolet rays in the UV-A region of from 320 to 400 nm, by which the skin is sun-tanned, cause blotches and freckles and promote the skin aging. Therefore, ultraviolet rays in the UV-A region, as well as ultraviolet rays in the UV-B region of from 250 to 320 nm, by which the skin is sun-burned, are considered to be harmful to the skin. In view of the above, absorbers for UV-A region ultraviolet rays was developed recently (refer to Japanese Patent Application Laid-Open No. 62517/1984).

However, these ultraviolet ray (UV-A) absorbers are organic compounds and yet involve various problems in the safety and the lasting effect thereof.

On the other hand, there have been made various studies on absorption and scattering of UV-ray and it has been known that a certain kind of inorganic powder has a great effect particularly for interrupting ultraviolet rays.

It has generally be known that powder having a higher reflective index has greater hiding power and has greater UV-ray interrupting effect. Upon measuring the optical transmittance of various metal oxides (those conventionally used for cosmetics having particle size of 0.5 μ m) having a high reflective index, it was confirmed that the optical transmittance at the wavelength region from 250 to 700 nm was substantially constant (FIG. 1).

The metal oxides having an adequate UV prevention effect, thus, involve an excessive hiding power which gives unacceptable feeling to the users, so that they are not suitable as an ingredient of anti-suntan cosmetic compositions, although they are easily available.

As described above, there have not yet been provided those absorbers for ultraviolet rays in the UV-A region, which are harmless, useful, and easily and inexpensively available.

SUMMARY OF THE INVENTION

In view of the above, the present inventors have made an earnest study for developing those cosmetic compositions that can easily be available at a reduced cost, with a high safety and having a high UV-ray preventive performance in the UV-A region. We noted that zinc oxide shows an absorption, although small, at

370 nm in the measurement of the optical transmittance for metal oxides (FIG. 1) and, as a result of a further study, found that zinc oxide of a certain particle size could selectively decrease the transmittance to the light in the UV-A region and that anti-suntan cosmetic compositions having excellent transparent feeling could be obtained by incorporating such zinc oxide of a predetermined amount.

We further found that when a specific titanium oxide was incorporated in combination with the above fine particulate zinc oxide, an anti-suntan cosmetic composition which is effective for ultraviolet rays in both the UV-A region and UV-B region and excellent in the safety and in the lasting effect could be obtained.

This invention was accomplished based on the above findings, in which the first invention provides anti-suntan cosmetics compositions comprising 1 to 25% by weight of fine particulate zinc oxide having an average particle size of from 70 to 300 μ m, and a second invention provides anti-suntan cosmetic compositions further containing titanium oxide having particle size of from 30 to 70 μ m.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph showing the transmittance of various metal oxides having an average particle size of about 0.5 μ m against the rays of a wavelength from 250 to 700 nm.

FIG. 2 is a graph showing the transmittance of zinc oxide having various particle size against the rays of a wavelength from 250 to 700 nm.

FIG. 3 is a graph showing relation between the minimum transmittance and an average particle size of zinc oxide.

FIG. 4 is a graph showing the transmittance of each powder foundation obtained in Example 5 against the rays of a wavelength from 250 to 700 nm.

FIG. 5 is a graph showing the transmittance of titanium oxides of various particle size against the rays of a wavelength from 250 to 700 nm.

FIG. 6 is a graph showing the transmittance of hydrophobicized titanium oxide against the rays of a wavelength from 250 to 700 nm.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

Zinc oxide to be incorporated in the cosmetic compositions of the present invention are fine particles of an average particle size from 70 to 300 μ m. The average particle size referred to in the present text is a diameter converted from the meso-pore specific surface area determined by the t-plot method (particle size converted excluding the specific surface area of micro pores of less than 20 Å). In detail, the average particle size D (μ), assuming the particle as spherical form, can be obtained by the following equation:

$$D = 6 / \rho S$$

where S (m^2/g) represents a meso-pore specific surface area and $\rho(g/cm^3)$ is the density.

If the particle size of the zinc oxide used in this invention is less than 70 μ m, it becomes transparent (light-permeable) against the rays in both for visible and ultraviolet wave-length regions, whereas if it is greater than 300 μ m, the hiding power is increased and the prevent-

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ing performance for the rays in the UV-A region becomes insufficient.

Zinc oxide prepared by any known methods may be used in the present invention. The known methods are; an indirect method (French Method) in which zinc oxide is obtained by melting to evaporate metal zinc and then oxidizing it in a gas phase, a direct method (American method) in which zinc oxide is obtained by sintering and reducing zinc ores together with cokes and then oxidizing the thus obtained metal zinc, and a wet method in which a water-soluble zinc salt such as zinc chloride and zinc sulfate is used as a starting material and zinc oxide is obtained by crystallizing and sintering them. Zinc oxide of about 300 to 800 m μ and of about 600 to 700 m μ can be obtained by the direct and indirect method, respectively. The thus obtained zinc oxide may be pulverized depending on the requirement. In the case of the wet method, zinc oxide of particle size greater than 70 m μ may be obtained by controlling the crystal growing conditions. In the indirect method, those having an aimed particle size can be obtained by controlling the reaction conditions of gas phase oxidation, for example, reaction temperature, zinc concentration and oxygen concentration to be lower.

The amount of the zinc oxide to be incorporated into the cosmetic composition is from 1 to 25% by weight (hereinafter simply referred to as %) and an appropriate amount can be selected depending on the type of cosmetic composition. For instance, in the case of preparing creams, incorporation amount of from 1 to 10% is preferred in order to obtain desired effects with no rough or frictional feelings. In the case of preparing a system such as make-up cosmetics in which a great amount of powder is incorporated, from 5 to 25% of zinc oxide can be incorporated.

The particle size of titanium oxide to be used in the second invention of the present invention is preferably from 30 to 70 m μ and, the rutile type one having particle size of from 40 to 70 m μ is particularly preferred. Titanium oxide is prepared, for example, by the wet method. That is, rutile type titanium oxide may be prepared by treating ilmenite with sulfuric acid into titanium oxysulfate and calcinating meta-titanic acid obtained by hydrolyzing the titanium oxysulfate at a temperature of about 1000° C. The particle size may be controlled also by pulverization after obtaining the rutile type titanium oxide or pulverization after the hydrophobicizing treatment described later, however, it is preferred to control the particle size at the hydrolyzing step or calcinating step. The rutile type titanium oxide having an average particle size of from 40 to 70 m μ exhibits increased absorption and scattering of the rays in the UV-A region near 320 nm in addition to the rays in the UV-B region. Accordingly, in the second invention, the rays in the entire region including the UV-B region and the UV-A region can be prevented by the combined use of titanium oxide with zinc oxide having UV-A absorption at a higher wavelength near 370 nm, thereby obtaining preferable anti-suntan cosmetic compositions. Further, while titanium oxide of other crystal forms than rutile type titanium oxide such as anatase type titanium oxide has a maximum absorption wavelength in the UV-B region, the low wavelength UV-A region can also be covered to some extent by increasing the incorporation amount. These titanium oxides are used in an amount from 1 to 20% and, preferably, from 5 to 10%.

Zinc oxide and titanium oxide described above provide satisfactory effects when they are used by themselves, however these powders may be hydrophobicized by silicone oils, metal soaps, dialkyl phosphate or the likes. By the hydrophobicizing treatment, frictional feeling of zinc oxide or titanium oxide is reduced and spreadability and water proofness are improved, so that they can be dispersed stably into a base of cosmetic composition. Preferred agents for the hydrophobicizing treatment are silicone oils and, particularly, methyl hydrogen polysiloxane, dimethylpolysiloxane and the like. Treatment with the silicone oils can be carried out without causing coagulation of zinc oxide or titanium oxide particles, and the water proofness can be improved extremely.

The hydrophobicizing treatment is carried out, for example, by sufficiently mixing titanium oxide with an average particle size of from 40 to 70 m μ and silicone oils dissolved in a solvent while heating them in a low speed blender, distilling off the solvent subsequently and then applying heat treatment at 90°-450° C. The amount of the solvent (silicone oil+solvent) used herein is such that the solvent can completely sinter zinc oxide or titanium oxide, or bring them into a slurry state, preferably, in the same amount as that for zinc oxide or titanium oxide. Prior to the hydrophobicizing treatment, titanium oxide or zinc oxide may previously be treated with silica and/or alumina.

Since titanium oxide has high surface activity, it tends to coagulate and has poor dispersibility. It has also a catalytic activity, so that other cosmetic ingredients are degraded. Accordingly, hydrophobicizing treatment to titanium oxide is particularly preferred for obtaining cosmetic compositions having higher quality.

In the cosmetic compositions of this invention, a compound capable of absorbing ultraviolet rays in the UV-B region can also be incorporated. Examples of such compound include those organic compounds having maximum absorption performance at 280-320 nm, for example, 2-ethylhexyl p-methoxy cinnamate and 2-ethylhexyl p-dimethylamino benzoate. The above compound can be incorporated in an amount from 0.5 to 10% and, preferably, from 1 to 5%.

In the cosmetic compositions according to this invention, the ultraviolet absorber described above is incorporated into a cosmetic carrier to prepare into various types of cosmetic compositions.

For example, they can be prepared into foundations by incorporating loading pigment, coloring pigment, oil and shaping agent; creams by incorporating oil, water and emulsifier; lotions by incorporating oil, water, solubilizing agent and lower alcohol; and lip sticks by incorporating oil and colorant.

The commercial value of the cosmetic compositions of the present invention can further be enhanced by the addition of a humectant, perfume, anti-oxidant, corrosion inhibitor or the like.

The cosmetic compositions according to this invention can prevent human skin from blotches and freckles and suppress the aging of the skin by scattering and absorbing ultraviolet rays in the UV-A region (and UV-B region) and preventing suntan. Further, zinc oxide incorporated therein has a skin astringent effect, which is effective particularly for skin care cosmetics or cosmetics used in the summer season.

This invention will further be explained in detail referring to Examples.

EXAMPLE 1

Effect of the particle size of zinc oxide to optical transmittance was examined. Zinc oxide powders having an average particle size of 30, 50, 250, 500 and 1000 μ m were dispersed each by 1% by weight in a diisostearyl malate, and then put between quartz glass cell of 0.03 mm of thickness and the optical transmittance was measured by a spectrophotometer (Model MPS 2000, manufactured by Shimazu Seisakusho). The results are shown in FIG. 2. The figure shows that zinc oxide used in this invention (average particle size of 250 μ m) has remarkably increased absorption near the wavelength at 370 nm.

EXAMPLE 2

The optical transmittance of zinc oxide powders shown in Table 1 below was measured. The results are shown in FIG. 3. As shown in the figure, remarkable reduction in the optical transmittance is observed at the average particle size between 70 and 300 μ m.

Symbol	a	b	c	d	e	f	g	h	i
Product name	ZINCA-20	ultrafine ZnO powder	EXTRAFINE GRAIN ZINC OXIDE	—	—	ultrafine zinc powder	—	—	Zinc powder No. 1
Manufacturer	Sakai Kogyo K.K.	Mitsubishi Kinzoku	Sumitomo Kinzoku Kozan	—	—	Sakai Kogyo K.K.	—	—	Sakai Kogyo K.K.
Manufacturing method	wet method	wet method (Japanese Patent Application Laid-Open No. 205319/1982)	indirect method	same as c	same as c	indirect method followed by wet pulverization	same as c (the reaction conditions of gas phase oxidation were controlled)	indirect method followed by wet pulverization	indirect method
	zinc chloride ↓ zinc carbonate (calcination) ↓ zinc oxide	zinc ion solution ↓ zinc oxalate ↓ zinc oxide	metal zinc ↓ zinc oxide						
Average particle size (μ m)	40.7	44.3	96.4	114	120	156	157	250	527
Minimum transmittance (%)	96.0	84.3	44.7	44.8	44.7	48.1	49.2	55.0	75.8
Wavelength at minimum transmittance (nm)	360	364	370	370	370	372	372	372	373

Example 3

Anti-suntan lotion

(1) ethanol	10%
(2) glycerine	4%
(3) zinc oxide: average particle size of 120 μ m (obtained by indirect method)	3%
(4) titanium oxide (200-300 μ m)	2%
(5) UV-absorber (2-ethylhexylparamethoxy cinnamate)	0.5%
(6) camphor	0.15%
(7) perfume	small amount
(8) purified water	appropriate amount

Ingredients (1), (2), (5) and (7) mixed and dissolved were added to a solution prepared by dispersing the ingredients (3) and (4) into (8) containing the ingredient (6). The mixture was well agitated and prepared into a product.

Example 4

Anti-suntan cream

(1) beeswax	5.5%
(2) cetanol	4.5%
(3) hydrogenated lanoline	7%
(4) squalane	33%
(5) fatty acid glycerine	3.5%
(6) oleophilic glycerine monostearate	2%
(7) polyoxyethylene sorbitan monolaurate (20 E.O)	2%
(8) zinc oxide: average particle size of 157 μ m (obtained by indirect process)	8%
(9) perfume	small amount
(10) preservative	appropriate amount
(11) antioxidant	appropriate amount
(12) propylene glycol	4.5%
(13) purified water	appropriate amount

Ingredients (8), (10), (12) and (13) were stirred to mix and then kept at 70° C. (aqueous phase). Other ingredients were mixed and dissolved under heating and kept

at 70° C. The thus obtained oil phase was added into the aqueous phase described above and the mixture was preliminarily emulsified, then emulsified by a homogenizer. The resultant emulsion was cooled down to 30° C.

Example 5
Anti-suntan powder foundation
Formulation:

Ingredient	Incorporation Amount (%)	
	Example 5	Comparative Example 1
(1) mica	appropriate amount	appropriate amount
(2) talc	20	20
(3) zinc oxide: average particle size of 156 μ m (pulverizate of the product obtained by the indirect method)	10	—
(4) rutile titanium oxide: average particle size of 50 μ m	10	10

-continued

Example 5 Anti-suntan powder foundation Formulation:		
Ingredient	Incorporation Amount (%)	
	Example 5	Comparative Example 1
(5) titanium oxide: average particle size of 200-300 m μ	8	8
(6) iron red oxide	0.8	0.8
(7) yellow iron oxide	2.5	2.5
(8) black iron oxide	0.1	0.1
(9) liquid paraffin	8	8
(10) beeswax	2	2
(11) preservative	appropriate amount	appropriate amount
(12) perfume	small amount	small amount

Preparation method

Ingredients (1)-(8) were mixed and pulverized. They were placed in a high speed blender, to which ingredients (9)-(11) mixed and dissolved at 80° C. were further added and homogenized. Further, after admixing the ingredient (12), the mixture was again pulverized and passed through a sieve, and then compression molded onto a metal disc.

Optical transmittance was measured for the thus obtained powder foundation and commercially available product A (containing titanium oxide of 200-300 m μ and having low UV-A absorbance, used as a pigment) to the light of 250-700 nm. Upon measurement, diisostearyl malate was used as a medium, to which 10% by weight of each foundation were dispersed, put between quartz glass cells of 0.03 mm thickness and the optical transmission was measured. The results are shown in FIG. 4. As shown in the figure, the foundation of Comparative Example 1 absorbs and scatters the rays in the UV-B region causing sunburn due to the effect of titanium oxide having an average particle size of 50 m μ , while the foundation of Example 5 absorbs and scatters the rays in the UV-A and UV-B regions due to the effect of both of titanium oxide of an average particle size of 50 m μ and zinc oxide of an average particle size of 156 m μ . The foundation of Example 5 shows weak hiding power to the visible region as comparable with that of the commercially available product A.

Example 6	
Creamy foundation	
(1) stearic acid	5.0%
(2) oleophilic glycerine monostearate	2.5%
(3) cetostearyl alcohol	1%
(4) propylene glycol monolaurate	3%
(5) squalane	7%
(6) olive oil	8%
(7) butyl paraoxybenzoate	appropriate amount
(8) purified water	appropriate amount
(9) triethanol amine	1.2%
(10) sorbitol	3%
(11) methylparaoxy benzoate	appropriate amount
(12) titanium oxide (200-300 m μ)	10%
(13) talc	5%
(14) coloring pigment (0.8% red iron oxide, 2.5% yellow iron oxide and 0.1% black iron oxide)	3.4%
(15) zinc oxide having an average particle size of 128 m μ (obtained by wet method)	11%
(16) perfume	small amount

Pigment ingredients (12)-(15) were mixed and pulverized. A solution comprising a mixture of aqueous phase ingredients (8)-(11) was prepared separately, to which pulverized pigments were added and dispersed followed by heating at 75° C. The oil phase ingredients (1)-(7) heated to dissolve at 80° C. were added under stirring to the previously conditioned aqueous phase and emulsified. The emulsion was cooled under stirring and the ingredient (16) was added at 50° C. and cooled to a room temperature under stirring.

Example 7	
Lip stick	
(1) beeswax	18%
(2) microcrystalline wax	12%
(3) paraffin wax	5%
(4) carnauba wax	7%
(5) lanoline	8%
(6) jojoba oil	balance
(7) liquid paraffin	12%
(8) isopropyl palmitate	8%
(9) silicon-covered titanium oxide (40 m μ)	5%
(10) zinc oxide having an average particle size of 100 m μ (obtained by the indirect Process)	5%
(11) colorant	appropriate amount
(12) antioxidant	appropriate amount
(13) perfume	appropriate amount

Ingredients (9), (10) and (11) were added to a portion of the ingredient (6) and then treated in a roller mill. Ingredients (1)-(5), (7), (8) and (12) are mixed and dissolved together with the remaining portion of the ingredient (6), to which the product treated by a roller mill was added and uniformly dispersed. At the last, the ingredient (13) was added and, after mixing, poured into a dye, cooled and then the thus obtained stick was inserted into a container. The thus obtained lip stick showed high dispersibility with no sedimentation and, after coating to lips, they were less discolored.

REFERENCE EXAMPLE 1

Independent effect of scattering and absorbing the rays in the ultraviolet region and visible region of titanium oxide having an average particle size from 35 to 70 m μ used in the second invention were studied. The results are shown below.

(Measuring Method)

1% by weight of titanium oxide was dispersed in a medium, isostearyl malate, and the dispersion was put between quartz cells of 0.03 mm thickness and the transmittance at the wavelength region from 250 to 700 m μ was measured by using a spectrophotometer (Model MPS-2000 made by Shimazu Seisakusho).

(Results)

The results of the measurement are shown in FIG. 5. Titanium oxide having a large average particle size (200 m μ) showed an optical transmittance substantially equal both to the ultraviolet rays and visible rays. Titanium oxide having an extremely small average particle size (15 m μ) had a selectivity to ultraviolet rays but the effect was not sufficient. On the other hand, titanium oxide having an average particle size from 35 to 75 m μ showed selectively excellent scattering and absorbing effects particularly to ultraviolet rays at a wavelength from 290 to 350 nm, which cause intense inflammation,

and had weak covering effect to the optical rays in the visible region. Among all, titanium oxide having a particle size of 50 m μ had highest interrupting effect and adequate maximum interrupting wavelength of 330 nm.

REFERENCE EXAMPLE 2

The variation of the ultraviolet ray absorbing effect of the hydrophobicized titanium oxide particles was studied and the results are shown below.

(Method)

Titanium oxide having an average particle size from 50 to 60 m μ and a hydrophobicizing agent dissolved in trichloroethylene were mixed under heating in a low speed blender. After distilling off trichloroethylene, the mixture was heated to 150° C. The effect of ultraviolet ray absorbance of the hydrophobicized titanium oxide thus obtained was measured in the same manner as described above.

(Results)

The results are shown in FIG. 6. FIG. 6 shows that titanium oxide treated with metal soaps was coagulated and the ultraviolet ray transmittance was increased remarkably, however titanium oxide subjected to silicon treatment (by 2% methyl hydrogen polysiloxane) possessed substantially the same ultraviolet interrupting effect as non-treated titanium oxide. Further, the thus obtained hydrophobicized titanium oxide had a reduced

surface activity and extremely preferable dispersibility into a base of the cosmetic compositions.

What is claimed is:

1. An anti-suntan cosmetic composition for selectively decreasing the transmittance of the UV-A region ultraviolet rays of 320-400 nm to prevent blotches and freckles in human skin, which comprises 1-25% by weight of fine particulate zinc oxide having an average particle size of 70-300 m μ .
2. An anti-suntan cosmetic composition for selectively decreasing the transmittance of the UV-A region ultraviolet rays of 320-400 nm and the UV-B region ultraviolet rays of 250-320 nm to prevent blotches and freckles in human skin, and to suppress aging of the skin, which comprises 1-25% by weight of fine particulate titanium oxide having an average particle size of 30-70 m μ and 1-25% by weight of fine particulate zinc oxide having an average particle size of 70-300 m μ .
3. An anti-suntan cosmetic composition as defined in claim 2, wherein said fine particulate zinc oxide and/or fine particulate titanium oxide is hydrophobicized.
4. An anti-suntan cosmetic composition as defined in claim 3, wherein said hydrophobicizing treatment is carried out with methyl hydrogen polysiloxane or dimethyl polysiloxane.
5. An anti-suntan cosmetic composition as defined in claim 2, wherein said fine particulate titanium oxide is in a rutile type crystal form.
6. An anti-suntan cosmetic composition according to claim 2, wherein said titanium oxide is contained therein in an amount of from 1 to 20% by weight.

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