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(54) **Socks and stockings comprising fiber containing metal.**

(57) This invention relates to socks and stockings comprising the fiber containing metal which comprises fiber materials mixed-spun with at least 2% polyurethane elastic fiber to which at least one of metal oxides selected from alumina, silica, and titania, as well as platinum are mixed as essential components, wherein, because metal oxides are mixed in the polyurethane elastic fiber with expandability, electromagnetic radiation (far infrared radiation) liberated from the metal oxides are emitted nearly in close contact with the human body, permitting electromagnetic radiation (far infrared radiation) to work effectively on the contact feeling at the wearing portion as well as when the socks and stockings are put on and thermal conductivity while they are worn, and enabling manifestation of an extremely excellent heat-retaining effect.

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Field of the Invention

This invention relates to socks and stockings comprising fiber containing metal and the object of the present invention is to provide socks and stockings comprising fiber containing metal which not only provides agreeable wear comfort while they are worn but also emits electro magnetic radiation liberated from the metal oxides nearly in close with the body of wearer to work effectively on contact feeling at the wearing portion as same as when they are put on and thermal conductivity while they are worn, enabling manifestation of an extremely good heat-retaining effect.

Description of Prior Art

In general, for fiber materials forming socks and stockings, cotton, nylon, polyester, acrylic, and urethane fiber are well-known, and these fiber materials are properly selected according to wearing seasons, such as for summer or for winter and mixed-spun at an optional ratio to form socks and stockings.

For example, socks and stockings for summer are formed with fiber materials primarily comprising cotton in view of permeability and absorbency, while socks and stockings for winter, in addition to said fiber materials, wool is frequently mixed to improve heat-retaining property.

Recently, in anticipation of heat-retaining property of far infrared radiation, socks and stockings using fiber mixed with far infrared irradiating ceramics as a component material have been known.

This socks and stockings use fiber having far infrared irradiating materials like alumina, girconia, or magnesia contained in polyethylene- and polyamide-based fiber materials which show high permeability to far infrared radiation and the fiber material containing this far infrared irradiating material further covered with a protection layer as part of the component fiber, and are formed in anticipation of the heat-retaining effect by wearing.

Problems to be Solved by this Invention

However, it is difficult that the socks and stockings mixed-spun with the wool manifest sufficient heat-retaining effect at soles of wearer, but mixed-spinning wool at high ratio to increase a heat-retaining effect causes bulkiness of the socks and stockings themselves, producing a problem that the socks and stockings are not worn readily.

On the other hand, the socks and stockings mixed with far infrared irradiating ceramics can eliminate the bulkiness as compared with said socks and stockings mixed-spun with wool but they have a problem that the intended effect is difficult to be achieved unless a large area is covered with the fiber material containing far infrared irradiating substance over the whole socks and stockings.

In addition, they have another problem that since in this socks and stockings a covered layer is provided to protect the far infrared irradiating layer but this covered layer absorbs far infrared radiation, the far infrared radiation emitted from the ceramics is unable to be effectively used.

Consequently, this socks and stockings have a problem that effect by the far infrared radiation is unable to work most effectively on the contact feeling when the socks and stockings are put on, thermal conductivity while they are worn, and skin temperature after they are worn, so that the excellent heat-retaining effects cannot be expected.

Therefore, in the industry, invention of socks and stockings which effects successfully on contact feeling when they are put on, thermal conductivity while they are worn, and the wearing temperature, with an extremely excellent heat-retaining property, has been required.

Means to Solve the Problems

All of the above-mentioned prior problems are solved by providing socks and stockings comprising fiber containing metal which comprises fiber materials mixed-spun with at least 2% polyurethane elastic fiber, to which at least one of metal oxides selected from alumina, silica, and titania as well as platinum are mixed as essential components.

Detailed Description of the Invention

The construction of socks and stockings comprising fiber containing metal relating to the present invention will be described in detail hereinafter.

In this invention, the fiber material mixed-spun with at least 2% polyurethane elastic fiber mixed with at least one of metal oxides selected from alumina (Al_2O_3), silica (SiO_2), and titania (TiO_2) as well as platinum (Pt) as essential components is designated as component fiber.

As alumina (Al_2O_3), silica (SiO_2), and titania (TiO_2) used in the present invention, those in the powder form with grain size of 1 μ or smaller are favorably used, but there is no restriction.

As platinum (Pt), that with grain size as fine as 7-40 $\text{\AA}$ and in a colloidal form is preferably used.

This is based on the experimental knowledge of the inventor that the use of colloidal-form platinum can yield the satisfactory heat-retaining property.

The mix ratio of these metal oxides and platinum is about 9-45% alumina (Al_2O_3), 50-80% silica (SiO_2), 8-15% each titania (TiO_2) and/or platinum (Pt), but there is no restriction.

To these metal oxides, oxides of calcium, zinc, and copper may be mixed by about 2-10%.

From the metal oxides comprised as above, electromagnetic radiation (far infrared radiation) with a 5-12 micron wavelength range to be effective for human bodies are stably and sufficiently emitted even at the temperature range of around 30 $^{\circ}\text{C}$, as clear from the following tests.

Polyurethane elastic fiber to which metal oxides and platinum are mixed is not particularly specified but SPANDEX which comprises a noncrystalline segments including either polyester or polyether portions and crystalline segment with urethane bonds and is popularly used in regular textile products is favorably used.

A method to mix metal oxides and platinum to said polyurethane elastic fiber is not particularly specified but any of the optional methods can be adopted as required, such as the method to mix the polymerized fiber material solution dispersedly in the solution before dry spinning or mix into the dry-spun yarns.

The blending ratio of metal oxides mixed in polyurethane elastic fiber is not particularly specified but any of the blending ratio can be favorably adopted if it is the blending ratio which emits electromagnetic radiation (far infrared radiation) with a wavelength range of about 5-12 microns to be effective for human bodies at the temperature around 30 $^{\circ}\text{C}$, successfully effects contact feeling and thermal conductivity during wearing and manifests an satisfactory heat-retaining effect and is within the range that enables to spin and that does not impair wear comfort as component fiber material of socks and stockings.

Furthermore, in the present invention, the reason why polyurethane elastic fiber is particularly used is that mixed-spinning polyurethane elastic fiber with generous expandability results in improved wear comfort of socks and stockings and at the same time mixing the above-mentioned metal oxides and platinum to this polyurethane elastic fiber enables emission of electromagnetic radiation (far infrared radiation) from the metal oxides into the body with the socks and stockings closely in contact with the body of the wearer, makes the best use of the effect of emitted electromagnetic radiation (far infrared radiation), and allows the electromagnetic radiation (far infrared radiation) to work effectively on the contact feeling when the socks and stockings are put on and the thermal conductivity, there by temperature variation in the body increases after the socks and stockings are worn and the blood flow rate at the wearing portion is easy to increase, as a result, a superior heat-retaining effect can be manifested.

The polyurethane elastic fiber mixed with at least one of metal oxides selected from the above-mentioned alumina (Al_2O_3), silica (SiO_2), and titania (TiO_2) as well as platinum (Pt) as essential components is mixed-spun with other regular fiber materials into socks and stockings through a regular method. In this event, polyurethane elastic fiber must be mixed-spun with metal oxides by at least 2%.

This is because in case that the mixed-spinning ratio of polyurethane elastic fiber containing metal oxides is less than 2%, emission of electromagnetic radiation from metal oxides using expandability of the above-mentioned polyurethane elastic fiber does not take place effectively and the superior heat-retaining property is not manifested.

As other fiber materials to be mixed-spun with polyurethane elastic fiber, ordinary natural and artificial fiber materials such as cotton, hemp, wool, acrylic, polyester, and nylon are favorably used and these fiber materials may be optimally mixed-spun to make socks and stockings at an optional ratio, and are not particularly specified.

Effects of the Invention

As described above in detail, because the present invention relates to socks and stockings comprising the fiber containing metal which are characterized in comprising fiber material mixed-spun with at least 2% polyurethane elastic fiber, to which at least one of metal oxides selected from alumina, silica, and titania as well as platinum are mixed as essential components, bulkiness of the socks and stockings themselves hardly exist and agreeable wear comfort is ensured when the socks and stockings are put on, and at the same time because electromagnetic radiation (far infrared radiation) by metal oxides is emitted nearly in

close contact with the wearer by making use of expandability of polyurethane elastic fiber, as clear from the results of said tests, electromagnetic radiation (far infrared radiation) is permitted to work effectively on contact feeling of the wearing portion as well as when the socks and stockings are put on and thermal conductivity while they are worn, enabling manifeststion of an extremely excellent heat-retaining effect.

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Brief Description of the Drawings

Figure 1 is a spectral emissivity chart for the fiber obtained in Example 2.

Figure 2 is a spectral emissivity chart for the fiber obtained in Example 3.

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Figure 3 is a spectral emissivity chart for the fiber obtained in Example 4.

Figure 4 is a spectral emissivity chart for the fiber obtained in Example 5.

Figure 5 is a spectral emissivity chart for the fiber obtained in Example 6.

Examples

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The effects of socks and stockings comprising fiber containing metal relating to the present invention will become more apparent from the following examples.

(Example 1)

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The 6.4% polyurethane elastic fiber mixed with metal oxides comprising alumina (Al_2O_3), silica (SiO_2), titania (TiO_2), and platinum (Pt) in the ratio 10:82:3:5 was mixed-spun with 56% cotton, 24.1% acrylic, and 13.5% nylon, and made into ladies' socks by an ordinary method.

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(Comparison 1)

Ladies' socks were made in the same manner of Example 1 except using polyurethane elastic fiber not mixed with metal oxides.

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(Comparison 2)

The 1.7% polyurethane elastic fiber mixed with metal oxides comprising alumina (Al_2O_3), silica (SiO_2), titania (TiO_2), and platinum (Pt) in the ratio 10:82:3:5 was mixed-spun with 64.7% cotton, 27.6% acrylic, and 5.2% nylon, and made into men's socks by an ordinary method.

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(Comparison 3)

Men's socks were made in the same manner of Comparison 2 except using polyurethane elastic fiber not mixed with metal oxides.

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(Test 1)

The ladies' and men's socks obtained in said Example 1 and Comparisons 1 through 3 were measured for various properties including density (g/m^2), thickness (cm), contact feeling (Q max), steady thermal conductivity ($\text{W/cm} \cdot ^\circ\text{C} \times 10^{-4}$), and heat-retaining ratio (%) with THERMOLABO 2-KES7 (KATOHTEC: heat property measuring equipment).

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Table 1 shows the results.

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TABLE 1

	[A]	[B]	[C]	[D]	[E]
EXAMPLE 1	286	0.102	0.083	3.525	42.3
COMPARISON 1	287	0.111	0.089	4.719	35.2
COMPARISON 2	438	0.221	0.064	8.495	39.7
COMPARISON 3	438	0.236	0.068	8.873	45.4

[A] ... DENSITY (g/m²)
 [B] ... THICKNESS (cm)
 [C] ... CONTACT FEELING (Q max) ※ 1
 [D] ... STEADY THERMAL CONDUCTIVITY (W/cm°C × 10⁻⁴) ※ 2
 [E] ... HEAT-RETAINING RATIO (%) ※ 3

※ 1 : The coldness felt by wearer in putting on;
 The bigger value indicates the more coldness.

※ 2 : The facility of thermal conduction of cloth;
 The bigger value indicates the more facility.

※ 3 : The ability of heat-retaining of cloth;
 The bigger value indicates the better ability.

(Test 2)

Using the ladies' and men's socks obtained in said Example 1 and Comparisons 1 through 3, tests were carried out on the living body.

First of all, skin temperature of right and left soles of a paneler were measured as the skin temperature before putting on socks, after adjusting on the living body for a specified period to harmonize the skin temperature of the right and left soles.

After the measure, the sock of Example 1 was put on the left foot, the sock of Comparison 1 was put on the right foot, and skin temperature (average, maximum) of the soles were measured in the situation after putting on and retaining heat for 900 seconds.

Then, the right and left socks was taken off, skin temperature (average, maximum) of the right and left soles were measured immediately after and about 61 seconds after the socks was taken off.

The overall temperature variation in skin temperature at the right and left soles while wearing the socks was calculated. Next, using the same paneler, skin temperature of right and left soles was adjusted on the living body for a specified period in the same manner, then the sock of Comparison 2 was put on the left foot, the sock of Comparison 3 was put on the right foot, and skin temperature (average, maximum) of the soles and the overall temperature variation in skin temperature were measured in the same manner.

The measured skin temperatures in this test were calculated from average and maximum values of the picture analysis temperature distribution of a specific region of the thermogram obtained from thermo analysis by thermograph (NEC San-Ei 6T/62 type (HgCdTe sensor, 8-13 μ m): infrared radiation thermometer - 50- 2000 ° C).

Table 2 shows the results.

TABLE 2

	[A]	[B]	[C]	[C]	[D]
EXAMPLE 1	29.3 31.5	29.1 31.5	31.1 (1.0) 33.8 (2.3)	31.1 33.8	1.8 ↑ 2.3 ↑
COMPARISON 1	31.2 33.5	30.2 32.3	32.8 (0.5) 34.7 (1.2)	32.8 34.7	1.6 ↑ 1.2 ↑
COMPARISON 2	32.6 34.3	32.1 34.0	33.1 (0.5) 35.2 (0.9)	32.8 34.6	0.2 ↑ 0.3 ↑
COMPARISON 3	31.6 33.7	32.0 34.0	32.6 (1.0) 34.2 (0.5)	32.6 34.2	1.0 ↑ 0.5 ↑
[A] ... BEFORE PUTTING ON [B] ... WEARING AND HEAT-RETAINING / HEAT-RETAINING FOR 900 SEC. [C] ... RIGHT AFTER TAKING OFF [D] ... RADIATION OF HEAT / RADIATION FOR 66 SEC. [E] ... OVERALL TEMPERATURE VARIATION THE UPPER ROW : AVERAGE TEMPERATURE (° C) THE LOWER ROW : MAXIMUM TEMPERATURE (° C) () indicates temperature of heat-retaining effect.					

(Test 3)

The ladies' socks of said Example 1 and Comparison 1 were respectively worn by the same paneler on the hand, and the blood flow rate (ml/min/100g) was measured by the laser Doppler method (Journal of the Laser Medical Society of Japan Vol. 12, No. 1, 7. 1988) using the laser Doppler rheometer (ADVANT: ALF-21) in both cases of retaining heat and heating by irradiation from a lamp.

Table 3 shows the results.

TABLE 3

	BLOOD FLOW OF FINGER (ml/min/100g)
EXAMPLE 1	23.5 24.0 ※
COMPARISON 1	22.0 24.0 ※

※ THE LOWER ROW ... CASE OF HEATING BY IRRADIATION FROM LAMP

As clear from TABLE 1, in case that mixed-spinning ratio of polyurethane elastic fiber is 6.4%, comparing ladies' socks mixed with metal oxide (Example 1) with that not mixed with metal oxide (Comparison 1) shows that the density and thickness are small, however small contact feeling results in small coldness when they are put on and small steady thermal conductivity results in small temperature variation due to the coldness of open-air, proving a high heat-retaining ratio.

In case that polyurethane elastic fiber is mixed-spun as low as 1.7% (Comparison 2), the effect is similar to that using polyurethane elastic fiber not containing metal oxides (Comparison 3), showing that heat-retaining effect is not sufficiently manifested.

As clear from TABLE 2, in case of mixed-spinning ratio of polyurethane elastic fiber is 6.4%, in the balance of heat-retaining and heat-radiation after putting on the socks, the socks containing metal oxides

(Example 1) provides overall temperature variation difference 0.2 °C higher on average and 1.1 °C higher on maximum than that of socks not containing metal oxides (Comparison 1), showing higher heat-retaining effect.

On the contrary, in case that the mixed-spinning ratio of polyurethane elastic fiber is low (Comparisons 2 and 3), heat-retaining effect by wearing socks is not manifested.

As clear from TABLE 3, the socks of Example 1 tend to increase the blood flow rate by heat-retaining as compared to the socks of Comparison 1.

(Example 2)

The 15% polyurethane elastic fiber containing metal oxides comprising alumina (Al_2O_3), silica (SiO_2), titania (TiO_2), and platinum (Pt) in the ratio 10:82:3:5 is mixed-spun with 85% cotton to make fiber.

(Example 3)

The 18% polyurethane elastic fiber same as said Example 2 are mixed-spun with 82% cotton to make fiber.

(Example 4)

The 28% polyurethane elastic fiber same as said Example 2 are mixed-spun with 72% cotton into fiber.

(Example 5)

The 50% polyurethane elastic fiber same as said Example 2 are mixed-spun with 50% staple fiber to make fiber.

(Example 6)

The 17% polyurethane elastic fiber same said above Example 2 are mixed-spun with 83% nylon to make fiber.

(Test 4)

For the fiber obtained by Examples 2 through 6, spectral emissivity was measured.

Measuring conditions are the wavelength range: 4.5-20.0 μm ; resolution: 16cm^{-1} ; detector: wide-range MCT; measuring temperature: 33 °C for surface temperature of texture; measuring position and time: four times in total, each once at two different positions and twice at the same position.

Figures 1 through 5 show the obtained relevant spectral emissivity.

As clear from the obtained spectral emissivity, in the fiber obtained in Examples 2 through 6, electromagnetic radiation (far infrared radiation) with wavelengths about 5-12 microns to be effective for human bodies is emitted even at the comparatively low temperature range of 33 °C.

Claims

1. Socks and stockings comprising fiber containing metal which are characterized in comprising fiber materials mixed-spun with at least 2% polyurethane elastic fiber, to which platinum and at least one of metal oxides selected from alumina, silica, and titania are mixed.

Fig. 1

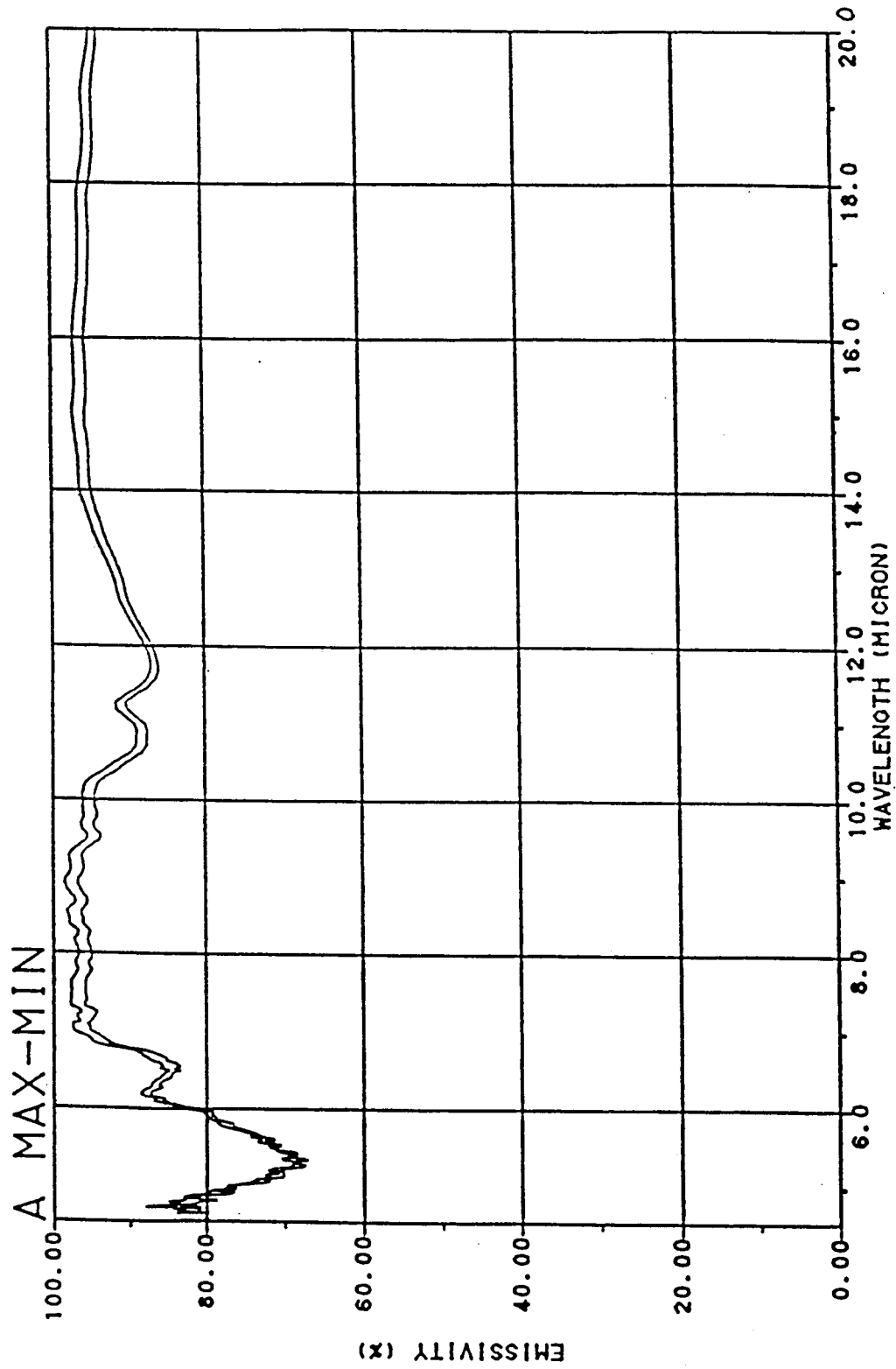


Fig. 2

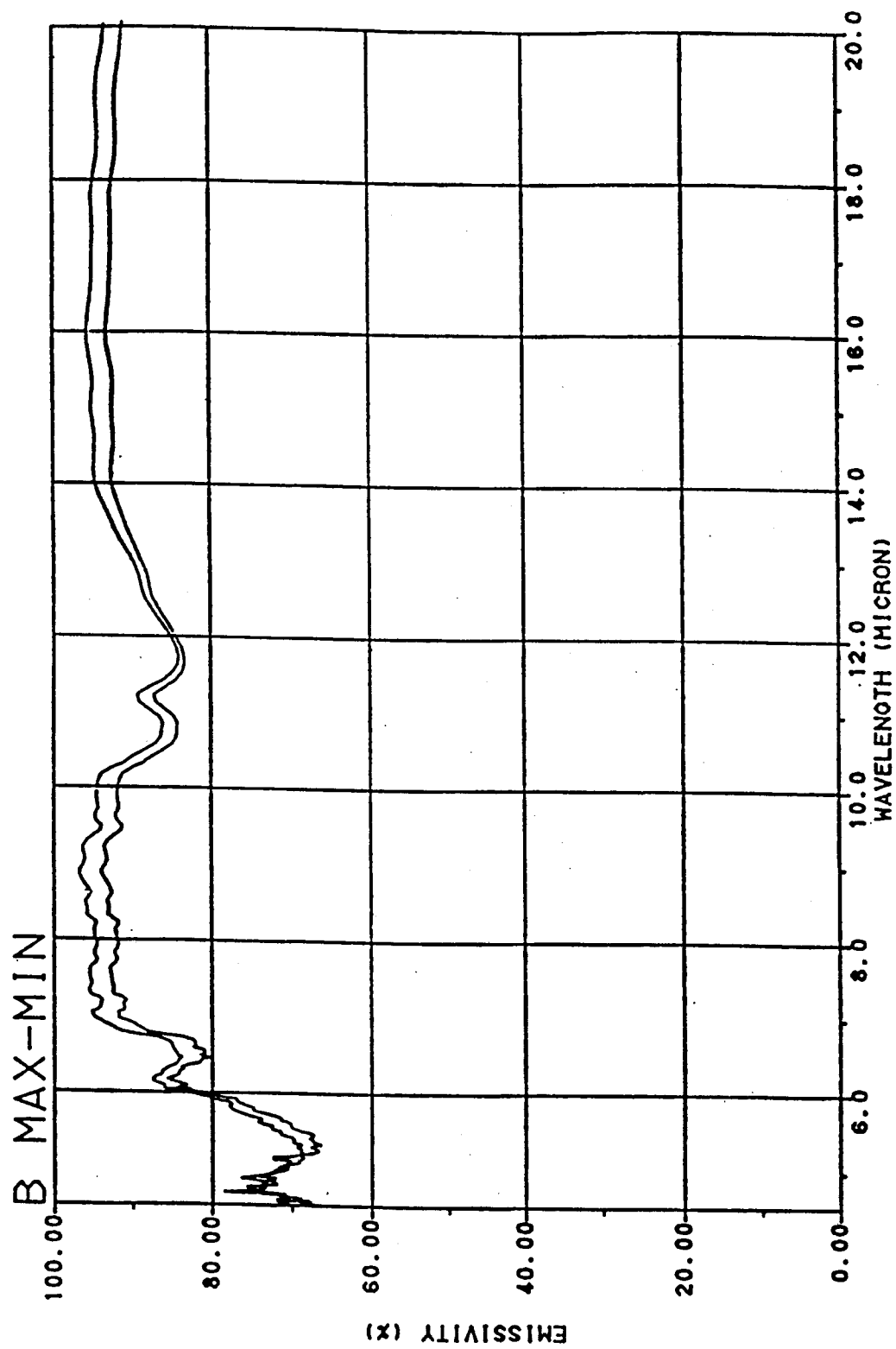


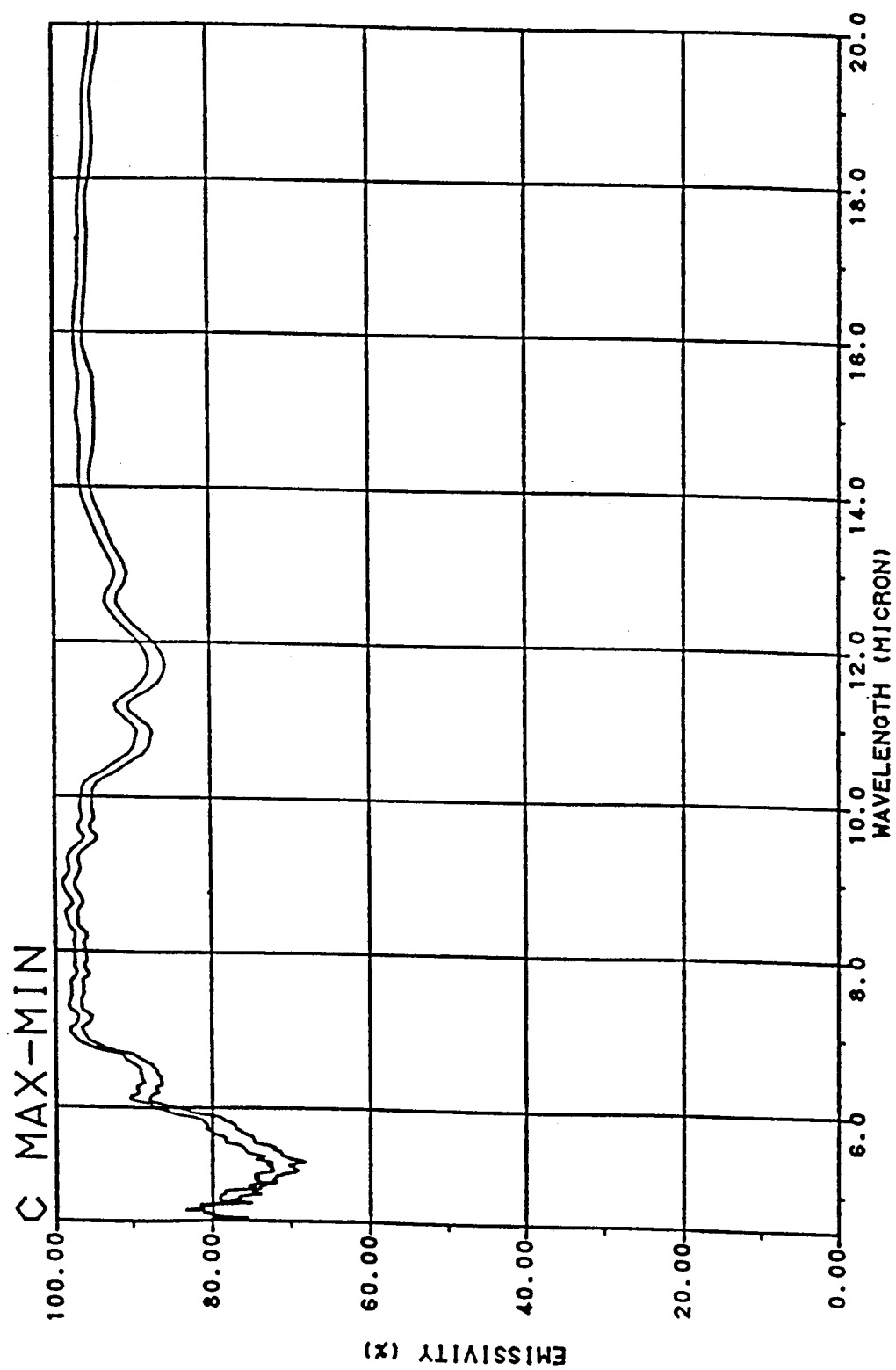
Fig. 3

Fig. 4

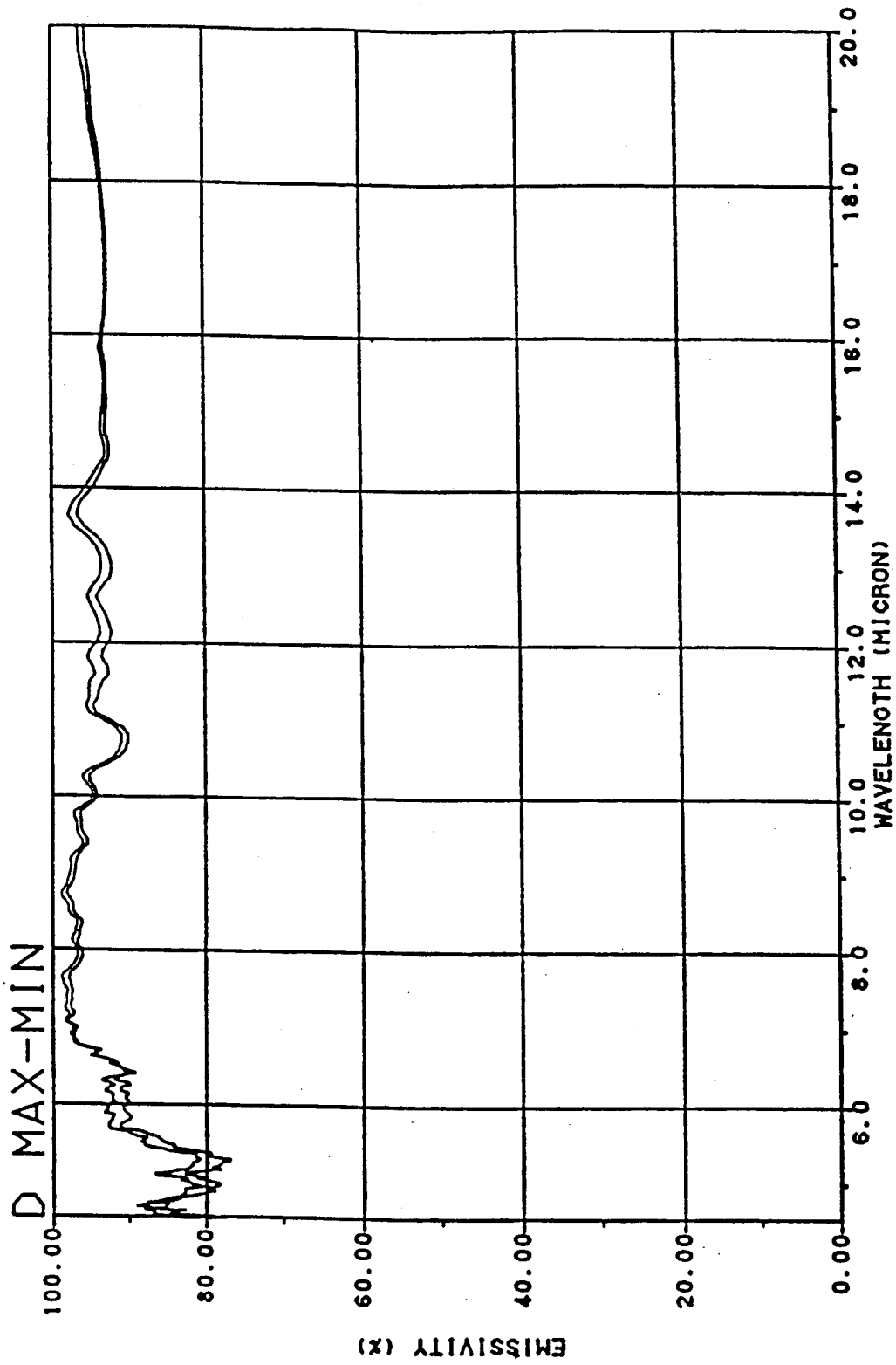
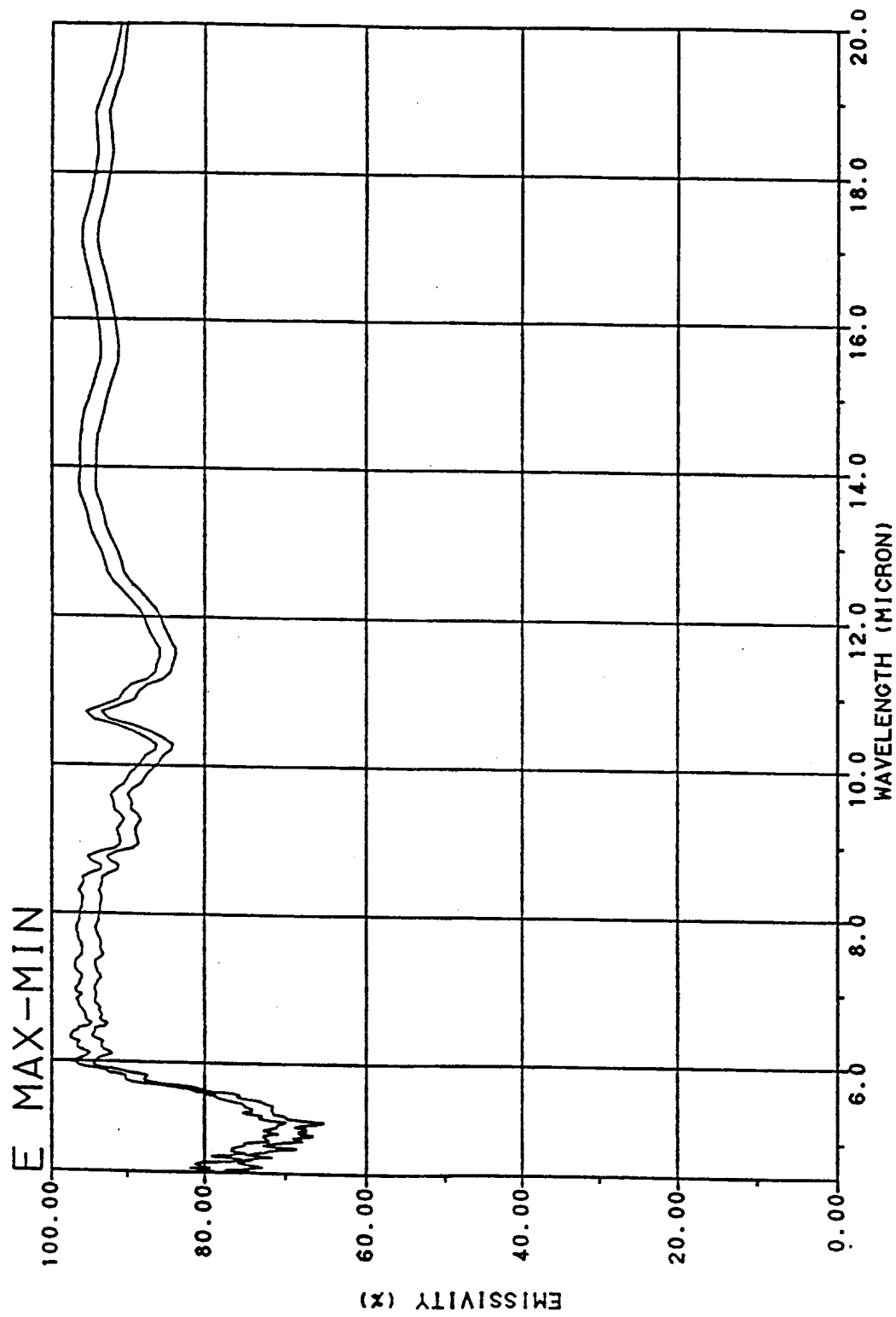


Fig. 5





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EUROPEAN SEARCH REPORT

Application Number
EP 93 10 1479

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	DATABASE WPI Week 8825, Derwent Publications Ltd., London, GB; AN 88-173138 & JP-A-63 112 701 (EARTH CLEAN KK DAIWA SPINNING KK) 17 May 1988 * abstract *	1	A41B11/00 A41B17/00
A	DATABASE WPI Week 9212, Derwent Publications Ltd., London, GB; AN 92-091763 & JP-A-4 034 001 (TORAY IND INC) 5 February 1992 * abstract *	1	
A	DATABASE WPI Week 9216, Derwent Publications Ltd., London, GB; AN 92-128857 & JP-A-4 073 226 (JPU KK) 9 March 1992 * abstract *	1	
A	DATABASE WPI Week 8847, Derwent Publications Ltd., London, GB; AN 88-335284 & JP-A-63 249 701 (ASAHI CHEMICAL IND KK) 17 October 1988 * abstract *	1	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 25 October 1993	Examiner GARNIER, F
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	