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(11) **EP 0 873 769 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
28.10.1998 Bulletin 1998/44

(21) Application number: **97939143.0**

(22) Date of filing: **03.09.1997**

(51) Int. Cl.⁶: **A63C 5/044**, A63C 5/12,
A63C 5/00, A63C 5/056,
C09G 3/00

(86) International application number:
PCT/JP97/03075

(87) International publication number:
WO 98/11958 (26.03.1998 Gazette 1998/12)

(84) Designated Contracting States:
AT CH DE FR LI

(30) Priority: **17.09.1996 JP 269323/96**

(71) Applicant: **ASICS CORPORATION**
Chuo-ku Kobe-shi Hyogo-ken (JP)

(72) Inventors:
• **IMAZATO, Katsuhiro**
Asics Corporation
Chuo-ku Kobe-shi Hyogo-ken 650 (JP)

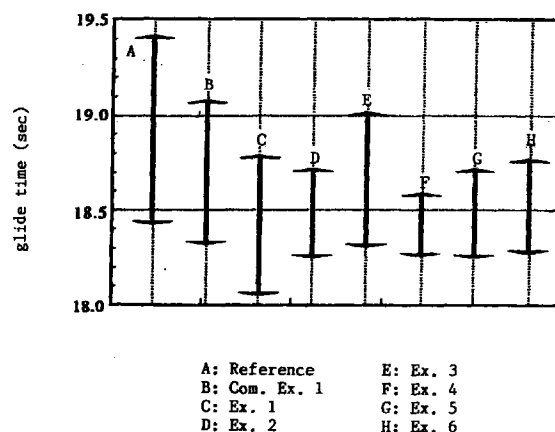
• **TOKUI, Yasuyuki**
Asics Corporation
Chuo-ku Kobe-shi Hyogo-ken 650 (JP)

(74) Representative: **Barz, Peter, Dr.**
Patentanwalt
Kaiserplatz 2
80803 München (DE)

(54) **SKI AND SNOWBOARD OF EXCELLENT SLIDING CHARACTERISTICS AND METHOD OF MANUFACTURING THE SAME**

(57) A ski or snowboard having a sole impregnated with a wax, characterized in that the ski or snowboard has a body attached by an adhesive layer to a wax impregnation preventing film formed over one surface of the sole, and a process for producing these articles.

Fig. 3



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Description

TECHNICAL FIELD

5 The present invention relates to skis and snowboards which are outstanding in gliding properties and strength and to a process for producing these articles.

BACKGROUND ART

10 Skiing events include races, such as a slalom and giant slalom, competing in time of the order of 1/100 second. In these races, the resistance of the sole providing the glide face is of extreme importance. Immediately before skiing, a wax is applied by ironing (so called hot wax, waxing) to the surface of the sole which is usually made of polyethylene, and the waxed surface is further ironed to ensure a smooth glide. However, almost no portion of the hot wax applied by this method penetrates into the sole, so that the sole needs to be elaborately ironed repeatedly even when the ski is to
 15 be used again soon after a single run, whereas the gliding properties still remain to be improved to be satisfactory.

From this viewpoint, on the other hand, it has been attempted to obtain soles from a mixture of polyethylene and wax by injection molding, but the polyethylene for use in injection molding needs to have a low molecular weight. As a result, the ski soles obtained are very low in strength, and none of them have found actual use.

20 An object of the invention is to provide skis and snowboards which are excellent in gliding properties and strength and a process for producing these articles.

DISCLOSURE OF THE INVENTION

25 The present invention provides a ski or snowboard having a sole impregnated with a wax, characterized in that the ski or snowboard has a body attached by an adhesive layer to a wax impregnation preventing film formed over one surface of the sole.

The invention also provides a process for producing a ski or snowboard having a wax-impregnated sole which process is characterized by forming a wax impregnation preventing film over one surface of a sole for the ski or snowboard, immersing the sole in a bath of molten wax to impregnate the sole with the wax, withdrawing the sole from the bath,
 30 removing the wax adhering to a surface of wax impregnation preventing film and a glide face, and attaching the wax impregnation preventing film to a ski or snowboard body with an adhesive.

While the present invention relates to the production of skis and snowboards, the glide faces of these two types of articles are similar, so that the invention will hereinafter be described with reference to skis for the sake of simplicity.

35 The sole to be used in the present invention is made from a polyethylene having a molecular weight of at least 500,000, preferably a superhigh molecular weight of 500,000 to 6,000,000, more preferably 3,000,000 to 4,000,000, whereby sufficiently increased strength can be given to the sole, therefore, to the ski.

40 The wax to be used in the present invention is preferably a mixed wax consisting primarily of n-alkanes having a melting point of 30 to 70°C and 18 to 40 carbon atoms. Examples of such waxes are PF115, PF125, PF135, HNP-11, SP-0110, ET-0073K, etc. manufactured by Nippon Seiro Co., Ltd. Mixtures of such a wax and other wax are of course usable insofar as the mixture is compatible with the sole.

According to the invention, a wax impregnation preventing film is formed over one surface of the sole, and the sole is then immersed in a bath of the wax as melted to impregnate the sole with the wax. Preferably, the surface of the sole to be formed with the preventing film is treated by a chemical or physical method in advance and thereby given an improved adhering property. Examples of chemical methods are treatment with a chemical such as chromium sulfate
 45 or nitric acid, and treatment with a coupling agent. Examples of physical methods are treatment with flames, treatment by corona discharge, glow discharge or ultraviolet rays, sandpapering and embossing. Examples of coupling agents are vinyltriethoxysilane and γ -methacryloxypropyl-trimethoxysilane.

The wax impregnation preventing film can be formed, for example, by applying to the sole an epoxy coating composition, urethane coating composition or acrylic coating composition which is incompatible with the wax. The sole is
 50 coated with the composition over the surface thereof to be adhered to the body of the ski, for example, by a brush, applicator or spray. Alternatively, the preventing film may be prepared in the form of a sheet first and then adhered to the sole. The thickness of the preventing film is usually about 5 to about 200 μm , preferably about 10 to about 100 μm , more preferably about 10 to about 60 μm . The hardness of the wax impregnation preventing film is usually about HmV 0.3 to about 10, preferably about HmV 0.4 to about 2, more preferably about HmV 0.5 to about 1.2, in terms of micro-Vickers
 55 hardness (JIS Z 2244, load 10 gf, hold time 30 seconds). If the hardness is less than 0.3, the strength of adhesion between the film and the ski body is low, whereas when the hardness is over 10, the preventing film is liable to develop cracks. The sole having the wax impregnation preventing film thus formed over one surface thereof is immersed in the molten wax bath. Usually, the wax melting temperature is preferably about 70 to about 110 °C. The immersion time is

at least 0.1 hour, preferably about 0.1 to about 7 hours.

The sole is taken out from the wax bath, and the wax adhering to the surface of the wax impregnation preventing film and the glide face are removed. For the removal of the wax, a major portion of the wax is removed first by a physical method using a plastic or rubber scraper or fabric or paper wiper, and the remaining wax is then removed by a chemical method using a wax remover, such as n-hexane or white gasoline, which will not dissolve the adhesive.

In this way, a wax-impregnated sole can be obtained which is excellent in gliding properties and strength and which exhibits excellent adhesion to the body of the ski.

The adhesive for adhering the wax impregnation preventing film to the ski body is preferably one having affinity for the coating composition used for forming the preventing film. For example, an epoxy adhesive is desirable when the epoxy coating composition is used for the preventing film, and a urethane adhesive is preferred when the urethane coating composition is used, although these examples are not limitative.

According to the invention, the concentration of the wax in the sole has such a gradient as to decrease from the surface of the sole to the interior thereof. The average concentration of $C_{24}H_{50}$, one of n-alkanes, in the sole surface portion ranging, for example, from 0 to 100 μm in depth from the surface is preferably at least about 0.1 $\mu\text{mole/cm}^3$ as measured by gas/mass chromatography. In this case, the sole has a scorching time of at least 5 minutes, usually at least 7 minutes, and is fully useful for events which will be completed within this period of time.

The object of the invention can be fully achieved when at least the surface of the sole is impregnated with the wax. The term the "surface" refers, for example, to the portion of the sole ranging from 0 to 100 μm in depth from the surface. Although a so-called ironing of hot wax is unnecessary for the ski of the invention, this ironing is used more preferably for the ski of the invention. Presumably ironing permits the hot wax to penetrate deep into the sole in a large quantity owing to the high affinity of the hot wax for the wax impregnating the sole, consequently affording excellent gliding properties. The amount of the wax impregnating the sole is dependent on the impregnation temperature and impregnation time; the higher the temperature and the longer the time, the greater is the amount of wax impregnating the sole. The depth of impregnation is less affected by the temperature; the sole can be impregnated with the wax to a position proximate to the wax impregnation preventing film regardless of whether the temperature is low or high. The amount of impregnating wax is limited since an excess of wax lowers the strength of the sole. The amount is preferably such that the sole is at least about 80 MPa in shearing modulus and at least about HmV 3.0 in micro-Vickers hardness.

The amount of impregnating wax was measured by the following method in the present invention. Preparation of specimens

Pieces, $2 \times 5 \times 0.01$ mm, were cut from the surface of the sole using the microtome stated below, and 10 pieces (0.1 mm in thickness) were checked as a unit to quantitatively determine the wax concentration.

Microtome:

Name	supermicrotome
Model	AS 500
Manufacturer	Angria Scientific (Germany)

Analysis

Ten 0.01-mm-thick specimens had a combined weight of about 1.00 ± 0.3 mg.

The wax alone was selectively extracted from the sole by the thermal desorption method and quantitatively determined by gas/mass chromatography (GC/MS) to obtain an absolute amount.

Thermal desorption device:

Name	Curie point-type pyrolyzer
Manufacturer	Nippon Bunseki Kogyo Co., Ltd.

GC/MS:

Model	HP5890II (GC), HP5971 (MS)
Manufacturer	Hewlett Packard

The wax-impregnated sole of the invention is usable for skis, for example, of the sandwich type, cap type, etc.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph showing amounts of $C_{24}H_{50}$, a component of wax, per unit volume in the soles of Examples 1 to 6 of the invention and Comparative Example 1 at varying depths;

FIG. 2 is a graph showing the relationship between the friction (sliding) time and the coefficient of dynamic friction (μ) as established for four kinds of soles which are different in the average concentration of wax in the surface; and

FIG. 3 is a graph showing the gliding test results achieved by the skis of Examples 1 to 6 and Comparative Example 1 and skis not treated with any wax for reference.

BEST MODE OF CARRYING OUT THE INVENTION

The present invention will be described in greater detail with reference to the following examples and comparative examples.

Example 1

One surface of a ski sole (IMS Kunststoff AG, P-TEX 2000) having a thickness of 1.35 mm and made of polyethylene having a molecular weight of 3,500,000 and a density of 0.937 g/cm^3 was oxidized by a gas burner and then coated with a urethane coating composition (Kashu Co., Ltd., STRON ACE 22) by spraying to form a wax impregnation preventing film having a thickness of $50 \pm 10 \text{ }\mu\text{m}$ and HmV 8.46 in micro-Vickers hardness. The sole was then immersed in a bath of molten wax (PF125, m.p. 52.5°C , density 0.911 g/cm^3 , consisting primarily of 15.4% of $C_{24}H_{50}$ and 16.5% of $C_{25}H_{52}$) at 90°C for 10 minutes, whereby the sole was impregnated with the wax. The sole was taken out from the wax bath, the wax adhering to the surface of the wax impregnation preventing film and the glide face was removed by a scraper first, and the remaining wax was then removed with white gasoline.

The urethane film of the wax-impregnated sole was subsequently bonded to a ski body with an epoxy adhesive [two pack type, Araldite AW106 (main agent), HV953U (hardener)]. In this way, skis of the invention were obtained. The sole was 230 MPa in shearing modulus and HmV 3.8 in micro-Vickers hardness.

Example 2

Skis of the invention were prepared in the same manner as in Example 1 except that the impregnation time was 60 minutes.

Example 3

Skis of the invention were prepared in the same manner as in Example 1 except that the impregnation temperature was 70°C .

Example 4

Skis of the invention were prepared in the same manner as in Example 1 with the exception of coating each sole with a urethane coating composition (Origin Co., Ltd., U-03) by spraying to form a wax impregnation preventing film having an average thickness of $35 \text{ }\mu\text{m}$ (HmV 0.7 in micro-Vickers hardness) and bonding the urethane film to a ski body with an urethane adhesive [two pack type, US100 (main agent), F-1 (hardener)] serving as an adhesive.

Example 5

Skis of the invention were prepared in the same manner as in Example 1 with the exception of coating each sole with an epoxy coating composition (Origin Co., Ltd., #HS N-7) by spraying to form a wax impregnation preventing film having an average thickness of $35 \text{ }\mu\text{m}$ (HmV 0.4 in micro-Vickers hardness).

Example 6

Skis of the invention were prepared in the same manner as in Example 1 with the exception of coating each sole with an acryl-urethane coating composition (Kashu Co., Ltd., STRON ACE HD2) by spraying to form a wax impregnation preventing film having an average thickness of $35 \text{ }\mu\text{m}$ (HmV 1.04 in micro-Vickers hardness).

Comparative Example 1

Skis were prepared using the same soles as those used in Example 1, and the same wax as used in Example 1 was applied to the soles by ironing ten times.

Test Example 1

The soles of Examples 1 to 6 and Comparative Example 1 were checked for the amount of $C_{24}H_{50}$, a component of the wax, per unit volume at varying depths of the sole by the aforementioned method using the microtome. The results are shown in FIG. 1, wherein A to F represent Examples 1 to 6, respectively, and G, Comparative Example 1.

The drawing shows that the higher the impregnation temperature, the longer the impregnation time and the smaller the hardness of the wax impregnation preventing film, the greater is the amount of wax, and that the depth of impregnation is not substantially dependent on the impregnation temperature or time. It is seen that the amount of impregnating wax and the depth of impregnation are much smaller in the sole of Comparative Example 1 than in those of Examples. It is also seen that the wax concentration in the sole has such a gradient as to decrease from the surface to the interior.

Test Example 2

Four kinds of soles having the respective average concentrations of wax ($C_{24}H_{50}$ component) given below in the surface portion ranging from 0 to 100 μm in depth were checked for the relationship between the friction (sliding) time and the coefficient of dynamic friction (μ) by a thrust collar type friction tester (test conditions: sliding velocity 150 cm/sec, load 0.26 MPa, ambient temperature 25 °C). FIG. 2 shows the results.

Sole S1 0.20 $\mu\text{mole/cm}^3$
 Sole S2 0.10 $\mu\text{mole/cm}^3$
 Sole S3 0.05 $\mu\text{mole/cm}^3$
 Sole S4 0.00 $\mu\text{mole/cm}^3$

The diagram shows that scorching occurs in Sole S4 impregnated with no wax about 2 minutes later, and that Sole S3 becomes scorched about 5 minutes later. Sole S2 is scorched about 7 to 8 minutes later, but is usable free of trouble since races are usually completed within 2 to 3 minutes. Sole S1 remains free of scorching even upon lapse of 15 minutes.

Test Example 3

The skis of Examples 1 to 6 and Comparative Example 1 and skis not treated with any wax for reference were checked for gliding properties under the following conditions.

A course was used which had a gentle slope having an overall length of 350 m including a distance of 200 m from the starting point to an intermediate point and a distance of 150 m from the intermediate point to the goal.

Photoelectric tubes were provided at the three locations of the starting point, intermediate point and the goal.

Under the conditions of 2 °C in atmospheric temperature, -5 °C in snow temperature, 0 in wind force and about 80 km/h in the speed at the goal, the skis were used for 10 runs to measure the glide times. The result is expressed in the range of times measured.

The skis of Examples 1 to 6 and Comparative Example 1 were ironed before use. FIG. 3 shows the results. The diagram reveals that the average for the 10 runs was 18.45 seconds with the skis of Example 1, 18.50 seconds with Example 2, 18.65 seconds with Example 3, 18.40 seconds with Example 4, 18.50 seconds with Example 5, 18.55 seconds with Example 6, 18.7-odd seconds with Comparative Example 1 and 18.95- odd seconds with the reference. There is a difference of 0.3-odd second between Example 4 and Comparative Example 1. This difference corresponds to differences of 0.34 to 3.00 seconds when calculated for downhill, giant slalom, slalom and super-giant slalom races as listed in Table 1, indicating that the skis of the invention are very superior in gliding properties.

Table 1

Alpine event	Difference in elevation (m)	Skiing distance (m)	Time difference (sec)
downhill (DH)	800~ 1000	2500~ 3500	2.14~ 3.00

Table 1 (continued)

Alpine event	Difference in elevation (m)	Skiing distance (m)	Time difference (sec)
giant slalom (GSL)	250~ 400	1000~ 1200	0.86~ 1.03
slalom (SL)	140~ 220	400~ 500	0.34~ 0.43
super-giant slalom (SGSL)	500~ 650	1500~ 2000	1.28~ 1.71

INDUSTRIAL APPLICABILITY

The skis and snowboards having a wax-impregnated sole of the invention are entirely novel articles heretofore unavailable. When applied by ironing, hot wax penetrates deep into the sole in a large quantity owing to the high affinity thereof for the wax impregnating the sole, consequently affording excellent gliding properties. The sole of the invention is made of polyethylene having a high molecular weight and therefore has exceedingly high strength.

Further, the amount of the wax impregnating the sole can be enhanced by selecting a low level of the hardness of the wax impregnation preventing film.

Claims

1. A ski or snowboard having a sole impregnated with a wax, characterized in that the ski or snowboard has a body attached by an adhesive layer to a wax impregnation preventing film formed over one surface of the sole.
2. A ski or snowboard as defined in claim 1 wherein the sole is formed of a polyethylene having a superhigh molecular weight of at least 500,000.
3. A ski or snowboard as defined in claim 1 wherein the wax is a mixed wax consisting primarily of an n-alkane having 18 to 40 carbon atoms and a melting point of 30 to 70 °C.
4. A ski or snowboard as defined in claim 1 wherein the concentration of the wax in the sole decreases from a surface of the sole to the interior thereof with a gradient.
5. A process for producing a ski or snowboard having a wax-impregnated sole which process is characterized by forming a wax impregnation preventing film over one surface of a sole for the ski or snowboard, immersing the sole in a bath of molten wax to impregnate the sole with the wax, withdrawing the sole from the bath, removing the wax adhering to a surface of the wax impregnation preventing film and a glide face, and attaching the wax impregnation preventing film to a ski or snowboard body with an adhesive.
6. A process for producing a ski or snowboard as defined in claim 5 wherein the sole is formed of a polyethylene having a superhigh molecular weight of at least 500,000.
7. A process for producing a ski or snowboard as defined in claim 5 wherein the wax is a mixed wax consisting primarily of an n-alkane having 18 to 40 carbon atoms and a melting point of 30 to 70 °C.
8. A process for producing a ski or snowboard as defined in claim 5 wherein the surface of the sole to be formed with the wax impregnation preventing film is treated by a chemical method or physical method in advance and thereby given an improved adhering property.
9. A process for producing a ski or snowboard as defined in claim 5 wherein a major portion of the wax adhering to the surface of the preventing film is removed by a physical method first, and the remaining wax is further removed by a chemical method using a wax remover and the like.

Fig. 1

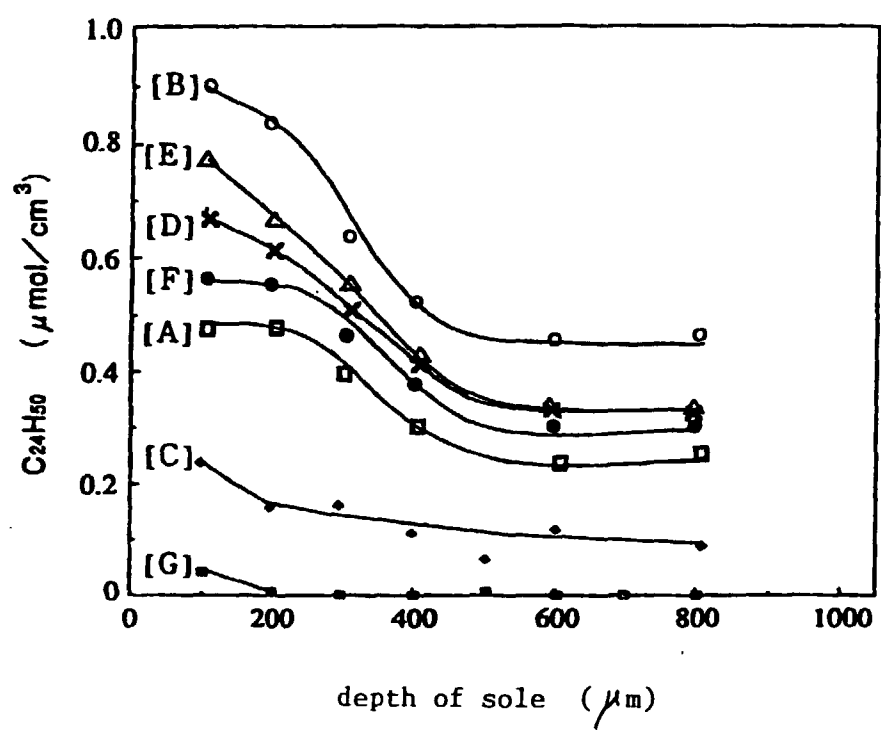


Fig. 2

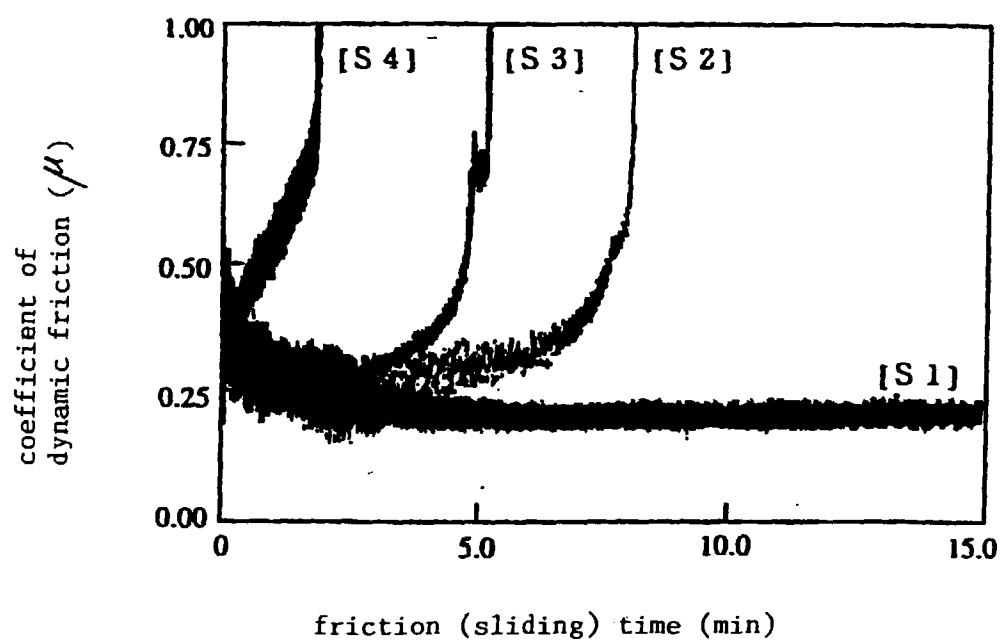
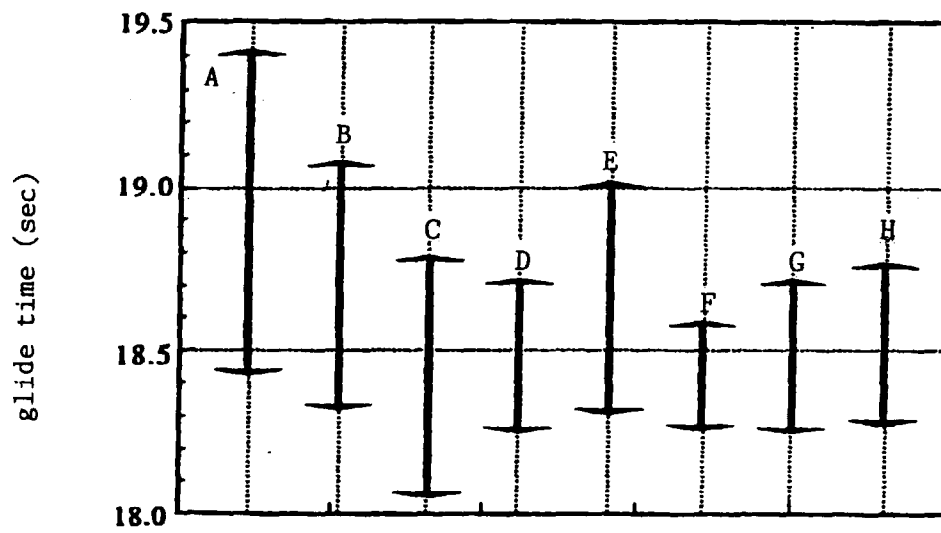


Fig. 3



A: Reference	E: Ex. 3
B: Com. Ex. 1	F: Ex. 4
C: Ex. 1	G: Ex. 5
D: Ex. 2	H: Ex. 6

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP97/03075

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl⁶ A63C5/044, A63C5/12, A63C5/00, A63C5/056, C09G3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl⁶ A63C5/04-044, A63C5/12, A63C5/00, A63C5/056, A63C11/08, C09G3/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922 - 1996	Jitsuyo Shinan Toroku
Kokai Jitsuyo Shinan Koho	1971 - 1997	Koho
Toroku Jitsuyo Shinan Koho	1994 - 1997	1996 - 1997

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 49-43729, A (Nippon Gakki Co., Ltd.), April 24, 1974 (24. 04. 74), Full text; all drawings	1, 4, 8-9
Y	Full text; all drawings (Family: none)	2-3, 5-7
Y	JP, 54-98834, A (Nippon Gakki Co., Ltd.), August 4, 1979 (04. 08. 79), Full text (Family: none)	5
Y	JP, 61-82772, A (Nitto Electric Industrial Co., Ltd.), April 26, 1986 (26. 04. 86), Full text (Family: none)	2, 6
Y	JP, 7-76350, B2 (ASICS Corp.), August 16, 1995 (16. 08. 95), Full text & EP, 421303, A2	3, 7

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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Date of the actual completion of the international search

November 27, 1997 (27. 11. 97)

Date of mailing of the international search report

December 9, 1997 (09. 12. 97)

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