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(54) **CONDUCTIVE POWDER AND TRANSPARENT CONDUCTIVE COMPOSITION**

(57) An electrically conductive powder prepared by coating amorphous silica fibers, obtainable by treating calcium silicate fibers with an acid, with one or more metal oxides selected from tin oxide, indium oxide and zinc oxide.

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Description**TECHNICAL FIELD**

- 5 [0001] The present invention relates to an electrically conductive powder excellent in transparency and electrical conductivity and also to a transparent conductive composition incorporating the electrically conductive powder.

BACKGROUND ART

- 10 [0002] There often is a need for shaped products, such as a coating film, film, sheet and the like, which have imparted thereto appropriate transparency and electrical conductivity for antistatic purpose or for utility as electrodes, heating elements or the like. Several methods have been proposed whereby such transparency and electrical conductivity can be imparted, including (1) subdividing antimony-doped tin oxide particles to sizes of below the wavelength range of visible light, mixing the subdivided particles in a resin to prepare a film-forming or coating composition which is subsequently processed to form a film or coating film, and (2) depositing, in the form of a thin film, a compound, e.g., indium oxide/tin oxide as widely used for formation of ITO film, onto surfaces as by a sputtering technique.

- 15 [0003] However, the powder particles used in the method (1), because of their fine sizes, exhibit high cohesive strength that facilitates the formation of agglomerates as secondary particles. The problem of poor dispersion arises when they are formulated into a coating composition. Also, the amount of those particles must be increased if they are to be effective in forming electrically conductive paths.

- 20 [0004] The method (2), while effective to provide thin metal films having excellent levels of electrical conductivity and transparency, needs expensive film-forming materials and a large-scale film-forming apparatus, which are problems.

- 25 [0005] Another method has been proposed which involves loading into a resin the electrically conductive powder prepared by coating amorphous silica or mica particles, known as being capable of imparting relatively high transparency to a coating film or regular film when incorporated therein, with electrically conductive metal oxide such as tin oxide (Japanese Patent Laid Open Nos. Hei 2-218768 and Hei 5-116930).

- 30 [0006] However, if the resin is to obtain a desired level of electrical conductivity, the electrically conductive powder must be incorporated therein in a large amount. The higher loading of the electrically conductive powder has created a problem of reducing transparency of the resin.

DISCLOSURE OF THE INVENTION

- 35 [0007] It is an object of the present invention to provide an electrically conductive powder having improved transparency and electrical conductivity compared to the above-described conventional electrically conductive powders, as well as a transparent conductive composition incorporating such an electrically conductive powder.

- [0008] A first aspect of the present invention is characterized in that amorphous silica fibers, obtainable by treating calcium silicate fibers with acid, are coated with one or more metal oxides selected from tin oxide, antimony oxide, indium oxide and zinc oxide.

- 40 [0009] A second aspect of the present invention is characterized in that amorphous silica fibers having a fiber length of 1 - 500 μm and an aspect ratio of 5 - 5,000 are coated with one or more metal oxides selected from tin oxide, antimony oxide, indium oxide and zinc oxide.

- [0010] Such amorphous silica fibers can be obtained by treating calcium silicate fibers with acid, as analogous to the first aspect.

- 45 [0011] Accordingly, the amorphous silica fibers for use in the second aspect may be those obtained by treating calcium silicate fibers with acid.

- [0012] In the first and second aspects, the amorphous silica fibers preferably have a refractive index in the range of 1.4 - 1.8. Maintaining their refractive index within the above-specified range allows a resin or polymer including such amorphous silica fibers to obtain the further improved transparency.

- 50 [0013] In the first and second aspects, the amount of the coated metal oxide is preferably in the range of 10 - 100 parts by weight, based on 100 parts by weight of the amorphous silica fibers. If it is excessively small, the sufficient electrical conductivity may not be obtained for the electrically conductive powder. On the other hand, if it is excessively large, an economical disadvantage becomes significant while not showing the proportional improvement in electrical conductivity. Also, the transparency of the conductive powder shows a decreasing trend.

- 55 [0014] As stated earlier, the metal oxide to be coated is selected from tin oxide, antimony oxide, indium oxide and zinc oxide. Preferably used are tin oxide containing antimony oxide, a metal oxide consisting of indium oxide/tin oxide, generally called ITO, and zinc oxide. For the purpose of imparting high electrical conductivity by the uniform coverage of amorphous silica fiber surfaces, the use of tin oxide containing antimony oxide is preferred. The amount of antimony

oxide incorporated is preferably in the range of 1 - 50 parts by weight, more preferably in the range of 1 - 20 parts by weight, based on 100 parts by weight of tin oxide. Tin oxide, when doped with antimony, exhibits the enhanced level of electrical conductivity.

[0015] In the present invention, the amorphous silica fibers may be coated with the metal oxide, for example, according to the following procedure. A selected metal oxide, such as in the form of its hydroxide, is deposited onto amorphous silica fiber surfaces in an aqueous solution. Subsequent dewatering, drying and heat treatment provides a coating film of electrically conductive metal oxide on surfaces of the amorphous silica fibers. The hydroxide or the like of the metal oxide can be prepared by hydrolyzing a metallic compound. The preferred metallic compounds are those which can be solubilized into water or water-soluble organic solvent, including those soluble in water in an acidic or base condition, such as halides and oxides, and those soluble in water-soluble organic solvents, such as metal alcoholates and metal acetyl acetonates.

[0016] A specific manufacturing method involves adding a solution of the aforementioned metallic compound to an aqueous dispersion of amorphous silica fibers. Subsequent hydrolyzing results in deposition of insolubles thereof onto fiber surfaces. The metallic compound solution may be added to the aqueous dispersion of fibers under a hydrolyzing condition. Alternatively, hydrolyzing may be achieved after the addition of the solution to the aqueous dispersion.

[0017] A first hydrolyzing method utilizes an organic compound, such as alcoholate or acetyl acetonate, for the metallic compound. The organic compound, after dissolved in a water-soluble organic solvent, is added to the above-described aqueous dispersion of amorphous silica fibers, whereby the metallic compound is hydronized to deposit onto fiber surfaces. Such a hydrolysis reaction may be effected under the application of heat or in the presence of an alkaline substance. Useful alkaline substances include hydroxides and carbonates of alkaline metals, and ammonium compounds, for example.

[0018] A second hydrolyzing method utilizes a halide for the metallic compound. A halide solution in alcohol is added to the aqueous dispersion of amorphous silica fibers. In this method, the hydrolysis reaction may be effected under the application of heat or in the presence of an alkaline substance. A useful alkaline substance can be chosen from those described in the aforementioned first method.

[0019] A third hydrolyzing method involves adding an aqueous solution of the metallic compound to the aforementioned aqueous dispersion of amorphous silica fibers. This method, because of its exclusion of organic solvents, is favored from the following points; working atmosphere, environmental pollution, prevention of disasters, and economics. Also in this method, the hydrolysis reaction can be effected under the application of heat or in the presence of an alkaline substance.

[0020] In the first aspect, the amorphous silica fibers used are those prepared by treating calcium silicate fibers with an acid. Useful calcium silicate fibers may be those comprised of wollastonite, xonotlite and the like, for example.

[0021] The acid treatment of calcium silicate fibers results in the removal of calcium therefrom, so that the amorphous silica fibers are obtained. The acid treatment is not particularly specified, so long as it can convert the calcium silicate fibers to amorphous silica fibers while maintaining the original fibrous form of the calcium silicate fibers. However, the acid treatment using a weak acid is generally preferred. For example, the preferred acid treatment employs a carbonic acid. Preferably, a carbonic acid gas is blown into the aqueous dispersion of calcium silicate fibers. With such a treatment, calcium in calcium silicate can be removed in the form of calcium carbonate, resulting in the provision of amorphous silica fibers which maintain the original fibrous form of the calcium silicate. After the acid treatment using the carbonic acid gas, the produced calcium carbonate may in some cases remain on the amorphous silica fibers. In such cases, calcium carbonate can be decomposed for removal therefrom by adding thereto an acid, such as oxalic acid, nitric acid or the like.

[0022] The amorphous silica fibers, as obtained in the manner as stated above, retain the original fibrous form of the starting material, i.e., calcium silicate fibers. The amorphous silica fibers can thus be obtained which have the fiber length and aspect ratio approximate in levels to those of the starting calcium silicate fibers. Therefore, the fiber length and aspect ratio of the amorphous silica fibers can be adjusted by suitably selecting the fiber length and aspect ratio of starting wollastonite fibers. The fibrous configuration of the amorphous silica fibers is represented preferably by a fiber length of 1 - 500 μm and an aspect ratio of 5 - 5,000, more preferably by a fiber length of 10 - 50 μm and an aspect ratio of 10 - 100. In order to assure transparency when the electrically conductive powder of the present invention is loaded in a resin or the like, it is preferred that a refractive index of the electrically conductive powder loaded is as close to that of the resin or the like as possible. In view thereof, the refractive index of the electrically conductive powder is preferably in the range of 1.4 - 1.8, more preferably in the range of 1.4 - 1.6.

[0023] The transparent conductive composition of the present invention is characterized in that the aforementioned electrically conductive fibers of the present invention is included in a binder. Examples of binder materials include synthetic polymer compounds such as thermoplastic and thermosetting resins; natural resins and their derivatives; metal-containing organic compounds; inorganic binder materials; and emulsions of organic or inorganic compounds. Specific examples of thermoplastic resins are engineering plastics such as polyolefins, polyvinyl chloride, ABS resin, polystyrene, acrylics, POM resin, PBT resin and PPS resin. Specific examples of thermosetting resins are phenol resin, epoxy

resin and the like. Other synthetic polymer compounds include polyphosphazene and the like. One or more of the above-listed binder materials can be selectively employed depending upon the particular purposes and uses sought.

[0024] In the case where the transparent conductive composition of the present invention is provided in the form of the conductive resin composition, an additive such as a filler, reinforcer, pigment, anti-oxidant, antistatic agent, lubricant, heat stabilizer, or flame retarder may suitably be incorporated therein within the limits not to lose the required transparency. Also, the electrically conductive powder of the present invention may be subjected to surface treatment with a coupling agent or the like before it is mixed with the binder.

[0025] Also in the preparation of the transparent conductive resin composition, conventional mixing operations may suitably be employed including, for example, Banbury mixing, internal mixing, extrusion pelletizing and the like.

[0026] Also, the transparent conductive composition of the present invention, because of its excellent transparency, becomes advantageous when used in the processed forms such as a coating film, film, sheet and the like. It can be formed into a coating film when used in the form of conventional coating compositions such as solvent-based, water-based and emulsion coating compositions. Also, it can be rendered into a film or sheet by a conventional film- or sheet-forming process.

[0027] Preferably, the transparent conductive composition of the present invention contains 3 - 80 % by weight of the electrically conductive powder and has a volume resistivity of not exceeding $10^{10} \Omega \cdot \text{cm}$ and a total luminous transmittance of 30 - 100 %.

[0028] The excessively low loading of the electrically conductive powder may result in the failure to obtain the desired electrical conductivity. On the other hand, the excessively high loading of the electrically conductive powder may result in the reduced transparency. For uses which need electrical conductivity for antistatic purposes, the volume resistivity of not exceeding $10^{10} \Omega \cdot \text{cm}$ is mostly required. Also, the total luminous transmittance is preferably not below 30 %, more preferably not below 50 %.

[0029] In accordance with the present invention, electrically conductive powders can be provided which, when loaded in a resin or the like, are able to impart both transparency and electrical conductivity thereto.

[0030] In accordance with the present invention, transparent conductive compositions can be provided which have excellent transparency and electrical conductivity.

[0031] The electrically conductive powder of the present invention are also useful for electrostatic coating and electrodeposition primer in the coating field of steel plates and the like.

[0032] The electrically conductive powder of the present invention, when added to a base layer made from a metallic coating composition commonly used in the coating field of steel plates and the like, can make the base layer directly coatable without the interposition of a primer. A coating composition for use in such a base layer may contain the electrically conductive powder of the present invention, an aluminum paste, a pigment and a polyester-melamine binder, for example.

[0033] Also, the electrically conductive powder of the present invention, when formulated in a coating composition, not only imparts the desired electrical conductivity but also exhibits the excellent flatting effect, which makes it very suitable for applications in the aforementioned coating fields.

BEST MODES IN CARRYING OUT THE INVENTION

[0034] The present invention will be now described with reference to specific examples.

(PREPARATION OF ELECTRICALLY CONDUCTIVE POWDERS)

Preparation Example (Preparation of amorphous silica fibers)

[0035] 200 g of calcium silicate fibers (product name "BISTAL", manufactured by Otsuka Chemical Co. Ltd., an average fiber length of 25 μm , an average fiber diameter of 0.77 μm) was dispersed in 4 liter deionized water, and subjected to a treatment for 20 hours which allowed a CO_2 gas to bubble through the dispersion at a flow rate of 100 ml/min, while the dispersion was stirred and maintained at 70 °C. After the treatment was terminated, the dispersion was cooled to 40 °C. 240 ml of a concentrated (67.5 %) nitric acid was added dropwise to the dispersion, while stirred, over 10 minutes, followed by an additional 1 hour of stirring. Thereafter, the product was suction filtered, washed with water, dewatered and dried. The resulting product was amorphous silica fibers having an average fiber length of 23 μm , an average fiber diameter of 0.77 μm , an average aspect ratio of 30 and a refractive index of 1.5.

EXAMPLE 1

[0036] 250 g of the amorphous silica fibers obtained in Preparation Example, as a base material, was dispersed in 2.5 liter of deionized water. A mixed solution of tin chloride and antimony chloride in hydrochloric acid and an aqueous

solution of sodium hydroxide were concurrently but separately added dropwise to the dispersion while stirred and maintained at 70 °C. The dispersion was stirred for an additional 2 hours, while its pH was kept at about 3. The dispersion was then filtered, washed with water, dewatered, dried at 110 °C for 10 hours, and then heat treated at 450 °C to obtain a fibrous-form electrically conductive powder of the present invention. Its tin oxide and antimony oxide contents were 25 parts by weight and 5 parts by weight, respectively, based on 100 parts by weight of the base material.

COMPARATIVE EXAMPLE 1

[0037] The procedure of the above Example 1 was followed, with the exception that white carbon (product name "NIPSIL", manufactured by Nippon Silica Kogyo Co., Ltd., comprised principally of SiO₂, an average particle size of 16 μm, a refractive index of 1.48) was used as a base material, to prepare an electrically conductive powder.

COMPARATIVE EXAMPLE 2

[0038] The procedure of the above Example 1 was followed, except that muscovite (product name "Z-20", manufactured by Hikawa Kogyo Co., Ltd., flake-form, an average particle size of 50 μm, a refractive index of 1.56) was used as a base material, to prepare an electrically conductive powder.

(PREPARATION OF TRANSPARENT CONDUCTIVE SHEETS)

EXAMPLE 2

[0039] A transparent conductive sheet incorporating the electrically conductive powder of Example 1 was prepared according to the following procedure.

[0040] A pellet-form polypropylene resin was melt in a twin-screw kneader, the electrically conductive powder of Example 1 was supplied from a side hopper, and the mixture was kneaded and extruded into a sheet-form, i.e. an electrically conductive sheet, which had a thickness of 30 μm. A blending proportion of the electrically conductive powder in the sheet was 30 % by weight.

COMPARATIVE EXAMPLE 3

[0041] The procedure of the above Example 2 was followed, except that the electrically conductive powder of Comparative Example 1 was used, to prepare a sheet.

COMPARATIVE EXAMPLE 4

[0042] The procedure of the above Example 2 was followed, except that the electrically conductive powder of Comparative Example 2 was used, to prepare a sheet.

COMPARATIVE EXAMPLE 5

[0043] The procedure of the above Example 1 was followed, except that titanium oxide fibers (product name "FTL-200", manufactured by Ishihara Sangyo Co., Ltd., rutile-form, an average fiber length of 5 μm, a refractive index of 2.90) was used as the base material, to prepare an electrically conductive powder.

[0044] The procedure of the above Example 2 was followed with the use of this electrically conductive powder to prepare a sheet.

[0045] The sheets obtained in Example 2 and Comparative Examples 3 - 5 were respectively measured for volume resistivity and total luminous transmittance in accordance with the following procedures. The results are shown in Table 1.

Procedure for determining volume resistivity

[0046] A sample piece was placed between two electrodes. A DC voltage was applied across the sample piece, and a value of the current flowing through the sample piece was measured. A volume resistivity (numerical value given by dividing the voltage by the current flowing through a unit volume of the sample piece: a unit of Ω • cm) was determined from this measured value.

Procedure for determining total luminous transmittance

[0047] Each sheet obtained was cut to an 8 cm by 8 cm square sample piece (thickness of not exceeding 1 mm). A total luminous transmittance (%) of the sample was measured utilizing a Haze computer (model number HGM-2DP: manufactured by Suga Shikenki Co., Ltd.).

Table 1

	Electrically Conductive Powder	Volume Resistivity ($\Omega \cdot \text{cm}$)	Total Luminous Transmittance (%)
Example 2	Example 1	1×10^5	85.3
Comp. Example 3	Comp. Example 1	2×10^7	69.0
Comp. Example 4	Comp. Example 2	3×10^6	81.2
Comp. Example 5	Titanium Oxide Fiber	2×10^6	19.7

(PREPARATION OF TRANSPARENT CONDUCTIVE COATING FILMS)EXAMPLE 3

[0048] The electrically conductive powder of the above Example 1 was loaded in a solvent-containing solution-type urethane resin in the concentration of 40 % by weight, based on a total solids weight, followed by mixing thereof with sufficient stirring. The mixture was then applied onto a PET film and cured by heat drying to obtain a coating film having a dry film thickness of 10 μm .

COMPARATIVE EXAMPLE 6

[0049] The procedure of the above Example 3 was followed, except that the electrically conductive powder of Comparative Example 1 was used, to form a coating film.

COMPARATIVE EXAMPLE 7

[0050] The procedure of the above Example 3 was followed, except that the electrically conductive powder of Comparative Example 2 was used, to form a coating film.

COMPARATIVE EXAMPLE 8

[0051] The procedure of the above Example 3 was followed, except that the same electrically conductive powder as used in Comparative Example 5, i.e., the electrically conductive powder prepared from titanium oxide fibers as the base material was used, to form a coating film.

[0052] The coating films obtained in Example 3 and Comparative Examples 6 - 8 were measured, respectively, for volume resistivity and total luminous transmittance according to the same procedures as described above. The results are shown in Table 2.

Table 2

	Electrically Conductive Powder	Volume Resistivity ($\Omega \cdot \text{cm}$)	Total Luminous Transmittance (%)
Example 3	Example 1	4×10^4	91.2
Comp. Example 6	Comp. Example 1	3×10^6	77.6
Comp. Example 7	Comp. Example 2	5×10^5	83.5
Comp. Example 8	Titanium Oxide Fiber	4×10^4	27.6

[0053] As can be clearly seen from Tables 1 and 2, the sheet of Example 2 and the coating film of Example 3, respectively prepared by using the electrically conductive powder of Example 1 in accordance with the present invention, exhibit the reduced levels of volume resistivity, markedly increased levels of total luminous transmittance and improved degrees of electrical conductivity and transparency, compared to those of Comparative Examples 3 - 8.

AVAILABILITY IN INDUSTRY

[0054] The present invention is applicable to members for which transparency and electrical conductivity have been conventionally sought, such as display device parts, antistatic films or packages, transparent electrodes and transparent heating units.

Claims

1. An electrically conductive powder characterized in that amorphous silica fibers, obtainable by treating calcium silicate fibers with an acid, are coated with one or more metal oxides selected from tin oxide, indium oxide and zinc oxide.
2. The electrically conductive powder as recited in claim 1, characterized in that a refractive index of said amorphous silica fibers is 1.4 - 1.8.
3. The electrically conductive powder as recited in claim 1, characterized in that the loading of said metal oxide is 10 - 100 parts by weight, based on 100 parts by weight of the amorphous silica fibers.
4. An electrically conductive powder characterized in that amorphous silica fibers having a fiber length of 1 - 500 μm and an aspect ratio of 5 - 5,000 are coated with one or more metal oxides selected from tin oxide, indium oxide and zinc oxide.
5. The electrically conductive powder as recited in claim 4, characterized in that said amorphous silica fibers are those obtained by treating calcium silicate fibers with an acid.
6. The electrically conductive powder as recited in claim 4, characterized in that a refractive index of said amorphous silica fibers is 1.4 - 1.8.
7. The electrically conductive powder as recited in claim 4, characterized in that the loading of said metal oxide is 10 - 100 parts by weight, based on 100 parts by weight of the amorphous silica fibers.
8. A transparent conductive composition characterized in that an electrically conductive powder, prepared by coating amorphous silica fibers having a fiber length of 1 - 500 μm and an aspect ratio of 5 - 5,000 with one or more metal oxides selected from tin oxide, indium oxide and zinc oxide, is included in a binder.
9. The transparent conductive composition as recited in claim 8, characterized as containing 3 - 80 % by weight of the electrically conductive powder and having a volume resistivity of not exceeding $10^{10} \Omega \cdot \text{cm}$ and a total luminous transmittance of 30 - 100 %.
10. The transparent conductive composition as recited in claim 8, characterized in that said binder is a polymer.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP99/01516

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl.⁶ C01B33/18, C08K3/34, 9/02, H01B1/08

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.Cl.⁶ C01B33/18, C08K3/34, 9/02, H01B1/08

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

Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-1999
 Kokai Jitsuyo Shinan Koho 1971-1999 Jitsuyo Shinan Keisai Koho 1996-1999

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.
Y	JP, 05-116930, A (The Nippon Chemical Industrial Co., Ltd.), 14 May, 1993 (14. 05. 93), Claims ; Par. Nos. [0021], [0023], [0036] (Family: none)	1-10
Y	JP, 63-004503, A (Sumitomo Chemical Co., Ltd.), 9 January, 1988 (09. 01. 88), Claims ; page 2, upper right column, lines 6 to 9 ; page 3, lower left column, lines 9 to 13 (Family: none)	1-10
Y	JP, 62-122005, A (Sumitomo Chemical Co., Ltd.), 3 June, 1987 (03. 06. 87), Claims ; page 2, lower left column, lines 7 to 10 ; page 3, lower right column, lines 13 to 20 (Family: none)	1-10

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

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
22 June, 1999 (22. 06. 99)Date of mailing of the international search report
29 June, 1999 (29. 06. 99)Name and mailing address of the ISA/
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP99/01516

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, 62-005507, A (Sumitomo Chemical Co., Ltd.), 12 January, 1987 (12. 01. 87), Claims ; page 2, upper right column, lines 11 to 16 ; page 3, upper left column, lines 17 to 20 (Family: none)	1-10
Y	JP, 55-080715, A (Tokuyama Soda Co., Ltd.), 18 June, 1980 (18. 06. 80), Claims ; page 2, upper left column, line 5 to upper right column, line 12 ; page 3, lower right column, line 16 to page 4, upper left column, line 4 (Family: none)	1-10

Form PCT/ISA/210 (continuation of second sheet) (July 1992)