

**IN THE UNITED STATES DISTRICT COURT
FOR THE DISTRICT OF DELAWARE**

E. I. DU PONT DE NEMOURS AND COMPANY,)	
)	
Plaintiff,)	
)	C.A. No. 11-773-SLR-CJB
v.)	
)	JURY TRIAL DEMANDED
HERAEUS PRECIOUS METALS NORTH AMERICA CONSHOHOCKEN LLC,)	
)	
Defendant.)	

FIRST AMENDED COMPLAINT

Plaintiff E. I. du Pont de Nemours and Company (“DuPont”) brings this First Amended Complaint for patent infringement against Defendant Heraeus Precious Metals North America Conshohocken LLC (“Heraeus”) and alleges as follows:

NATURE OF THE ACTION

1. This is an action for patent infringement arising under the patent laws of the United States, including 35 U.S.C. § 271 and §§ 281-285.
2. This lawsuit pertains to Heraeus’s infringement of U.S. Patent Number 7,767,254 (the “254 Patent”), entitled “Paste for Solar Cell Electrode and Solar Cell.”

PARTIES

3. Plaintiff DuPont is a corporation organized and existing under the laws of the state of Delaware, with a principal place of business located at 1007 Market Street, Wilmington, Delaware 19898. DuPont is a world leader in science innovation in markets including agriculture and food, building and construction, electronics and communications, general industry, and transportation. DuPont is also a leading supplier of front-side silver photovoltaic pastes.

4. Defendant Heraeus Precious Metals North America Conshohocken LLC is a corporation organized and existing under the laws of the state of Delaware, with a principal place of business at 24 Union Hill Road, West Conshohocken, Pennsylvania 19428. Upon information and belief, Heraeus is a business involved in, among other things, the processing of precious and platinum group metals as well as a comprehensive range of special metals. Heraeus Precious Metals North America Conshohocken LLC is a wholly owned subsidiary of Heraeus Holding GmbH.

JURISDICTION AND VENUE

5. This action arises under the Patent Laws of the United States, 35 U.S.C. § 101 *et seq.*, including 35 U.S.C. § 271. This Court has subject matter jurisdiction over this matter pursuant to 28 U.S.C. §§ 1331, 1338(a).

6. This Court has personal jurisdiction over Heraeus. Heraeus Precious Metals North America Conshohocken LLC is incorporated in Delaware and maintains substantial, continuous, and systematic contacts in Delaware. Heraeus has thus purposefully availed itself of the benefits and protections of Delaware's laws such that it should reasonably anticipate being haled into court here.

7. Venue is proper in the District of Delaware pursuant to 28 U.S.C. §§ 1391, §1400(b).

FACTUAL BACKGROUND

8. Plaintiff DuPont is the owner, by assignment, of all rights, title and interest in the '254 Patent. Inventors Takuya Konno, Takashi Kitagaki, and Hiroki Kojo filed their application for the '254 Patent on August 26, 2009. The '254 Patent issued on August 3, 2010. A true and correct copy of that patent is attached as Exhibit A.

9. The '254 Patent claims a method of producing a light-receiving surface electrode of a solar cell using a conductive paste. The conductive paste is comprised of silver particles with a specific surface size, as well as glass frit and resin binder.

**COUNT I - INFRINGEMENT
OF UNITED STATES PATENT NO. 7,767,254**

10. DuPont restates and realleges each of the assertions set forth in Paragraphs 1 through 10 above.

11. Upon information and belief, Heraeus's manufacture and use of solar cells made using front side photovoltaic pastes including but not limited to those numbered 94XX, 92XX, and 96XX series at its West Conshohocken, Pennsylvania research facility infringes one or more claims of the '254 Patent under 35 U.S.C. § 271.

12. DuPont is entitled to recover from Heraeus the damages sustained by DuPont as a result of Heraeus's wrongful acts in an amount subject to proof at trial, including lost profits and an amount not less than a reasonable royalty, together with interest and costs as fixed by this Court under 35 U.S.C. § 284.

13. The infringement by Heraeus of the '254 Patent will continue to cause DuPont irreparable injury and damage for which there is no adequate remedy at law unless and until Heraeus is enjoined from infringing said patent.

**COUNT II – INDIRECT INFRINGEMENT
OF UNITED STATES PATENT NO. 7,767,254**

14. DuPont restates and realleges each of the assertions set forth in Paragraphs 1 through 13 above.

15. Upon information and belief, Heraeus has been on notice of the '254 Patent at least from September 2, 2011.

16. Upon information and belief, Heraeus has knowingly, deliberately, and actively induced and is continuing to actively induce the infringement by others of the '254 Patent by knowingly selling front side photovoltaic pastes to customers with the intent that those customers will infringe the '254 Patent by practicing the method disclosed therein to produce a light-receiving surface electrode of a solar cell using a conductive paste.

17. Upon information and belief, Heraeus makes and fires solar cells using the patented method at its R&D facility in West Conshohocken to optimize its pastes to meet specific customer needs, such as qualifying the paste to work with the specific type of silicon that its customer uses. Upon information and belief, Heraeus then sells its paste to its customers knowing and intending that they will use the optimized paste to make a light-receiving surface electrode of a solar cell in a manner that infringes the '254 Patent.

18. Upon information and belief, Heraeus knowingly and deliberately instructs its customers to apply its conductive pastes when manufacturing a solar cell in a manner that infringes the '254 Patent, and specifically intends that its customers will use its pastes in a manner that infringes the '254 Patent.

19. Upon information and belief, Heraeus has knowingly induced SolarWorld Industries America, Inc. ("SolarWorld") to infringe the '254 Patent by selling SolarWorld a conductive paste that Heraeus developed utilizing a process covered by the '254 Patent. On further information and belief, Heraeus has qualified this conductive paste to work with SolarWorld's silicon, and sold that paste to SolarWorld with the knowledge and intent that SolarWorld will use that paste to make a light-receiving surface electrode of a solar cell in a manner that infringes the '254 Patent.

20. Upon information and belief, Heraeus will continue to induce others to infringe the '254 Patent unless and until enjoined by this Court.

PRAYER FOR RELIEF

WHEREFORE, DuPont respectfully requests that the Court enter judgment in its favor against Heraeus, granting the following relief:

- a. An adjudication that Heraeus has infringed one or more claims of the '254 Patent literally and/or under the doctrine of equivalents;
- b. An adjudication that Heraeus has knowingly, deliberately, and actively induced others to infringe the '254 Patent;
- c. A grant of a permanent injunction pursuant to 35 U.S.C. § 283, enjoining Heraeus and its agents, servants, officers, directors, employees, affiliated entities, and all persons in active concert or participation with them from continued infringement of the '254 Patent;
- d. An award to DuPont of damages adequate to compensate DuPont for Heraeus's acts of infringement of the '254 Patent;
- e. An award to DuPont equal to any profits that Heraeus gained from its infringement of the '254 Patent;
- f. An award of prejudgment and post-judgment interest on all sums awarded;
- g. A post-verdict and post-judgment accounting for any infringement the '254 Patent not otherwise covered by a damages award and the requested injunctive relief; and
- h. Any such other and further relief as the Court may deem just and proper under the circumstances.

DEMAND FOR JURY TRIAL

Pursuant to Rule 38(b) of the Federal Rules of Civil Procedure, DuPont respectfully requests a trial by jury of any and all issues on which a trial by jury is available under applicable law.

Respectfully submitted,

POTTER ANDERSON & CORROON LLP

OF COUNSEL:

Sean G. Gallagher
Adam K. Mortara
Asha L.I. Spencer
Matthew W. Brewer
BARTLIT BECK HERMAN
PALENCHAR & SCOTT LLP
54 W. Hubbard Street, Suite 300
Chicago, IL 60654
Tel: (312) 494-4400

By: /s/ David E. Moore
Richard L. Horwitz (#2246)
David E. Moore (#3983)
Hercules Plaza, 6th Floor
1313 N. Market Street
Wilmington, DE 19801
Tel: (302) 984-6000
rhoorwitz@potteranderson.com
dmoore@potteranderson.com

*Attorneys for Plaintiff
E. I. du Pont de Nemours and Company*

Dated: March 1, 2013
1096591 / 20120-574

Exhibit

A



US007767254B2

(12) **United States Patent**
Konno et al.

(10) **Patent No.:** US 7,767,254 B2
 (45) **Date of Patent:** *Aug. 3, 2010

(54) **PASTE FOR SOLAR CELL ELECTRODE AND SOLAR CELL**

(75) **Inventors:** Takuya Konno, Tochigi-Ken (JP);
 Takashi Kitagaki, Utsunomiya (JP);
 Hiroaki Kojo, Tochigi (JP)

(73) **Assignee:** E. I. du Pont de Nemours and
 Company, Wilmington, DE (US)

(*) **Notice:** Subject to any disclaimer, the term of this
 patent is extended or adjusted under 35
 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal dis-
 claimer.

(21) **Appl. No.:** 12/547,814

(22) **Filed:** Aug. 26, 2009

(65) **Prior Publication Data**
 US 2009/0317940 A1 Dec. 24, 2009

Related U.S. Application Data

(62) Division of application No. 12/162,509, filed on Jul.
 29, 2008, now Pat. No. 7,648,730.

(30) **Foreign Application Priority Data**
 Feb. 2, 2006 (JP) 2006-026340

(51) **Int. Cl.**
B05D 5/12 (2006.01)
H01B 1/22 (2006.01)

(52) **U.S. Cl.** 427/96.1; 252/514
 (58) **Field of Classification Search** 252/514;
 427/96.1, 99.2, 125; 136/256
 See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,766,516 A	6/1998	Fukuta et al.
6,406,646 B1	6/2002	Lee et al.
6,556,419 B2	4/2003	Suzuki et al.
6,815,073 B2	11/2004	Tanei et al.
2006/0107791 A1	5/2006	Fujino et al.
2007/0181858 A1	8/2007	Matsushima et al.
2008/0035895 A1	2/2008	Ogi et al.

FOREIGN PATENT DOCUMENTS

JP	2003257243 A	9/2003
WO	2006/008896 A1	1/2006

OTHER PUBLICATIONS

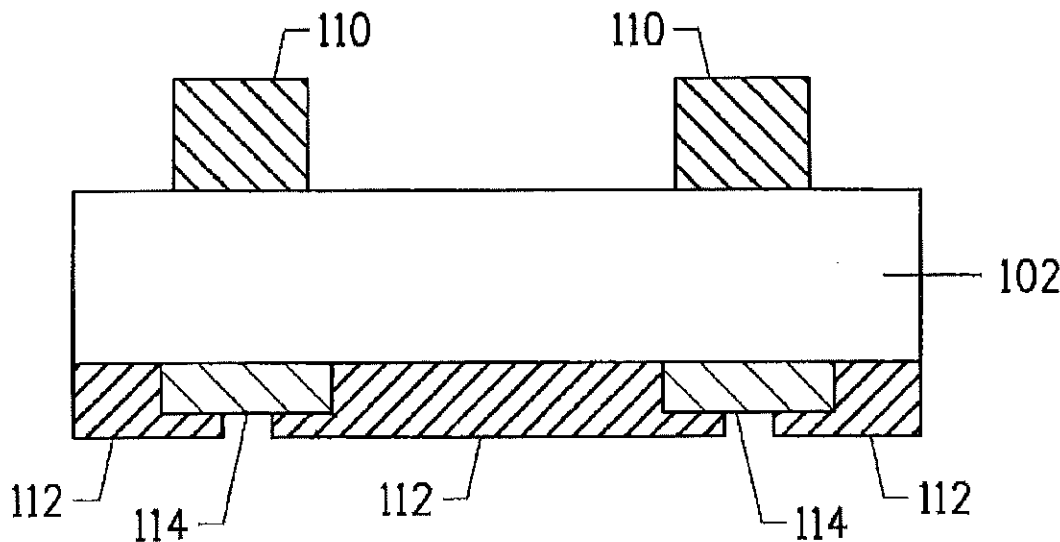
PCT International Search Report and Written Opinion for Interna-
 tional Application No. PCT/US2006/029942 dated Jan. 26, 2007.

Primary Examiner—Mark Kopec

(57) **ABSTRACT**

In a paste for a solar cell light-receiving surface electrode
 including silver particles, glass frit, resin binder, and thinner,
 silver particles with a specific surface of 0.20-0.60 m²/g are
 used as the silver particles. The silver particles are preferably
 included at 80 mass % or more to the total amount of silver
 particles being included in the paste.

10 Claims, 1 Drawing Sheet



U.S. Patent

Aug. 3, 2010

US 7,767,254 B2

FIG. 1A

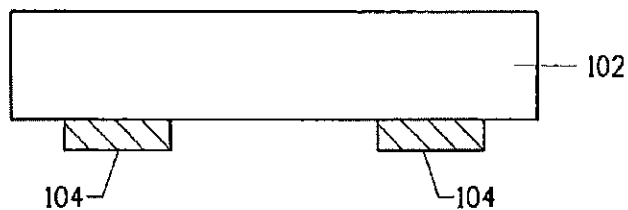


FIG. 1B

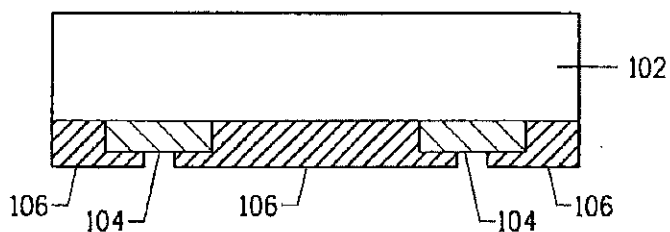


FIG. 1C

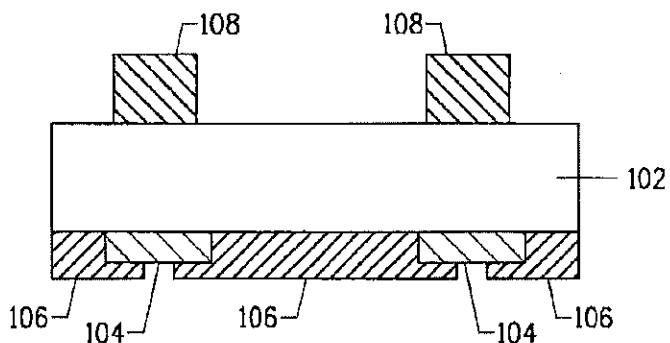
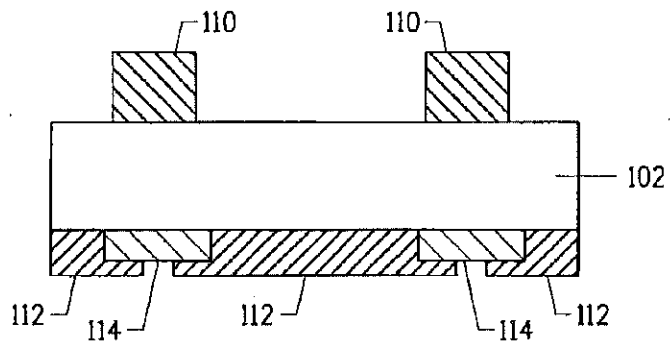


FIG. 1D



US 7,767,254 B2

1

PASTE FOR SOLAR CELL ELECTRODE AND SOLAR CELL

This application is a divisional of U.S. patent application Ser. No. 12/162,509 filed on Jul. 29, 2008 now U.S. Pat. No. 7,648,730.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention pertains to a solar cell. More specifically, the present invention pertains to an electrode paste for a solar cell light-receiving surface being used in the manufacture of an electrode in a solar cell and a solar cell being obtained by using said paste.

2. Description of Related Art

In manufacturing an electrode for a solar cell, the electrode is formed at the side in which an anti-reflection film is formed. The generally used method for manufacturing the electrode is a method that spreads a paste containing glass frit, resin binder, thinner, and if necessary, additives on an anti-reflection film and [then] sinters it.

In order to raise the power generation characteristics in the solar cell, the characteristics of the electrode are important. For example, the power generation efficiency is raised by lowering the resistance value of the electrode. In order to achieve this purpose, various methods are proposed.

Silver particles are generally known as the electroconductive metal in the electrode of the solar cell. However, the relationship between the specific surface of the silver particles being used and the power generation characteristics is not deeply reviewed. In paragraph [0009] of Japanese Kokai Patent Application No. 2003-257243, "BET diameter" is defined as "the particle diameter attained, assuming that the particles have a spherical shape, based on the specific surface (m²/g) of the particles measured in the BET method." According to said publication, the BET diameter of the silver particles being used is 0.10-0.50 μm. As application examples and comparative examples, silver powders with a BET diameter of 0.02-0.50 μm are presented.

Here, if the silver density=10.5 g/cm³=10.5×10⁶ g/m³, the radius=R (μm)=R×10⁻⁶ m, and the specific surface=S (m²/g), the following equation is established.

$$\text{Weight of one silver particle} = 4\pi(R \times 10^{-6})^2 S / (4\pi(R \times 10^{-6})^3) \times 10.5 \times 10^6$$

If this equation is solved with respect to S,

$$S = 3 / (10.5 \times R)$$

Since the BET diameter is a diameter, the radius R is its half. Considering this, if the specific surface of the silver powder with a BET diameter of 0.02-0.50 μm, its [specific surface] is 1.1-28.6 m²/g.

$$\text{BET diameter of } 0.02 \mu\text{m} = \text{radius of } 0.01 \mu\text{m} = \text{specific surface of } 28.6 \text{ m}^2/\text{g}$$

$$\text{BET diameter of } 0.10 \mu\text{m} = \text{radius of } 0.05 \mu\text{m} = \text{specific surface of } 5.7 \text{ m}^2/\text{g}$$

$$\text{BET diameter of } 0.50 \mu\text{m} = \text{radius of } 0.25 \mu\text{m} = \text{specific surface of } 1.1 \text{ m}^2/\text{g}$$

BRIEF SUMMARY OF THE INVENTION

The purpose of the invention is to provide an electroconductive paste contributing to the improvement of the power generation efficiency of a solar cell.

2

An embodiment of the present invention is a paste for a solar cell light-receiving surface electrode including silver particles with a specific surface of 0.20-0.60 m²/g, glass frit, resin binder, and thinner. The silver particles are preferably included at 80 mass % or more to the total amount of silver particles being included in an electrode.

An embodiment of the present invention is a solar cell light receiving surface electrode having an electrode surface that consists of a paste for a solar cell-light receiving surface electrode including silver particles with a specific surface of 0.20-0.60 m²/g, glass frit, resin binder, and thinner. The silver particles, optimally includes 80 mass % or more to the total amount of silver particles being included in the electrode. The solar cell having an electrode prepared using the paste for a solar cell electrode of the present invention has excellent power generation efficiency.

Disclosed is a method of producing a light-receiving surface electrode of a solar cell comprising the steps of:

applying a conductive paste on a silicon substrate; wherein the conductive paste comprises silver particles with a specific surface of 0.20-0.60 m²/g, and wherein the conductive paste further comprises glass frit, resin binder and thinner; and firing the applied conductive the applied conductive paste.

BRIEF DESCRIPTION OF THE DRAWING(S)

FIG. 1 explains the manufacturing processes in manufacturing a solar cell using the electroconductive paste of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

It has been clarified that the power generation characteristics of the solar cell being obtained are improved by using silver particles with a small specific surface as the silver being included as an electroconductive metal in the paste. The present invention is based on this knowledge.

The present invention pertains to a paste for a solar cell light-receiving surface electrode including silver particles with a specific surface of 0.20-0.60 m²/g, glass frit, resin binder, and thinner. The electroconductive paste of the present invention is used in forming a light-receiving surface electrode (surface side electrode) of a solar cell.

Next, each component of the electroconductive paste of the present invention is explained.

1. Electroconductive Metal

In the paste of the present invention, silver (Ag) particles are used as an electroconductive metal. The silver particles of the present invention have a specific surface smaller than that of general silver particles. Specifically, the specific surface of the silver particles is 0.20-0.60 m²/g, preferably 0.25-0.50 m²/g. The power generation characteristics tend to be improved with the decrease of the specific surface, however if the specific surface is too small, the adhesive strength is likely to be lowered. With the use of silver particles with a small specific surface, the power generation characteristics of the obtained solar cell are improved.

The specific surface [measured] can be attained by a BET-point method (JIS-Z-8830). An apparatus on the market may used, and for example, it can be measured using NOVA3000 made by Quantachrome Co. In the present invention, if a meaningful difference is made in the specific surface by the measuring apparatus, the value measured by NOVA3000 made by Quantachrome Co. is adopted.

The content of the silver particles is not particularly limited. One or two kinds of silver particles with a specific surface [requirement] that is regulated in the present inven-

US 7,767,254 B2

3

tion can be used. Sometimes, other silver particles may also be used. In case silver particles which deviate from the specific surface [requirement] that is regulated in the present invention are used, the amount being used is preferably 20 wt % or less [compared] to the total amount of silver particles. In other words, the content of the silver particles that meet the specific surface [requirement] that is regulated in the present invention is 80 mass % or more to the total amount of silver particles being included in the paste. The content is preferably 90 mass % or more, more preferably 95 mass % or more, and especially preferably 100 mass %. The obtained power generation characteristics tend to be improved with the increase of the content of the silver particles with a specific surface [requirement] that is regulated in the present invention.

The silver particles that meet the specific surface [requirement] that is regulated in the present invention can be manufactured by the atomizing method, wet-reducing method, etc. The specific surface can be controlled by controlling the conditions in each manufacturing method. In general, the specific surface can be reduced by setting conditions in which the particle diameter is increased.

It has been considered that it is preferable for the silver particles used in the light-receiving surface of the electrode of the solar cell to be fine and to have a large specific surface. The reason for this is considered to be that fine silver particles with a large specific surface are easily introduced into the depressions and projections of the wafer surface to prevent the reflection. On the other hand, according to these inventors, it was clarified that the power generation characteristics of the solar cell being obtained were improved by using silver particles with a small specific surface. Specifically, the characteristics such as Eff: conversion efficiency (%), R_s : series resistance ($\Omega\text{-cm}^2$), FF: fill factor (%), V_{oc} : open voltage (mV), J_{sc} : short circuit current ($\text{mA}\cdot\text{cm}^2$), and R_{sh} : shunt resistance ($\Omega\text{-cm}^2$) are improved. The present invention is based on this knowledge.

The particle diameter and the specific surface of the silver particles have a fixed relation, and if the particle diameter of the silver particles is large, the specific surface tends to be decreased. For this reason, in obtaining the silver particles with a small specific surface of the present invention, the particle diameter is apt to be increased. Also, in case the silver particles are used for a general electroconductive paste, the particle diameter of the silver particles is not particularly limited in terms of technical effects, however the particle diameter has an influence on the sintering characteristics of the silver (for example, the silver particles with a large particle diameter are sintered at a speed slower than that of the silver particles with a small particle diameter). Furthermore, it is necessary for the silver particles to have a particle diameter suitable for a method for spreading an electroconductive paste (for example, screen printing).

In consideration of these requirements, the average particle diameter of the silver particles is preferably 0.1-14 μm , more preferably 2.0-8.0 μm . With the use of the silver particles with such a particle diameter, a paste suitable for spreading of the electroconductive paste can be formed. Also, silver particles with excellent sintering characteristics are easily obtained. For example, the average particle diameter is calculated as an average particle diameter (50% point) by the measured value of LA-920 made by Horiba Seisakusho K.K.

Usually, it is preferable for the silver to have a high purity (99%+). However, a substance with low purity can also be used by an electrical requirement of an electrode pattern.

The content of the silver particles in the paste is not particularly limited, however the content is preferably 70-90 wt % based on the weight of the paste.

4

2. Glass Frit

It is preferable for the electroconductive paste of the present invention to include a glass frit as an inorganic binder. The glass binder usable in the present invention is a glass frit with a softening point of 450-550° C. so that the electroconductive paste may be sintered at 600-800° C., appropriately wetted, and appropriately adhered to a silicon substrate. If the softening point is lower than 450° C., the sintering is advanced, and the effects of the present invention cannot be sufficiently obtained. If the softening point is higher than 550° C., since a sufficient melting flow is not caused during sintering, a sufficient adhesive strength is not exerted, and the liquid-phase sintering of the silver cannot be accelerated in some cases.

Here, the "softening point" is a softening point obtained by the fiber stretch method (fiber elongation method) of ASTM C338-57.

Since the chemical composition of the glass frit is not important in the present invention, any glass frit being used in electroconductive paste for an electronic material can be used. For example, silver borosilicate glass, etc., can be appropriately used. Silver silicate glass and the lead borosilicate glass are excellent materials in the present invention in terms of both the range of the softening point and the glass fusibility. In addition, a leadless glass such as zinc borosilicate can also be used.

The content of the glass frit is not particularly limited as long as it is an amount that can achieve the purpose of the present invention, however the content is preferably 0.5-10.0 wt %, more preferably 1.0-3.0 wt % based on the weight of the electroconductive paste.

If the amount of glass frit is smaller than 0.5 wt %, the adhesive strength is sometimes not sufficient [sic; sufficient]. If the amount of glass frit is more than 10.0 wt %, a trouble is sometimes caused in the soldering postprocess by glass rise, etc.

3. Resin Binder

The electroconductive paste of the present invention includes a resin binder. In this application example, the "resin binder" is a concept including a mixture of a polymer and a thinner. Therefore, an organic liquid (also called a thinner) may also be included in the resin binder. In the present invention, the resin binder in which organic liquid is included is preferable, and if the viscosity is high, if necessary, the organic liquid can be separately added as a viscosity regulator.

In the present invention, an optional resin binder can be used. In the present invention, a pine oil solution or ethyl cellulose or ethylene glycol monobutyl ether monoacetate solution of resin (polymethacrylate, etc.), terpineol solution of ethyl cellulose, etc., can be mentioned. In the present invention, a terpineol solution of ethyl cellulose (ethyl cellulose content=5-50 wt %) is preferably used. Also, in the present invention, a solvent containing no polymers, such as water or organic liquid, can be used as a viscosity regulator. As the usable organic liquid, for example, alcohol, ester of alcohol (for example, acetate or propionate), and terpene (for example, pine oil, terpineol, etc.) can be mentioned.

The content of the resin binder is preferably 5-50 wt % based on the weight of the electroconductive paste.

4. Additives

In the electroconductive paste of the present invention, a thickener and/or a stabilizer and/or other general additives may also be added or may not be added. In case the additives are added, tackifier (thickener), stabilizer, etc., can be added. Also, as other general additives, dispersant, viscosity regulator, etc., can be added. The amount of tackifier, etc., being

US 7,767,254 B2

5

added is changed in accordance with the viscosity of the electroconductive paste, however it can be appropriately determined by the concerned party.

Also, several kinds of additives may be added.

As explained below, it is preferable for the electroconductive paste of the present invention to have a prescribed range of viscosity. In order to render an appropriate viscosity to the electroconductive paste, if necessary, a tackifier (thickener) can be added. As examples of the tackifier, the above-mentioned substances can be mentioned. The amount of tackifier, etc., being added is changed in accordance with the viscosity of the final electroconductive paste and can be appropriately determined by the party concerned.

The electroconductive paste of the present invention is favorably manufactured by mixing each above-mentioned component with a three-roller kneader. The electroconductive paste of the present invention is preferably spread on a desired part of the light-receiving surface of the solar cell by screen printing, however in spreading it in such a printing, it is preferable to have a prescribed range of viscosity. The viscosity of the electroconductive paste of the present invention is preferably 50-300 PaS when it is measured at 10 rpm and 25° C. by a utility cup using a #14 spindle as a Brookfield HBT viscometer.

As mentioned above, the electroconductive paste of the present invention is used to form an electrode mainly composed of silver on the light-receiving surface of the solar cell. In other words, the paste of the present invention is printed and dried on the light-receiving surface of the solar cell. Separately, a back face electrode composed of aluminum or silver is also formed on the back face of the solar cell. These electrodes are preferably simultaneously sintered.

Then, the solar cell of the present invention is explained. The solar cell of the present invention has a light-receiving surface electrode formed of silver particles with a specific surface of 0.20-0.60 m²/g, glass frit, resin binder, and thinner. Preferably, the silver particles are included at 80 mass % or more [compared] to the total amount of silver particles being included in the electrode. The silver particles and the glass frit are the same as those mentioned above, their explanation is omitted.

An example for preparing the solar cell using the electroconductive paste of the present invention is explained referring to FIG. 1.

First, a Si substrate 102 is prepared. An electroconductive paste 104 for a solder connection is spread on the back face of the substrate by screen printing and dried (FIG. 1(a)). As the electroconductive paste, a conventional silver conductive paste containing silver particles, glass particles, and resin binder can be used. Next, aluminum paste for the back face electrode for the solar cell (there is no particular limitation as long as it is used for the solar cell, however for example, PV333, PV322 (applicant of the patent of this case)) 106, etc.,

6

are spread by screen printing, etc., and dried (FIG. 1(b)). The drying temperature of each paste is preferably 180° C. or lower. Also, the film thickness of each electrode of the back face is the thickness after drying, and the thickness is preferably 20-40 μm in the aluminum paste and 15-30 μm in the electroconductive silver paste. Also, the overlapping part of the aluminum paste and the electroconductive silver paste is about 0.5-2.5 mm.

Next, an electroconductive paste 108 of the present invention is spread by screen printing, etc., and dried (FIG. 1(c)). For the substrate obtained, the aluminum paste and the electroconductive silver paste are simultaneously sintered at a temperature of about 600-900° C. for about 2-15 min in an infrared sintering furnace, so that an intended solar cell can be obtained (FIG. 1(d)).

The solar cell being used by using the electroconductive paste of the present invention, as shown in FIG. 1(d), has an electrode 110 formed of the electroconductive paste of the present invention on the light-receiving surface (surface) of the substrate (for example, Si substrate) 102 and has an Al electrode (first electrode) 112 mainly composed of Al and a silver electrode (second electrode) mainly composed of Ag on the back face.

EXAMPLES

1. Preparation of Electroconductive Paste

Application Example 1

A mixture containing silver particles with a specific surface of 0.25 m²/g, Si.B.Pb.O system glass frit, and sintering auxiliary material was prepared. A terpineol solution containing 20% ethyl cellulose was added as an organic vehicle to the mixture. Furthermore, terpineol was added as a thinner to adjust the viscosity. The content of each component is shown in Table I. The silver particles were 83.4 wt %, the glass frit was 1.6 wt %, the organic vehicle was 10.0 wt %, the sintering auxiliary material was 3.5 wt %, and the terpineol added as a thinner to adjust the viscosity was 0.9 wt %.

This mixture was premixed in a universal mixer and kneaded by a three-roll kneader, so that a paste for a solar cell electrode was obtained. The particle diameters, the contents, and the characteristics of the materials used were shown in Table I.

Application Examples 2-4 and Comparative Examples 1-3

Pastes for a solar cell electrode were obtained similarly to Application Example 1 except for changing the kind of silver particles being used and the amount being used to the amounts shown in Table I.

TABLE I

		Application Example 1	Application Example 2	Application Example 3	Application Example 4	Comparative Example 1	Comparative Example 2	Comparative Example 3
Silver particles A	specific surface (m ² /g)	0.25	0.30	0.51	0.59	0.62	0.84	.084
	wt %	83.4	83.4	71.0	71.0	71.0	83.4	71.0
	wt % vs Ag total	100.0	100.0	85.1	85.1	85.1	100.0	85.1

US 7,767,254 B2

7

8

TABLE I-continued

		Application Example 1	Application Example 2	Application Example 3	Application Example 4	Comparative Example 1	Comparative Example 2	Comparative Example 3
Silver particles B	Specific surface (m ² /g)	—	—	1.9	1.9	1.9	—	1.9
	wt %	—	—	12.4	12.4	12.4	—	12.4
	wt % vs Ag total	—	—	14.9	14.9	14.9	—	14.9
Glass frit	wt %	1.6	1.6	1.6	1.6	1.6	1.6	1.6
Organic vehicle	wt %	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Additive	wt %	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Thinner	wt %	0.9	0.9	0.9	0.9	0.9	0.9	0.9

3. Preparation of Solar Cell

Using four kinds of obtained pastes, solar cells were manufactured. First, a Si substrate was prepared. An electroconductive paste (silver paste) for a soldering connection was spread on the back face of the Si substrate by screen printing and dried. Next, an aluminum paste (PV333 (made by E.I. du Pont de Nemours and Company)) for a back face electrode was spread in a partially overlapping fashion with the dried silver paste by screen printing and dried. The drying temperature of each paste was set to 120° C. Also, the film thickness of each electrode of the back face being spread [upon] was 35 μm of the aluminum paste and 20 μm of the silver paste as a film thickness after drying.

trode (first electrode) 112 mainly composed of Al on the back face and the silver electrode (second electrode) 114 mainly composed of Ag.

4. Evaluation of Cells

The electric properties (I-V characteristic) of the solar cell substrates obtained were evaluated by a cell tester. As the cell tester, an equipment (NCT-M-150AA) made by NPC Co., was used.

Eff: conversion efficiency (%) and Rs: serial resistance (Ω·cm²) were measured. The higher Eff, the more excellent power generation performances as a solar cell. The lower Rs, the more excellent power generation performances as a solar cell. The results are shown in Table II. The numerical values of each electric property shown in Table II are the average of measured values of 5 sheets of solar cell substrate samples and are relative values of the case where each numerical value of Comparative Example 1 was assumed as 1.

TABLE II

	Application Example 1	Application Example 2	Application Example 3	Application Example 4	Comparative Example 1	Comparative Example 2	Comparative Example 3
Eff	1.123	1.221	1.034	1.048	1	0.641	0.464
Rs	0.552	0.432	0.817	0.799	1	2.492	5.611

Furthermore, the paste of the present invention was spread on the light-receiving side surface (surface) by screen printing and dried. A printer made by Price Co., and a mask having an 8 inch and 10 inch frame and a stainless wire with a mesh of 250 were used. A pattern for evaluation for 1.5 in consisting of finger lines with a width of 100μ and bus bars with a width of 2 mm was employed, and the film thickness was 13 μm after sintering.

Next, for the obtained substrate, the spread pastes were simultaneously sintered under the conditions of a peak temperature of about 730° C. and IN-OUT for about 5 min in an infrared sintering furnace, so that intended solar cells were obtained.

The solar cells being obtained using the electroconductive pastes of the present invention, as shown in FIG. 1, have the Ag electrode 110 on the light-receiving surface (surface) of the substrate 102 (for example, Si substrate) and the Al elec-

As mentioned above, the characteristics of the obtained solar cells are improved using the silver particles with a small specific surface.

What is claimed is:

1. A method of producing a light-receiving surface electrode of a solar cell comprising the steps of:

applying a conductive paste on a silicon substrate, wherein the conductive paste comprises silver particles with a specific surface of 0.20-0.60 m²/g, and wherein the conductive paste further comprises glass frit, resin binder and thinner; and

firing the applied conductive the applied conductive paste.

2. A method of producing a light-receiving surface electrode of a solar cell of claim 1, wherein firing temperature is 600-900 degree C. in the firing step.

3. A method of producing a light-receiving surface electrode of a solar cell of claim 1, wherein firing time is 2-15 minutes in the firing step.

4. A method of producing a light-receiving surface electrode of a solar cell of claim 1, wherein the above-mentioned

US 7,767,254 B2

9

silver particles are included at 80 mass % or more of the total amount of silver particles being included in the paste.

5 5. A method of producing a light-receiving surface electrode of a solar cell of claim 1, wherein the specific surface of the silver particles is 0.25-0.50 m²/g.

6. A method of producing a light-receiving surface electrode of a solar cell of claim 1, wherein the average particle diameter of the silver particles is 0.1-14 μm.

7. A method of producing a light-receiving surface electrode of a solar cell of claim 1, wherein the average particle diameter of the silver particles is 2.0 μm.

10

8. A method of producing a light receiving surface electrode of a solar cell of claim 1, wherein the content of the silver particles in the paste is 70-90 wt % upon the weight of the paste.

5 9. A method of producing a light receiving surface electrode of a solar cell of claim 1, wherein the content of the glass frit is 0.5-10 wt % based upon the weight of the paste.

10 10. A method of producing a light receiving surface electrode of a solar cell of claim 1, wherein the softening point of the glass frit is 450-550° C.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 7,767,254 B2
APPLICATION NO. : 12/547814
DATED : August 3, 2010
INVENTOR(S) : Takuya Konno, Takashi Kitagaki and Hiroki Kojo

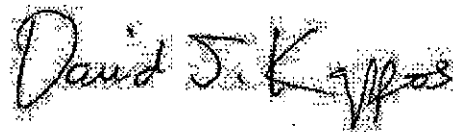
Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 2, Line 23: "firing the applied conductive the applied conductive paste" should read
-- firing the applied conductive paste --

Column 8, Line 59: "firing the applied conductive the applied conductive paste" should read
-- firing the applied conductive paste --

Signed and Sealed this
Thirtieth Day of August, 2011



David J. Kappos
Director of the United States Patent and Trademark Office