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W. DÜRR

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METHOD OF PRODUCING A PHOTOCONDUCTIVE LAYER

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Fig. 1

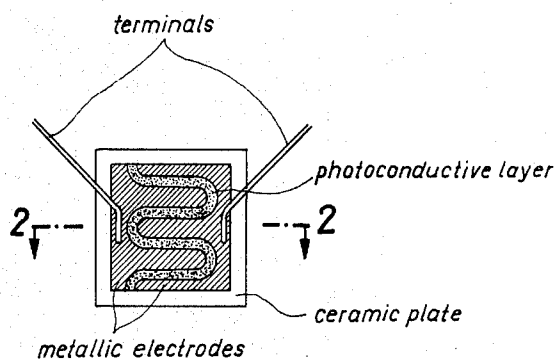
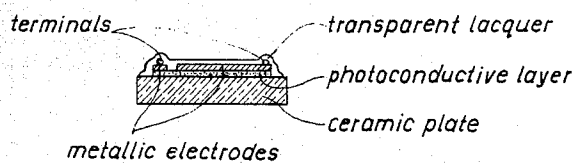


Fig. 2



Inventor:

W. DÜRR

by Michael J. Striker
Attorney

1

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METHOD OF PRODUCING A PHOTO-CONDUCTIVE LAYER

Walter Dürr, Schulstrasse 15, Wolfschlugen, Kreis
Nürtingen, Germany

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13 Claims. (Cl. 117—201)

The present invention relates to a method of producing a photoconductive layer and, more particularly, to a method of producing a photoconductive layer of the type which consists mainly of cadmium sulfide, cadmium selenide or cadmium sulfo-selenide and an activating agent such as a copper or silver salt. Conductive layers which comprise a polycrystalline layer of cadmium sulfide, cadmium selenide, or cadmium sulfo-selenide have been found to be particularly advantageous for many applications, primarily in light meters, and are thus produced in a great variety of shapes, sizes and adapted for a variety of current loads.

According to one of the known methods for producing such photoconductive layers, cadmium sulfide is vaporized in a partial vacuum and condensed on a suitable carrier. The thus-formed layers generally are not light sensitive and have to be further treated, for instance suitably heated in order to be activated.

It also has been proposed to form a coherent layer of microcrystalline pulverulent photoconductive material, without first to vaporize such material. For this method it is usually presupposed that the starting material has been made photoconductive in a special process prior to formation of the layer. The photoconductive powder may then be embedded in a synthetic resin or in another suitable non-conductive binder material, and a thin layer formed thereof on a carrier plate. However, photoconductive layers produced in this manner do not have a favorable relationship between the conductivity in light-exposed and in dark condition. Furthermore, photoconductive cells formed with such photoconductive layers do not show a linear correlation between the applied voltage and current. The reason for this disadvantageous behavior may be found in the fact that a relatively high contact resistance exists between the abutting individual small crystals, which contact resistance is superposed upon the light-variable resistance and, furthermore, is voltage-dependent.

In an attempt to overcome the above discussed disadvantages it has been suggested to achieve a better contact between the individual cadmium sulfide or the like particles, by adding a solvent for cadmium sulfide, for instance cadmium chloride. The layer which is formed for instance of cadmium sulfide and cadmium chloride is heated to about 600° C., whereby the cadmium chloride will melt and in such molten condition will dissolve part of the cadmium sulfide. Upon further heating, the cadmium chloride will be vaporized and thus the cadmium sulfide will again precipitate from the solution, due to vaporization of the solvent, i.e., the cadmium chloride.

It has also been proposed, to press small plates of pulverulent cadmium sulfide without using a binder, and to sinter the thus-formed layer or small plate at high temperatures, for instance at about 1000° C., so as to form a solid sintered body. The individual pulverulent crystals bake or sinter together during such heat treatment at about 1000° C., and in this manner, the contact between the individual crystals is improved and the contact resistance reduced. Finally, it also has been proposed to apply finely crystalline photoconductive material to a porous or easily softening carrier and to sinter the par-

2

ticles of the photoconductive material to each other and to the carrier at high temperatures, for instance higher than 1000° C. However, this method is relatively difficult to carry out, partly because very high temperatures are required and thus, for instance, there exists the danger of undesirable and disadvantageous dissociation of the material. It is usually required to carry out the last mentioned method in a protective gas atmosphere with high gas or vapor pressure.

It is therefore an object of the present invention to overcome the above discussed disadvantages.

It is a further object of the present invention to provide a method of producing a photoconductive layer, particularly of cadmium sulfide, cadmium selenide, cadmium sulfo-selenide and the like, which method can be carried out in a simple and economical manner.

It is another object of the present invention to provide a method of producing such photoconductive layer, which method can be carried out at relatively lower temperatures, such as temperatures of about 600° C., and, in any event, will not require heating to about 1000° C. or more.

It is still another object of the present invention to provide a method for producing such photoconductive layers, which will be characterized by their high photoconductive sensitivity.

Other objects and advantages of the present invention will become apparent, from a further reading of the description and of the appended claims.

With the above and other objects in view, the present invention contemplates in a method of producing a photoconductive layer of high sensitivity, the steps of forming a stratum including a substance having inherent photoconductive properties, and an activating agent therefor, and heating the stratum to the sintering temperature of the substance in the presence of a gas adapted to promote sintering of the substance into a state of improved photoconductive sensitivity.

According to a preferred embodiment, the method of the present invention comprises the steps of forming a pulverulent layer consisting essentially of precipitated finely subdivided particles of a substance selected from the group consisting of sulfides, selenides and sulfo-selenides of cadmium, and an activating agent therefor, said activating agent including a salt of a member of the group consisting of copper and silver and sintering the layer at a temperature of about 600° C. and for a period of about 15 minutes in the presence of a gas adapted to improve crystallization and sintering of the same and selected from the group consisting of hydrogen chloride, hydrogen bromide and hydrogen iodide.

The present invention is also concerned with a method of producing a photoconductive layer, which method comprises the steps of introducing into a reaction chamber a layer consisting essentially of a substance selected from the group consisting of sulfides, selenides and sulfo-selenides of cadmium, an activating agent therefor, also introducing into the reaction chamber a material adapted to form at the sintering temperature of the substance a gas selected from the group consisting of hydrogen chloride, hydrogen bromide and hydrogen iodide, said material being selected from the group consisting of ammonium chloride, methyl-ammonium chloride, hydrazindihydrochloride, aniline-hydrochloride, hydroxylaminohydrochloride and the corresponding bromides and iodides, and heating the layer in the reaction chamber to the sintering temperature of the substance so as to sinter the same and to form the gas, the latter improving crystallization and sintering of the substance so as to form a sintered layer of improved photoconductive sensitivity.

The novel features which are considered as characteristic for the invention are set forth in particular in the

appended claims. The invention itself, however, both as to its construction and its method of operation, together with additional objects and advantages thereof, will be best understood from the following description of specific embodiments when read in connection with the accompanying drawing, in which:

FIG. 1 is a plan view of a photoconductive layer on a support, in accordance with the present invention; and

FIG. 2 is a cross sectional view taken along line 2—2 of FIG. 1.

The various elements of the illustrated structure are fully identified by legends appearing in the drawing.

Thus, according to the present invention a mixture of very small particles of cadmium sulfide, cadmium selenide or of other more or less similarly acting photoelectrically active substances may be formed with an activating agent such as a copper or silver salt, a layer of such mixture is then formed on a suitable carrier for instance of ceramic material, and the thus formed layer is heated to sintering temperature of the cadmium sulfide or the like in the presence of the crystallization promoting gas such as hydrogen chloride. Thereby it will be achieved that due to the presence of the gaseous hydrogen chloride or the like, a sintered layer of photoelectrically highly active and usually somewhat larger crystals is formed.

Surprisingly it has been found that the presence of gaseous hydrogen chloride, hydrogen bromide or hydrogen iodide will promote sintering and/or crystal formation so that a layer will be produced under such conditions at relatively low temperatures such as temperatures of about 600° C., which layer will be of high photoelectric or photoconductive sensitivity.

Generally, in order to sinter cadmium sulfide powder or the like into a coherent body or layer, it is necessary to apply temperatures as high as 900 or 1000° C. or even higher. Such sintering at high temperatures is carried out in an inert gas atmosphere such as a nitrogen or argon atmosphere. Surprisingly, it has been found that by carrying out the sintering and crystallization in the presence of hydrogen chloride or the like, that under such conditions sintering will be successfully accomplished at much lower temperatures which are in the vicinity of about 600° C. In the absence of such hydrogen halide, cadmium sulfide does not sinter at such considerably lower temperatures than the previously applied about 1000° C., or at least sintering could not be accomplished within comparable periods of time. Sintering allows the conclusion that a growth of the crystals took place and this can also be confirmed directly by measuring the particle size of the cadmium sulfide or the like prior and after the sintering process. Thus, it appears justified to refer to the action of the hydrogen halide, particularly hydrogen chloride, bromide or iodide, not only as sintering-promoting but also as crystallization-promoting gas, whereby in the presence of such hydrogen halide the sintering temperature can be considerably reduced below the temperature required when the sintering is carried out without the inventive addition of such hydrogen halide gas.

According to the present invention, a layer of finely subdivided cadmium sulfide and/or selenide and of activating agents is formed on a suitable carrier and the pulverulent layer is then heated in the presence of a sintering and crystallization promoting gas.

Very good results are achieved by using as such promoting gas hydrogen chloride or hydrogen bromide or hydrogen iodide. However, it is also possible and frequently desirable to utilize a compound such as hydrazine-dihydrochloride which at the elevated temperatures applied to the layer will split off a suitable hydrogen halide, in this case hydrogen chloride. The heat treatment preferably is carried out at about 600° C. and for a period of about 15 minutes.

In a somewhat similar manner, it would seem also pos-

sible to produce a photoconductive layer of cadmium telluride, zinc sulfide, zinc selenide, zinc telluride, or mixtures of any of the above mentioned substances as well as of cadmium sulfide and cadmium selenide in any desired proportions. However, for practical purposes, the present invention is primarily concerned with layers formed of cadmium sulfide and/or cadmium selenide.

As activating agents for cadmium sulfide and cadmium selenide, copper and silver salts have given good results, particularly copper chloride, copper nitrate and silver nitrate. The concentration of such activating agents relative to the photoconductive material such as cadmium sulfide or cadmium selenide preferably will be between 10^{-3} and 10^{-6} , most preferably about 10^{-4} atomic parts, in other words 1 atom of silver or copper should be present for between 10^3 and 10^6 , or preferably 10^4 molecules of cadmium sulfide or cadmium selenide.

The use of copper salts such as copper chloride or copper nitrate rather than silver salts such as silver nitrate is preferred.

The pulverulent particles of the cadmium sulfide and/or cadmium selenide of which the pulverulent layer on the support is to be formed should be of a particle size of less than 0.5 micron. The activating agent is preferably admixed in aqueous solution.

The temperature at which the sintering of cadmium sulfide and/or cadmium selenide is carried out according to the present invention preferably will be between about 550 and 700° C., and most preferably about 600° C.

The length of time for which the cadmium sulfide or selenide is to be subjected to the sintering temperature will vary between about 5 minutes and 60 minutes depending on whether the temperature is closer to about 550° C. or closer to about 700° C. At the preferred temperature of about 600° C., sintering preferably will be carried out for about 15 minutes when either cadmium sulfide or cadmium selenide or a mixture thereof is to be sintered. To a certain degree, optimum temperature and optimum length of sintering will also depend on the other variables of the process such as the type and dimensions of the reaction vessel, the type, concentration or amount of the crystallization and sintering promoting gas, the particle size and thickness of the layer, etc. It is possible without difficulty to determine within the above range the optimum time and temperature for any given process condition.

It is noted that the melting point of cadmium sulfide and cadmium selenide actually is higher than 1000° C., nevertheless by proceeding according to the present invention, the particles or small crystals will grow into larger units and will grow together so as to form a coherent solid body. Surprisingly, this sintering of the mass can be carried out according to the present invention at the relatively very low temperature of about 600° C. Without venturing to give a theoretical explanation of the influence of the hydrogen halide such as hydrogen chloride, there is not doubt that surprisingly according to the present invention, namely in the presence of such promoting gas, the sintering can be carried out successfully at such relatively very low temperatures. The activating gas is homogeneously dispersed during the sintering by diffusion in solid condition so as to be evenly distributed throughout the entire photoconductive mass.

The carrier on which the layer of cadmium sulfide or the like is formed, preferably will consist of a material having thermal insulating properties, which will not be affected by the sintering temperature, and will be chemically inert with respect to the layer to be sintered and the sintering promoting gas. Such materials include quartz, mica, glass and ceramic materials, the latter being preferred. The ceramic materials should be densely burnt and non-porous. Commercially available ceramic plates and the like which primarily contain either steatite or alumina are suitable for this purpose.

The following examples are given as illustrative only

of the present invention, without, however, limiting the invention to the specific details of the examples.

Example I

A photoconductive layer according to the present invention may be prepared as follows:

A suspension of a cadmium sulfide powder in water containing about 1 part by weight of cadmium sulfide powder and 4 parts by weight of water is formed and to the thus formed suspension a copper chloride solution is added of such concentration and in such amount that one copper atom will be present for about 10^4 cadmium atoms. The cadmium sulfide which is thus suspended is a finely pulverulent cadmium sulfide which may be either produced from a cadmium salt solution by precipitation with hydrogen sulfide, or by grinding cadmium sulfide in a ball mill, either until all particles have a size of less than 0.5 micron, or by sifting out such particles which are of larger size. In any event, the suspension is to be formed of a cadmium sulfide powder the particles of which have a size not exceeding 0.5 micron.

The suspension of cadmium sulfide in an aqueous solution containing the activating agent is then sprayed, brushed or in any other suitable manner applied to a ceramic support so that on such support an initially moist layer of finely subdivided pulverulent cadmium sulfide and including the activating agent is obtained.

According to the present example, the suspension is sprayed onto a plate of densely burnt heat-resistant ceramic material and thereafter dried thereon so that on the support a pulverulent layer is formed, weighing about 5 mg. per cm^2 . Thereafter, the carrier with the pulverulent material thereon is placed into a flat, covered porcelain dish and burnt for about 15 minutes at about 600°C .

In order to provide the crystallization and sintering promoting atmosphere in the porcelain dish, a small amount of hydrochloric acid is introduced into the same prior to the heating. The hydrochloric acid is vaporized during heating and will be prevented by the cover of the porcelain dish from quickly escaping therefrom. The amount of hydrochloric acid depends primarily on the interior dimensions of the porcelain dish. For instance, if the inner volume of the porcelain dish equals $7 \times 7 \times 1.5$ cm., then an amount of 0.05 ml. of 25% aqueous hydrochloric acid will be suitable and give good results. However, it is not of decisive importance how much hydrochloric acid is added, the amount of hydrochloric acid, i.e. of hydrogen chloride gas may vary within rather wide limits, provided that it does not fall below a minimum.

As discussed further above, the condition that is to be met according to the present invention is that during the heat treatment of the pulverulent layer i.e. during the sintering of the same a gaseous crystallization and sintering promoting material, preferably hydrogen chloride, hydrogen bromide or hydrogen iodide will be present. The hydrogen chloride or the like may be introduced prior to heating in the form of an aqueous solution, or it may also be introduced during the heating in gaseous form as by being blown into the dish or reaction chamber in gaseous form, preferably mixed with a carrier gas. It is also possible to produce the hydrogen chloride or the like by decomposition of a chemical compound such as hydrazindihydrochloride which at the prevailing sintering temperatures will split off hydrogen chloride.

Assuming that the sintering is carried out in a covered flat dish having a square area of about 50 cm^2 and a height of about 1.5 cm., i.e. an available volume of about 75 cm^3 , assuming that the weight of the cadmium sulfide layer which is to be sintered will be between 20 and 100 mg., preferably about 50 mg. and further assuming that hydrogen chloride is used as a crystallization and sintering promoting gas, then the following quantitative relationships are preferred:

Between 0.05 and 0.3 mg. HCl should be introduced per cm^3 of reaction space, and preferably 0.16 mg./ cm^3 .

This would correspond to a total amount of preferably 12 mg. HCl. This amount, namely 12 mg. HCl would be present in about 0.05 ml. aqueous 25% hydrogen chloride solution. When it is desired to use instead of hydrogen chloride a compound such as hydrazindihydrochloride, which during sintering will split off HCl by thermal decomposition, then an equivalent amount of such substance is to be used. For instance, 18 milligram hydrazindihydrochloride will split off about 12 mg. of hydrogen chloride.

If hydrogen bromide or hydrogen iodide is to be used in place of hydrogen chloride, then equivalent concentrations should be used. For instance, instead of 12 mg. HCl, 27 mg. hydrogen bromide may be used. However, it is preferred to use hydrogen chloride as the crystallization and sintering promoting gas.

By way of example only, there are listed several other substances which under the sintering conditions of the present invention will split off hydrogen chloride and which may be used to provide the crystallization and sintering promoting gas:

Ammonium chloride (NH_4Cl)
Methylammoniumchloride ($\text{CH}_3\text{NH}_2\text{Cl}$)
Hydrazindihydrochloride ($\text{H}_2\text{N.NH}_2.2\text{HCl}$)
Anilinehydrochloride ($\text{C}_6\text{H}_5.\text{NH}_2\text{HCl}$)
Hydroxylaminohydrochloride ($\text{NH}_2\text{OH.HCl}$)

The corresponding bromides and iodides, if HBR or HI are to be formed.

During the sintering as described in Example I the following takes place:

The starting material, i.e. cadmium sulfide produced by precipitation with hydrogen sulfide from a cadmium salt solution, will consist of very small particles which should not exceed and preferably will be smaller than 0.5 micron. The layer formed of the suspension of such particles by spraying onto the support is not sensitive to light and non-conductive. The reason for this lack of photoconductive properties may be found in the very large contact resistance between individual particles, as well as in the insensitivity of the individual particles. In order to endow the precipitated cadmium sulfide or the like with photosensitivity, it is necessary not only to add the proper proportion of activating agents, but also to subject the material to a crystallization process during which due to crystal growth relatively large crystals will be formed. In order to obtain not only a powder of enlarged crystals but a compact body or a firmly coherent layer, it is furthermore necessary to cause sintering of the growing crystals.

According to the present invention, a sintered, photoconductive, firmly adhering layer is obtained by heating the above described pulverulent layer in the presence of hydrogen chloride at a temperature of about 600°C . If the process is repeated under equal conditions, however, omitting the hydrogen chloride, it will be found that the initial pulverulent layer does change its character only slightly, remains pulverulent and does not become photo-sensitive or photoconductive. In the presence of hydrogen chloride gas, however, quick crystal growth can be observed. Individual crystals or particles grow at the expense of adjacent material and eventually a reduced number of somewhat round crystalline bodies is formed. During continuing heating at about 600°C ., the starting material of smallest particle size will be completely used up, i.e. incorporated in the larger crystal and the remaining crystals will grow together forming a dense structure. The size of the individual crystalline bodies in the finished sintered layer may be, for instance, between 4 and 10 microns.

During the burning, in addition to crystal growth and growing together of the crystals, there will also be achieved incorporation of the activating agents into the crystal lattice. As stated above, silver and preferably copper may be used as activating agents. The activating agent should be present in such quantity that one

atom of silver or copper will be available for between 10³ and 10⁶, preferably about 10⁴ atoms of cadmium. The most convenient way of producing the activating agent is in the form of a water soluble salt, for instance, copper chloride.

Photoconductive layers of cadmium sulfoselenide can be easily produced by mixing pulverulent cadmium sulfide and cadmium selenide in the desired proportion, and to treat this mixture as described above with respect to pulverulent cadmium sulfide alone. During this sintering, due to diffusion, homogeneous mixed crystals will be formed so that the finished layer will not represent a mere mixture of cadmium sulfide and cadmium selenide crystals but will consist of cadmium sulfoselenide crystals. Photoconductive layers of cadmium sulfoselenide are of particular importance when it is desired to obtain a maximum of spectral sensitivity at a certain point somewhere between the point of maximum spectral sensitivity of pure cadmium sulfide and pure cadmium selenide.

While the present invention has been described in connection with the forming of a photoconductive layer of cadmium sulfide and/or cadmium selenide, it is also possible to work up in a substantially similar manner other potentially photoconductive materials or mixtures of the same.

Example II

100 grams cadmium sulfide having a particle size of less than 0.5 micron are mixed for several minutes under stirring with 6.9 cm.³ of 0.01 molar copper chloride solution and 400 cm.³ distilled water. A yellow suspension is formed. The suspension is then sprayed onto circular carrier plates of ceramic material having a diameter of 12 mm. and dried thereon. A pulverulent layer weighing about 5 mg. per cm.² is thus formed on the carrier plates.

Eight of the carrier plates with the pulverulent layers thereon are then placed into a flat porcelain dish having an inner volume of about 75 cm.³, a bottom surface of 50 cm.² and a height of about 1.5 cm.

In order to provide the crystallization and sintering promoting atmosphere in accordance with the present invention, 0.05 cm.³ of 25% aqueous hydrochloric acid are introduced into the dish, the same is then closed with a cover and heated at 600° C. for 15 minutes. The cover prevents quick escape of the hydrogen chloride vapors formed during the heating. As stated further above, the amount of hydrochloric acid may vary within wide ranges.

Upon completion of the heating and cooling, it will be found that the initially pulverulent layer has completely changed its character and has become a firm, coherent crystalline layer which is resistant against mechanical stress and adheres firmly to its support. The photo-sensitivity of the layer is very high.

Example III

100 grams cadmium selenide having a particle size of less than 0.5 micron, 5.2 cm.³ of a 0.01 molar aqueous copper nitrate solution and 400 cm.³ distilled water are mixed under mechanical stirring until a black suspension is formed. The suspension is brushed with a fine paint brush onto circular plates of ceramic material having a diameter of 12 mm., and dried thereon. The thus formed dried pulverulent layer will weigh about 5 mg./cm.². Eight ceramic plates with the respective layers thereon are placed into the porcelain dish described in Example II. 18 mg. of hydrazindihydrochloride are also introduced into the dish and the same is then covered. The covered dish is then heated to 600° C. for 15 mm. in a protective nitrogen gas atmosphere.

Example IV

The procedure described in Example II, is followed, however, a mixture of 75 grams cadmium sulfide, 33.1 grams cadmium selenide, 6.9 cm.³ of 0.01 molar copper chloride solution and 400 cm.³ distilled water is formed. Upon completion of the process, a burnt layer has been formed which has a reddish appearance. During the burning or sintering, due to diffusion, homogeneous cadmium sulfoselenide crystals are formed so that the layer does not consist of a mere mixture of cadmium sulfide and cadmium selenide but of homogeneous mixed crystals.

The sintered photoconductive layers which are produced according to the above examples are then incorporated in a photosensitive cell, for instance, by applying to the layer two thin metallic electrodes. The electrodes are so shaped that a straight aperture of even width remains therebetween, exposing the photoconductive layer. Other types of electrodes may also be used such as electrodes in the shape of interlocking fingers, so that a long meandering aperture of even width is formed exposing the photoconductive layer. The preferred electrode metals are gold and indium. The electrode pattern is preferably applied by vapor deposition in a high vacuum and with a mask covering the portions of the photoconductive layer which are to remain exposed. The photoconductive layer with the electrodes thereon is then introduced into a glass flask provided with terminals which are connected to the electrodes, and the flask is then filled with an inert protective gas such as argon or nitrogen, and sealed by melting the opening of the flask. Or, the plate with the photoconductive layer thereon is provided with terminals and then covered with a protective transparent lacquer of a type which will not attack the light sensitive layer.

A potential of for instance 3 volts is then applied to the thus produced photoelectric cell. The current flowing through the cell will vary depending on the degree of illumination to which the free portion of the photoconductive layer is exposed.

The following table describes the current passing through cells which were produced in accordance with Example II-IV. The width of the exposed portion of the photoconductive layer was 0.04 cm. and the length of the exposed portion 1.0 cm. A potential of 3 volts was applied. The Table also describes the location of the maximum of spectral sensitivity which with photoconductive layers of pure cadmium sulfide will be found in the green part of the spectrum and with layers of pure cadmium selenide in the red part. The cadmium sulfoselenide layers, however, show maximum sensitivity in a portion of the spectrum inbetween the green and red portions thereof, whereby the exact location of maximum sensitivity depends on the proportion of cadmium selenide and cadmium sulfide in the cadmium sulfoselenide crystals. By suitable adjustment of this proportion, it is possible to obtain maximum spectral sensitivity at any intermediate point of the spectrum between the points of maximum sensitivity of cadmium sulfide on the one hand and cadmium selenide on the other hand.

Table

Composition	Copper Atoms per Cadmium Atoms	Current in ma. at 0.0 ft. candles	Current in ma. at 5.0 ft. candles	Maximum spectral Sensitivity at Angstrom
CdS.....	10 ⁻⁴	1.0	0.5	5,200
CdSe.....	10 ⁻⁴	0.7	1.7	7,500
CdS 0.75.....	10 ⁻⁴	0.8	0.6	5,900
CdSe 0.25.....				

Without further analysis, the foregoing will so fully reveal the gist of the present invention that others can by applying current knowledge readily adapt it for various applications without omitting features that, from the

standpoint of prior art, fairly constitute essential characteristics of the generic or specific aspects of this invention and, therefore, such adaptations should and are intended to be comprehended within the meaning and range of equivalence of the following claims.

What is claimed as new and desired to be secured by Letters Patent is:

1. A method of producing on a support a photoconductive layer, comprising the steps of forming on a support a pulverulent layer consisting essentially of at least one substance selected from the group consisting of cadmium sulfide and cadmium selenide, and an activating agent therefor, said activating agent including a salt of a member of the group consisting of copper and silver; and heating said layer in the presence of a gas adapted to improve crystallization and sintering of the same and selected from the group consisting of hydrogen chloride, hydrogen bromide and hydrogen iodide to a temperature of between 550° C. and 1000° C. so as to cause crystal growth and sintering of said layer to form a coherent solid body of improved photoconductivity.

2. A method of producing on a support a photoconductive layer, comprising the steps of introducing into a reaction chamber a support carrying a layer consisting essentially of at least one substance selected from the group consisting of cadmium sulfide and cadmium selenide, and an activating agent therefor; also introducing into said reaction chamber a material adapted to form at the sintering temperature of said substance a gas selected from the group consisting of hydrogen chloride, hydrogen bromide and hydrogen iodide; and heating said layer in said reaction chamber to a temperature of between 550° C. and 1000° C., said temperature being sufficiently high to form said gas and to sinter said substance in the presence of said gas, the latter improving crystallization and sintering of said substance so as to form a sintered layer of improved photoconductive sensitivity.

3. A method of producing on a support a photoconductive layer, comprising the steps of introducing into a reaction chamber a support carrying a layer consisting essentially of at least one substance selected from the group consisting of cadmium sulfide and cadmium selenide, and an activating agent therefor; also introducing into said reaction chamber an aqueous solution of a hydrogen halide selected from the group consisting of hydrogen chloride, hydrogen bromide and hydrogen iodide; and heating said layer in said reaction chamber to a temperature between 550° C. and 700° C., said temperature being sufficiently high to free said hydrogen halide in gaseous state and to cause crystal growth and sintering of said substance in the presence of said gaseous hydrogen halide, so as to form a sintered layer of improved photoconductive sensitivity.

4. A method of producing on a support a photoconductive layer, comprising the steps of introducing into a reaction chamber a support carrying a layer consisting essentially of at least one substance selected from the group consisting of cadmium sulfide and cadmium selenide, and an activating agent therefor; heating said layer in said reaction chamber for a period of between about 5 minutes and 60 minutes to a temperature of between 550° C. and 700° C. and in the presence of a gas including a hydrogen halide selected from the group consisting of hydrogen chloride, hydrogen bromide and hydrogen iodide, the latter improving crystallization and sintering of said substance so as to form a sintered layer of improved photoconductive sensitivity.

5. A method of producing on a support a photoconductive layer, comprising the steps of introducing into a reaction chamber a support carrying a layer consisting essentially of at least one substance selected from the group consisting of cadmium sulfide and cadmium selenide, and an activating agent therefor; also introducing into said reaction chamber hydrazindihydrochloride as a material adapted to form gaseous hydrogen chloride at the sintering

temperature of said substance; and heating said layer in said reaction chamber for a period of between about 5 minutes and 60 minutes to a temperature of between 550° C. and 700° C. so as to form gaseous hydrogen chloride and to sinter said substance, said gaseous hydrogen chloride improving crystallization and sintering of said substance so as to form a sintered layer of improved photoconductive sensitivity.

6. A method of producing on a support a photoconductive layer, comprising the steps of forming on a support a pulverulent layer consisting essentially of at least one substance selected from the group consisting of cadmium sulfide and cadmium selenide, and an activating agent therefor, said activating agent including a salt of a member of the group consisting of copper and silver; and sintering said layer at a temperature of about 600° C. and for a period of about 15 minutes in the presence of a gas adapted to improve crystallization and sintering of the same and selected from the group consisting of hydrogen chloride, hydrogen bromide and hydrogen iodide.

7. A method of producing on a support a photoconductive layer, comprising the steps of forming on a support a pulverulent layer consisting essentially of precipitated finely subdivided particles of at least one substance selected from the group consisting of cadmium sulfide and cadmium selenide, and an activating agent therefor, said activating agent including a salt of a member of the group consisting of copper and silver; and sintering said layer at a temperature of about 600° C. and for a period of about 15 minutes in the presence of a gas adapted to improve crystallization and sintering of the same and selected from the group consisting of hydrogen chloride, hydrogen bromide and hydrogen iodide.

8. A method of producing on a support a photoconductive layer, comprising the steps of forming on a support a pulverulent layer consisting essentially of cadmium sulfide and an activating agent therefor, said activating agent including a salt of a member of the group consisting of copper and silver; and sintering said layer at a temperature of about 600° C. and for a period of about 15 minutes in the presence of a gas adapted to improve crystallization and sintering of the same and selected from the group consisting of hydrogen chloride, hydrogen bromide and hydrogen iodide.

9. A method of producing on a support a photoconductive layer, comprising the steps of forming on a support a pulverulent layer consisting essentially of cadmium selenide and an activating agent therefor, said activating agent including a salt of a member of the group consisting of copper and silver; and sintering said layer at a temperature of about 600° C. and for a period of about 15 minutes in the presence of a gas adapted to improve crystallization and sintering of the same and selected from the group consisting of hydrogen chloride, hydrogen bromide and hydrogen iodide.

10. A method of producing on a support a photoconductive layer, comprising the steps of forming on a support a pulverulent layer consisting essentially of cadmium sulfoselenide and an activating agent therefor, said activating agent including a salt of a member of the group consisting of copper and silver; and sintering said layer at a temperature of about 600° C. and for a period of about 15 minutes in the presence of a gas adapted to improve crystallization and sintering of the same and selected from the group consisting of hydrogen chloride, hydrogen bromide and hydrogen iodide.

11. A method of producing on a support a photoconductive layer, comprising the steps of introducing into a reaction chamber a support carrying a layer consisting essentially of at least one substance selected from the group consisting of cadmium sulfide and cadmium selenide, and an activating agent therefor; also introducing into said reaction chamber a material adapted to form at a temperature of about 600° C. a gas selected from the group consisting of hydrogen chloride, hydrogen bromide

11

and hydrogen iodide, said material being selected from the group consisting of ammonium chloride, methyl-ammonium chloride, hydrazindihydrochloride, aniline-hydrochloride, hydroxylaminohydrochloride and the corresponding bromides and iodides; and heating said layer in said reaction chamber for about 15 minutes at a temperature of about 600° C. so as to form said gas and sinter said layer, said gas improving crystallization and sintering of said substance, so as to form a sintered layer of improved photoconductive sensitivity.

12. A method of producing on a support a photoconductive layer, comprising the steps of forming on a support a pulverulent layer consisting essentially of precipitated finely subdivided particles of at least one substance selected from the group consisting of cadmium sulfide and cadmium selenide, and an activating agent therefore, said activating agent including a salt of a member of the group consisting of copper and silver; and sintering said layer at a temperature of about 600° C. and for a period of about 15 minutes in the presence of a gas adapted to improve crystallization and sintering of the same and selected from

12

the group consisting of hydrogen chloride, hydrogen bromide and hydrogen iodide.

13. A support and a photoconductive layer thereon produced in accordance with the method of claim 1.

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JOSEPH B. SPENCER, *Primary Examiner*.

RICHARD D. NEVIUS, *Examiner*.