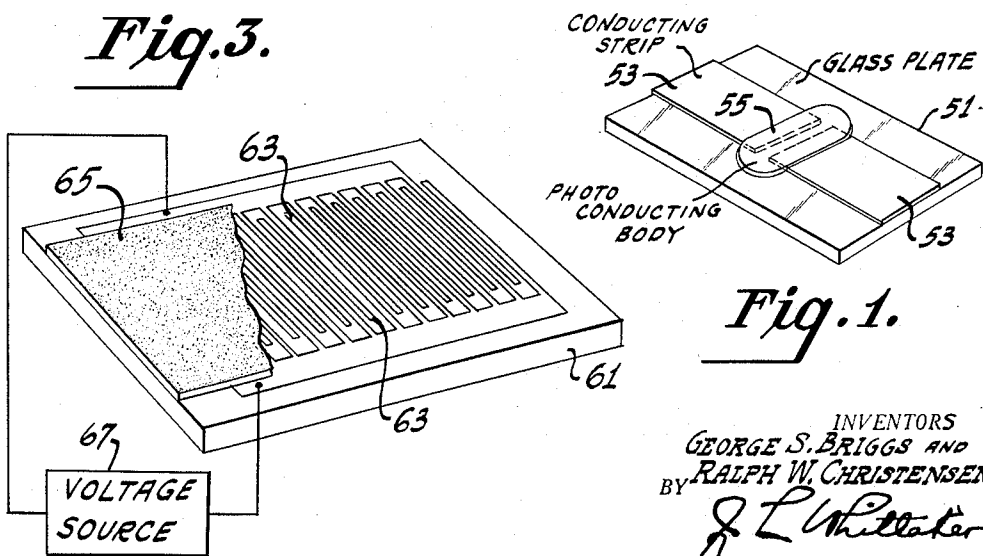
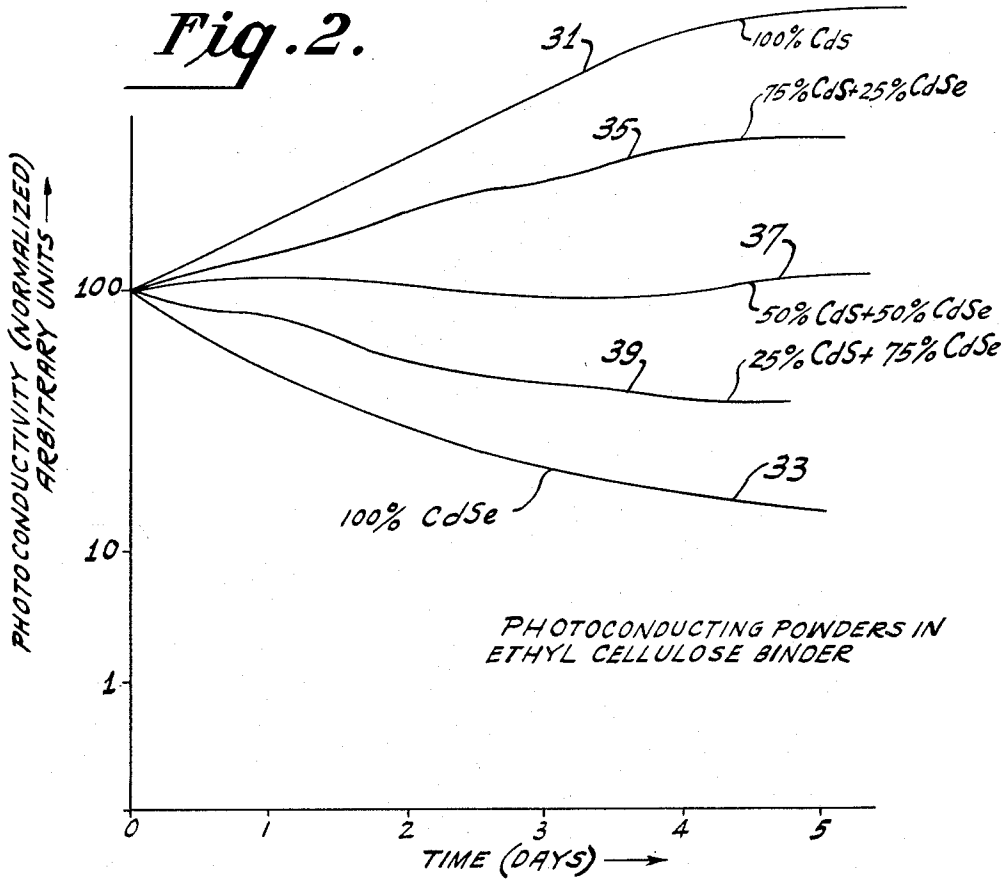


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G. S. BRIGGS ET AL  
PHOTOCONDUCTING DEVICES

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2,866,878

## PHOTOCONDUCTING DEVICES

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6 Claims. (Cl. 201—63)

This invention relates to improved photoconducting compositions which are particularly useful in gap type and area type photocells and in other devices utilizing photoconductive bodies. The invention includes improved methods for preparing the improved photoconducting compositions and improved devices utilizing the improved photoconducting compositions of the invention.

A photoconductive device is one which displays a reduced resistance to electric current flow when irradiated, for example, with light. In its simplest form, a photoconductive device comprises a photoconductive body and a pair of electrodes attached thereto. With a voltage applied to the electrodes, the device passes an increased amount of electric current when there is an increase in the intensity of light irradiating the device.

Ideally, a photoconductive device is a perfect insulator when light to which it is sensitive is absent, and is a perfect conductor when a maximum intensity of light to which it is sensitive is present. Actually, a photoconductive device behaves as a higher resistance conductor when light to which it is sensitive is absent, and behaves as a lower resistance conductor when light to which it is sensitive is incident upon the photoconductive body.

The change in conduction produced by a unit variation of light intensity is referred to as the photosensitivity of the device. The measure of photosensitivity is in terms of photocurrent under standard conditions. The current passed by the device in darkness is referred to as the dark current; the current passed when the device is irradiated is referred to as the light current; and the difference between the light current and the dark current is referred to as the photocurrent.

One type of photoconductive device comprises a single crystal of a photoconductive material and electrodes attached to the crystal. Such single crystal photocells exhibit large photocurrents and high ratios of light current to dark current. However, the crystals are small in size and consequently the total current passed by a single crystal is small. When greater currents are passed through the crystal, the crystal heats up and the photosensitivity of the crystal is reduced, either temporarily or permanently. Furthermore, single photoconductive crystals are difficult to grow and are fragile. Thus, the expense of manufacture and maintenance often prohibits the use of such single crystal photocells.

Another type of photoconductive device comprises a body including finely-divided photoconducting powder particles of a single composition and electrodes attached to said body. The body may include, for example, an unbonded powder or a powder mixed with a binder such as a synthetic resin. Such powder-type photocells may be made in any desired size, shape or current carrying capacity. Although such powder-type photocells often respond to a broader band of frequencies than crystal photocells, it is frequently desirable to provide photocells of this type that respond to still broader bands of frequencies.

It has been observed that previous powder-type photo-

cells of a single composition exhibit a change in photoconductivity over periods of time. In some cases the photoconductivity increases, while in other cases the photoconductivity decreases. It is desirable that such photocells maintain substantially constant photoconductivity so that they may be incorporated into apparatus without compensating networks and devices.

An object of the invention is to provide improved photoconducting compositions, improved bodies of said photoconducting compositions and improved photoconducting devices.

Another object is to provide improved photoconducting compositions, bodies and devices that are responsive to a broad band of frequencies in the electromagnetic spectrum.

Another object is to provide improved photoconducting compositions, bodies and devices that maintain substantially constant photoconducting properties with respect to time.

A further object is to provide improved methods for preparing the improved photoconducting compositions of the invention.

Photoconducting compositions according to the invention comprise an intimate physical mixture of finely-divided crystal particles of at least two different photoconducting materials, preferably dispersed in an electrically-insulating, film-forming vehicle. An intimate physical mixture of at least two photoconducting materials has been found to provide a broader spectral response and better electrical properties than finely-divided crystal particles of a single photoconducting material. Photoconducting devices comprising bodies of the improved compositions of the invention, are effectively more photosensitive due to the broader spectral response and are more stable with respect to time.

A method of the invention includes intimately mixing finely-divided crystal of at least two different photoconducting materials preferably by dispersing in an electrically-insulating, film-forming vehicle.

The devices of the invention include a body having a composition according to the invention and at least one electrode attached to said body.

The invention will be more fully described in the following detailed description when read in conjunction with the drawings herein:

Figure 1 is a perspective view of a first photocell according to the invention,

Figure 2 is a family of curves illustrating the change in photosensitivity with respect to time of compositions according to the invention and of the component photoconductors of said photoconducting composition, and

Figure 3 is a perspective view of a second photocell according to the invention.

Similar reference characters are used for similar elements throughout the drawings.

A preferred method for preparing a photoconducting composition according to the invention follows.

Fifty parts by weight of photoconducting cadmium sulphide and fifty parts by weight of photoconducting cadmium selenide are dispersed in fifty parts by weight of a 1% solution of ethyl cellulose in amyl alcohol. The mixture is then coated on a substrate and the amyl alcohol removed by evaporation. The composition of the resulting body calculated from the initial mixture is 50 parts photoconducting cadmium sulphide, 50 parts photoconducting cadmium selenide and 0.5 parts ethyl cellulose (all parts by weight).

*Cadmium sulphide photoconducting powder.*—A preferred photoconducting cadmium sulphide powder is prepared as follows: An intimate mixture of 100 grams of precipitated cadmium sulphide, 10 grams of cadmium chloride, 1 gram of ammonium chloride, 1.7 milliliters

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of 0.1 M cupric chloride, and 250 milliliters of water is prepared. This mixture may be prepared in a blender such as is used for mixing powders with water. The yellow, viscous slurry is dried at about 150° C. for about 15 hours.

The dried cake is then broken up into pea-size lumps and packed into a 12 inch test tube to a depth of about seven inches. The tube is provided with a stopper having an inlet tube therethrough for the purpose of maintaining a substantially stagnant atmosphere in the test tube while maintaining atmospheric pressure through the subsequent firing steps. The test tube filled with the dried mixture is fired at about 600° C. for about 20 minutes. The fired product is then removed from the test tube and allowed to soak in water until it disintegrates. This ordinarily takes about 20 minutes. The product is washed on a fine, sintered, glass filter, dispersing the cake once or twice in water until the washings contain less than 0.01 M cadmium chloride.

The product of the first firing is brown in color and of a relatively fine particle size. During the first firing, there is present in the charge about 10% cadmium chloride which is a solvent flux for cadmium sulphide. The small particles of cadmium sulphide partially or completely dissolved in the cadmium chloride and are recrystallized into small crystals which are of the order of 0.3 mil in size and have copper and halide incorporated therein. At this stage, the product is photoconducting.

The washed product of the first firing is moistened with a solution containing equal parts of 0.1 M aqueous cadmium chloride and 1.0 M ammonium chloride. The excess solution is removed by suction. After drying, the powder is passed through a 325 mesh sieve and the tailings discarded.

The dry sieved powder is placed in a test tube to a depth not greater than 4.5 inches and fired for about 20 minutes at 600° C. in a stagnant atmosphere. The fired mass is removed from the furnace and permitted to cool. During this second firing, the powder sinters to a stick, which is then grated through a 50 mesh sieve. During the second firing there is present only a controlled trace of superficial chloride. The slightly sintered stick is easily broken up into a powder which exhibits a low dark resistivity and high dark current.

About 0.2 gram of sulphur is placed in the bottom of a test tube and the sieved brown powder from the second firing is placed on top of the sulphur to a depth of about 4.5 inches. The powder in the test tube is fired at about 500° C. for about 10 minutes in a stagnant atmosphere and then while still in the third firing, a vacuum is applied to the powder by means of an inlet tube and the firing continued for about 10 minutes with the vacuum applied. The test tube is removed from the furnace, cooled and the product passed through a 325 mesh screen.

During the third firing, the sulphur vaporizes and passes through the mass of brown powder. The product of the third firing exhibits a high dark resistivity, a low dark current and a high photosensitivity. Typical measurements indicate the ratio of light current to dark current of about 10<sup>8</sup> and a high speed of response.

The cadmium sulphide photoconducting powder which is the product of the third firing is tan to dark brown in color, the color darkening with increases in either the proportions of copper or increases of the first firing temperature. The average particle size varies according to the first firing temperature, being of the order of 0.3 mil for 600° C. and of the order of 0.7 mil for 650° C. The powders exhibit a panchromatic absorption, although the spectral response is peaked in red and is practically nil in the blue region of the spectrum. The powder is non-luminescent, has substantially uniform particle size and is free-flowing.

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Since cadmium sulphide is partially soluble in molten cadmium chloride, it is believed that the presence of about 10% cadmium chloride in the mix during the first firing permits the growth of discrete uniformly sized crystals bonded by the water soluble cadmium chloride. The fired lump disintegrates readily in water. Thus, the content of cadmium chloride is not critical, its purpose being principally to provide a crystallizing medium for the cadmium sulphide host crystal. Although cadmium chloride is preferred, any crystallizing medium for the host crystal which does not otherwise adversely effect the product, may be used in place of cadmium chloride. Similar crystallizing media are used for other host crystals.

Ammonium chloride is introduced into the mix to (1) convert to cadmium chloride any cadmium oxide which may be present in the mix, and (2) to provide a firing atmosphere that prevents oxidation. An activator proportion of chloride is incorporated into the host crystal during the first firing. This amount is extremely small and may come from either the cadmium chloride or the ammonium chloride.

Copper is introduced into the mix in a proportion equivalent to 100 parts per million of copper with respect to cadmium sulphide. The amount of copper is not critical; however, it is preferred to use between 50 and 300 parts per million of copper. In place of copper, other monovalent cations may be incorporated into the cadmium sulphide host crystal. For example, 200 parts per million of silver in place of copper produces an orange-colored powder having an intermediate photosensitivity and a low rate of decay.

The firing temperature during the first firing is somewhat critical. The firing temperature should be above the melting point of cadmium chloride which is about 580° C. Below this temperature practically no crystal growth occurs and the copper does not diffuse into the host crystal. Higher temperatures during the first firing produces a powder which has a darker color, larger particle size, lower dark resistivity and higher dark current. The preferred temperature is the lowest temperature that insures prompt melting of the solvent material, produces a small particle size and a high dark resistivity in the final product. A temperature of about 600° C. is preferred.

The second firing sinters the powder into a stick and increases the conductivity and photosensitivity of the material. Small particles are probably sintered onto the surface of the larger ones, thus, reducing the number of particle-to-particle contacts. Again, a firing temperature of the order of 600° C. is preferred as the lowest temperature which insures the prompt melting of cadmium chloride.

During the third firing, the sulphur vapor which passes through the mass of photoconducting powder reduces the dark current of the powder, presumably by diminishing the chloride in the powder to a value substantially equivalent to the amount of copper present in the product. At 500° C., the powder does not sinter and the photosensitivity of the powder is only slightly affected. At higher temperatures, the loss in photosensitivity is greater.

In each of the firing steps enough time should be allowed to bring the entire charge to the furnace temperature. For tubes about one inch in diameter, about 20 minutes is required. Longer firings up to one hour make no noticeable difference in the powder. Similarly, the speed with which the product is cooled makes little or no difference in the final product.

Grinding the finished powder progressively reduces its photosensitivity, similar to the observations on single crystals. Grinding of an intermediate product is undesirable because it produces all particle sizes and shapes, and because grinding is inherently uncontrollable. It is best, therefore, to avoid grinding at any stage. The

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powder from the first firing is put through a 325 mesh sieve to eliminate the few lumps which may have formed in earlier steps in the process and also to establish an upper limit (such as 1.7 mils) to the particle size. After the second firing, the 50 mesh sieve is used to achieve a more uniform disintegration of the sintered stick and to avoid crushing. After the third firing the final product is passed through a 325 mesh sieve to eliminate any aggregates over 1.7 mils. Less than 5% is lost at this stage. In passing material through a sieve no hard rubbing is used.

The electrical properties of the final product are influenced by the amount of chloride present during the second firing. With too much chloride, the final product has a high dark current; with too little chloride, the final product has a low sensitivity.

*Cadmium selenide photoconducting powder.*—A preferred photoconducting cadmium selenide is prepared by the general method described for the cadmium sulphide photoconducting powder except that cadmium selenide is substituted for cadmium sulphide in the starting mixture. Thus, the starting mixture comprises 100 grams of cadmium selenide, 10 grams of cadmium chloride, 1 gram of ammonium chloride, 1.7 milliliters of 0.1 M copper chloride and 250 milliliters of water.

Referring to Figure 1, a photocell according to the invention comprises a pair of spaced electrodes 53 attached to a photoconducting body 55 of the invention. The device may be prepared according to the following procedure. A glass plate 51 is provided with a strip of conducting material 200 mils wide and having a 20 mil gap running across and at right angles to the strip forming two electrodes 53. Such a strip may be produced by masking the plate 51 and then spraying with a silver-resin composition. Other methods may be used, for example, painting or silk screening.

A mixture is prepared comprising about 100 parts by weight of photoconducting powder and 50 parts by weight of a solution containing one weight percent of ethyl cellulose resin dissolved in amyl alcohol. A drop 55 of this mixture is placed on the gap and allowed to dry. When the drop 55 is dry, the photocell is ready for use. The photoconducting body 55 comprises 100 weight parts of photoconductor and 0.5 weight parts of ethyl cellulose.

While the photocell of Figure 1 utilizes a photoconducting body 55 comprising a resin-bonded powder, an unbonded powder may also be used. A photoconducting body bonded with an electrically-insulating, film-forming vehicle is preferred. It is preferred to use 0 to 1 weight parts of a binder to 100 weight parts of the photoconducting powder. In the above described example, between zero and 100 parts of the 1% ethyl cellulose solution may be used with 100 parts of photoconducting powder. Increased amounts of ethyl cellulose increases the resistivity of the photocells although the above range of constituents is not critical. Other electrically-insulating, film-forming vehicles may be used as a binder, for example, a silicone resin, araldite resin or acryloid resin. In addition to photoconducting cadmium sulphide and photoconducting cadmium selenide, other photoconductors such as photoconducting cadmium sulfoselenide and cadmium telluride may be used. The photoconducting compositions of the invention comprise generally mixtures of finely-divided crystal particles of at least two different photoconductors which mixtures may be bonded or unbonded. The photoconducting cadmium sulphide and cadmium selenide may be mixed in any proportion, each mixture having its own distinctive electrical properties.

Referring to Figure 2, the photoconductivity of the photocells of Figure 1 comprising only the preferred photoconducting cadmium sulphide dispersed in ethyl cellulose increase with time as shown by the curve 31. The photoconductivity of the photocells of Figure 1

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comprising only the preferred cadmium selenide dispersed in ethyl cellulose decreases with time as shown by the curve 33. In either case, these photocells change with time, making it extremely difficult to design the photocells into circuits with other components. The stability of these photocells is improved by utilizing the compositions of the invention, preferably a mixture comprising 50% by weight of photoconducting cadmium sulphide and 50% by weight of photoconducting cadmium selenide bonded with ethyl cellulose. As shown by the curve 37, the photoconductivity of the mixture remains substantially constant with respect to time.

There is also shown characteristics of photocells comprising mixtures of 25% by weight photoconducting cadmium sulphide and 75% by weight photoconducting cadmium selenide bonded with ethyl cellulose by the curve 35, and 75% by weight of photoconducting cadmium sulphide and 25% by weight of photoconducting cadmium selenide bonded with ethyl cellulose by the curve 39. In each case there is shown an improvement in stability with respect to time over photocells made with only one constituent photoconducting powder.

Table I gives comparative data of the operation of typical photocells constructed according to Figure 1, when irradiated with 0.1 lumen (73 foot candles) of light from an incandescent source. The spectral response of photocells comprising only the preferred photoconducting cadmium sulphide powder bonded with ethyl cellulose is peaked at about 7500 Å. as shown in column 5. The spectral response of photocells comprising only the preferred photoconducting cadmium selenide powder bonded with ethyl cellulose is peaked at about 9250 Å. as shown in column 1. As shown in column 3, the spectral response of photocells comprising a mixture of equal parts of photoconducting cadmium sulphide and photoconducting cadmium selenide bonded with ethyl cellulose is peaked at about 7500 Å. and is more sensitive over a broader range of the spectrum than photocells comprising only one of the constituent photoconducting materials. Further, a photocell comprising one of the mixtures of the invention appears to have its own distinctive characteristics rather than having characteristics which is the mean of the characteristics of the constituents. As shown in columns 2 and 4 photocells comprising other mixtures of the component photoconducting powders bonded with ethyl cellulose exhibit an increased photoconductive response over a broader range of the spectrum than either component photoconductor, and, each mixture exhibits its own distinctive peak spectral response. A similar effect is obtained with photocells comprising mixtures of photoconducting powders without a binder.

Referring now to Figure 3, another type of photocell is the area type photocell which may comprise a substrate 61, such as porcelain, mica, Bakelite, but preferably glass, upon which has been formed a pair of interdigitated electrodes 63. A layer 65 comprising a photoconducting composition according to the invention is coated over the gap area of the electrodes. A typical device has a gap width of 20 mils and a gap length of 1000 mils. The electrodes 63 are then connected to a voltage source 67 external to the device.

The compositions of the invention may be utilized to prepare photoconductive devices and elements that are useful in meters, relays, picture converters, picture intensifiers, pickup devices, switches and so forth. The devices comprise a body of a photoconducting composition of the invention and an electrode attached to said body. The body may be any shape; however, it is preferred to prepare the body as a layer of material either upon the electrode structure or with the electrode structure deposited thereon.

There have been described improved photoconducting compositions having improved electrical characteristics.

There has also been described novel methods for preparing the improved photoconducting compositions of the invention, and photoconducting bodies and photoconducting devices comprising the improved photoconducting compositions of the invention. The improved photoconducting compositions of the invention provide a broader spectral response and better electrical properties than finely-divided crystal particles of a single photoconducting material.

TABLE I

Relative spectral response (normalized) of powder-type photocells in arbitrary units.

	Compositions.				
	1	2	3	4	5
CdSe, percent.....	100	75	50	25	0
CdS, percent.....	0	25	50	75	100
ethyl cellulose.....	0.5	0.5	0.5	0.5	0.5
$\lambda$ (A.)	Response.				
4,000.....	0	0	0	0	0
4,500.....	0	3	16	31	5
5,000.....	0	11	91	200	46
5,500.....	0	45	430	1,100	460
6,000.....	0	100	700	1,500	800
6,500.....	0	140	1,000	2,000	1,400
7,000.....	30	320	1,300	2,400	2,200
7,500.....	120	500	1,500	2,300	2,600
8,000.....	200	640	1,450	2,000	2,400
8,500.....	250	740	1,300	1,500	1,700
9,000.....	290	770	1,000	1,000	1,000
9,500.....	280	680	700	500	300
10,000.....	220	500	400	100	60

Irradiation=0.1 lumen from an incandescent source.  
 Gap=20 x 200 mils.  
 Applied voltage=90 volts D. C.

What is claimed:

1. A 25 to 75 weight percent photoconductive body consisting essentially of a physical mixture of finely-divided crystal particles of photoconducting cadmium sulphide and 25 to 75 weight percent photoconducting cadmium selenide dispersed in an electrically-insulating, film-forming vehicle.

2. A photoconductive body consisting essentially of a physical mixture of finely-divided crystal particles of photoconducting cadmium sulphide and photoconducting

cadmium selenide dispersed in a binder, said mixture comprising about 50 parts by weight of photoconducting cadmium sulphide, about 50 parts by weight of photoconducting cadmium selenide and about 0.5 part by weight of ethyl cellulose.

3. A photoconductive device comprising a body of a physical mixture of finely-divided crystal particles of photoconducting cadmium sulphide and photoconducting cadmium selenide dispersed in an electrically-insulating, film-forming vehicle, said mixture consisting essentially of 50 parts by weight of photoconducting cadmium sulphide, 50 parts by weight of photoconducting cadmium selenide and 0.5 part by weight of ethyl cellulose, and at least one electrode in contact with said body.

4. A photoconductive body consisting essentially of a physical mixture of finely-divided crystal particles of 25 to 75 weight percent photoconducting cadmium sulphide and 25 to 75 weight percent photoconducting cadmium selenide dispersed in up to one weight percent ethyl cellulose.

5. A photoconductive body consisting essentially of a physical mixture of finely-divided crystal particles of photoconducting cadmium sulphide and photoconducting cadmium selenide dispersed in a binder, said mixture comprising about 25 to 75 parts by weight photoconducting cadmium sulphide, about 25 to 75 parts by weight photoconducting cadmium selenide and about 0.5 part by weight of an electrically-insulating, film-forming vehicle; the total parts cadmium sulphide and cadmium selenide being 100.

6. A photoconductive device comprising a body consisting essentially of a physical mixture of finely-divided crystal particles of 25 to 75 weight percent photoconducting cadmium sulphide and 25 to 75 weight percent photoconducting cadmium selenide dispersed in an electrically-insulating, film-forming vehicle, and at least one electrode in contact with said body.

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 2,866,878

December 30, 1958

George S. Briggs et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 7, line 18, Table I, first column thereof, for "CdSE" read -- CdSe --; line 37, strike out "25 to 75 weight percent"; line 39, before "photoconducting" insert -- 25 to 75 weight percent --.

Signed and sealed this 21st day of July 1959.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON

Commissioner of Patents

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