

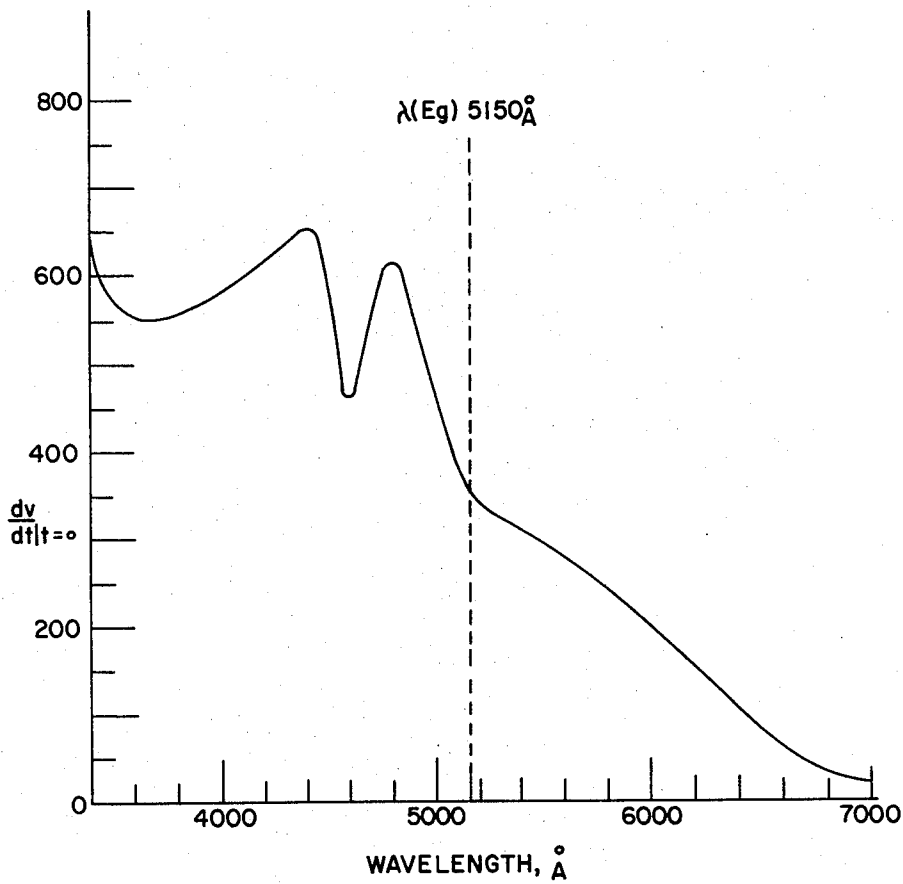
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METHOD FOR PHOTOCONDUCTIVE POWDER

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**METHOD FOR PHOTOCONDUCTIVE POWDER**

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5 Claims

**ABSTRACT OF THE DISCLOSURE**

Method of preparing copper-chlorine activated cadmium sulfide, cadmium selenide or cadmium sulfoselenide with a small percentage of cadmium chloride or zinc chloride to inhibit grain growth.

**BACKGROUND OF THE INVENTION**

This invention relates in general to a method of preparing photoconductive cadmium sulfide, cadmium selenide and cadmium sulfoselenide, particularly to such powders with improved properties.

The photosensitive properties of cadmium sulfide has been known for sometime and considerable effort has been expended to modify and improve its properties for use in specific devices.

For many applications, the ideal photoconductive device is one which is a perfect insulator when it is not subjected to activating radiation such as light and is a perfect conductor when it is subjected to a high intensity of activating radiation. The great majority of photoconductive devices, however, actually behave as fairly high resistance conductors in the absence of activating radiation and as lower resistance conductors in the presence of activating radiation. Depending upon the application, a photoconductive device may have a high or low resistivity. It is the signal to noise ratio which is significant. Relatively low dark resistivities on the order of  $10^{10}$  to  $10^{13}$  ohm-cm. may be tolerated as long as there is a sufficient signal to noise ratio coupled with adequate photoreponse for the specific image application using the photoreceptor. The minimum dark resistivity allowable, then would be indicative of this specific application. The signal to noise ratio requirements for most photoconductor applications are such that the material is generally made so to ensure quantum gain. That is to say, for each incident photon, the number of carriers which flow is unity. In this particular case of xerography, the maximum gain possible is unity. Carrier generation efficiency is thus the key feature of a photoconductor for xerographic application.

With binder layers, it is possible to use photoconductive pigments with relatively low resistivities when the matrix material intercedes between the pigment particles. The layer will not give effective cycling characteristics but can be used in the single mode q.v. phthalocyanine paper. With a single carrier type photoconductor, such as CdS, it is possible to work with relatively low resistivities. During charging the mobile carriers are swept out to form a depletion layer. As long as the charge density of the depletion layer is not too high, the xerographic performance can still be most effective.

The reason requiring a photoconductor having these characteristics becomes apparent after a short explanation of the most commonly used xerographic process. In the process as first described in U.S. Pat. 2,297,691 to C. F. Carlson, a photoconductor is first given a uniform electrostatic charge over its surface and is then exposed to an image of activating electromagnetic radiation. A latent electrostatic image then forms on the photoconductor because the illuminated areas of the photoconductor become relatively conductive allowing the charge in those

areas to be dissipated, while charge in the non-illuminated area is retained. This latent electrostatic image is then developed or made visible by the deposition of finely divided electroscopic marking material on the surface of the photoconductor which conforms to the pattern of the latent electrostatic image. The visible image may then be viewed or used in situ on the photoconductor or it may be transferred to a second surface, e.g. a copy paper. It thus becomes obvious that the photoconductive film must have a sufficiently high dark resistivity to hold its initial charge in areas which are not exposed for at least as long a time as is required to expose and develop the photoconductor. Depending upon the read-out method and machine application, it has been found that photoreceptors having minimum dark resistivities on the order of  $10^{13}$  ohm-cm. are required for this purpose.

Although vitreous selenium photoconductive insulators have been used with highly satisfactory results in the xerographic process, a constant search has gone on for improved materials which have the requisite dark resistivity along with increased sensitivity, wider spectral response and other desirable properties.

Cadmium sulfide, cadmium selenide and cadmium sulfoselenides are materials which have been investigated for use in photocells, e.g. meters, relays, etc. and also as practical alternatives for vitreous selenium. In a process described in U.S. Pat. 2,876,202 to Busanovich et al., the patentees describe a three step process which yields cadmium sulfide powder having a particulate size range of between 5 and 40  $\mu$ m. For use in a xerographic mode, the cadmium sulfide particles must be dispersed in a transparent binder or matrix with very high electrical resistivity in the order of  $10^{15}$  ohm-cm. It has been determined that particles in this size range present inherent obstacles to the fabrication of smooth surface layers having optimum xerographic development qualities. Particles in this size range necessarily have poor packing density with limitations on layer thickness which leads to inefficient utilization of light and an increased weight quantity of photoconductor per unit area of photoreceptor. Mechanically subdividing the particles to a micron and submicron size range, e.g. by grinding, does not solve the problem because grinding drastically reduces the photoconductivity of the material.

In a process described in U.S. Pat. 2,995,474 to Pearlman the patentee obtains cadmium sulfide powder in the order of 1  $\mu$ m. by treating copper doped cadmium sulfide with a carefully controlled environment of hydrogen, hydrogen chloride and hydrogen sulfide. The specialized equipment necessary for this technique and the criticality of maintaining proper flow rates, proportions and temperatures, may account for the reason why commercial use of this process has not followed.

The art of pigment impregnated matrix-type photoreceptor fabrication would be significantly advanced if Cu-Cl activated cadmium sulfide, cadmium selenide or cadmium sulfoselenide could be prepared as discrete particles of less than 5  $\mu$ m. surface mean diameter without the aforementioned specified environmental control.

Accordingly, it is an object of the invention to provide improved methods for preparing photoconductive powders.

Another object is to provide improved methods for preparing photoconducting powders of a particle size adapted for use in a xerographic mode.

Yet another object is to provide improved methods for preparing photoconducting powders having a surface mean diameter of less than 5  $\mu$ m.

**SUMMARY OF THE INVENTION**

This invention is directed to a method of preparing a photoconductive powder comprising firing at a tem-

perature between 500° C.-700° C. a member of the group consisting of cadmium sulfide, cadmium selenide and cadmium sulfoselenide with an activator proportion of a precursor containing a member of the group consisting of copper and silver, and with from 0.01 to 1 percent by weight of the composition of a member of the group consisting of cadmium chloride and zinc chloride.

By the foregoing technique powdered photoconductive cadmium sulfide, cadmium selenide and cadmium sulfoselenide of less than 5  $\mu$ m. particle size is obtained which is well suited for xerographic use.

#### BRIEF DESCRIPTION OF THE DRAWING

For better understanding of the invention as well as other objects and further features thereof, reference is made to the accompanying drawing, wherein:

The sole figure represents a curve showing the spectral response analysis of a material formed by the instant process.

#### DETAILED DESCRIPTION OF THE INVENTION

Using the following basic procedure, a series of activated cadmium sulfide compositions were prepared, where each composition differed in the percent by weight of cadmium chloride employed.

#### EXAMPLES 1-5

A cadmium sulfide powder, commercially available from General Electric Phosphor Division (Cleveland, Ohio) as Electronic Grade 118-8-2, and having a surface mean diameter,

$$d_{v-5}$$

( $\mu$ m.) of 2.6, is blended with an aqueous  $\text{CuCl}_2$  solution so as to introduce about 0.01% Cu by weight of CdS. The slurry is dried and the system reduced to a fine powder. The powder is divided into five equal portions and each is moistened with a separate aqueous solution of  $\text{CdCl}_2$  so as to introduce 0.03, 0.09, 0.16, 0.28 and 0.53 percent by weight  $\text{CdCl}_2$  into the respective portions. Each portion is dried at 140° C. for three hours and broken into small chunks. A 45 gm. quantity of each portion is calcined at 600° C. for five minutes in quartz tubes. Each portion is quenched in 600 cc. of deionized water and the disintegrated charges washed free of chloride ions. Each portion is filtered and dried at 140° C. The resulting powder is subjected to particle size and electrical analyses without further treatment.

#### EXAMPLE 6

By way of comparison, an activated cadmium sulfide powder was prepared by the method of Example I of U.S. 2,876,202.

A mixture of 90% by weight CdS, (same source as CdS of Examples 1-5) 9% by weight  $\text{CdCl}_2$ , 0.9% by weight  $\text{NH}_4\text{Cl}$  and 0.02% by weight  $\text{CuCl}_2$  is heated at 600° C. in air for 20 minutes. The resulting powder is washed free of water soluble salts, filtered and moistened with aqueous 1.0 M  $\text{NH}_4\text{Cl}$  and aqueous 0.1 M  $\text{CdCl}_2$ . The dried powder is sieved through a 325 mesh screen and calcined at 600° C. for twenty minutes. The powder from the second calcination is treated with 0.08-0.3% by weight sulfur at 500° C. for ten minutes under atmospheric conditions and then under reduced pressure in the order of  $10^2$   $\mu$ m. Hg. The resulting powder is subjected to particle size and electrical analyses.

The technique employed for particle size analyses is as follows:

#### Particulate size analyses

A microscopic examination of each powder system was made at a magnification of 500 $\times$  using a Leitz Microscope. This provided a screening procedure for examining the general size and shape of the particles and to lend visual support to the numerical analysis by Coulter counter method. Because many of the particles were

below minimum size for detection in the Coulter Counter (that is, <1  $\mu$ m.), the numerical data was programmed to a log-normal distribution which was found to accommodate the powder system and allowed the surface mean diameters

$$d_{v-5}$$

to be derived from the resulting geometric mean and standard deviation values through the following relation:

$$\log(d_{v-5}) = \log(d'_{v-5}) - 1.151(\log \sigma'_g)^2$$

In Equation 1,  $d'_g$  is the geometric means diameter by weight distribution corresponding to the 50% level on the log-probability plot;  $\sigma'_g$  is the standard deviation defined as the diameter ratio corresponding to the 84 and 50% levels on the log-probability curve, thus

$$\sigma'_g = \frac{d(80\% \text{ level})}{d(50\% \text{ level})}$$

The derived surface mean diameter,  $d_{v-5}$ , then accounts for the total particulate population in that

$$d_{v-5} = \frac{\sum f_i d_i^3}{\sum f_i d_i^2}$$

TABLE.—PARTICULATE CHARACTERIZATION

Example number:	Percent $\text{CdCl}_2$	$d_{v-5}$ ( $\mu$ m.), Coulter counter
1.....	0.03	2.88
2.....	0.09	2.77
3.....	0.16	2.74
4.....	0.28	2.63
5.....	0.53	2.97
6.....	9.0	15.0
G.E. CdS <sup>1</sup> .....	0.00	2.60

<sup>1</sup> Starting material.

As can be seen from the table, the process of Examples 1-5, utilizing comparatively small proportions of  $\text{CdCl}_2$ , resulted in no significant particle growth over the size of the original starting material. On the other hand, the process of Example 6, employing the comparatively large proportions of 9%  $\text{CdCl}_2$ , resulted in considerable particle growth as compared with the starting material.

In order to evaluate a representative powder formed by the process of this invention for its utility in a xerographic mode, a xerographic plate is prepared as follows: a mixture of the photoconductive powder of Example 2 and polyurethane, a thermosetting resin product commercially available as Zar from United Gilsonite Laboratory, Scranton, Pa., is prepared in a 1:1 volume ratio. A suitable organic solvent is used as the vehicle for the polyurethane. A layer 25-35 microns thick of this composition is silk screened onto a Nesa glass substrate, (glass coated with a thin transparent conductive tin oxide layer) providing visual inspection of the powder distribution in the organic plastic. The film is extremely smooth and the particles evenly distributed in good packing order throughout the plastic.

This plate was corona charged to -300 volts and then dark discharged. The rate was determined to be approximately 5 volts/second. On exposure to spectral light of  $2 \times 10^{12}$  hv./cm.<sup>2</sup>-sec. flux intensity, its spectral response is that represented by the curve of the drawing. This curve shows the initial photo-induced discharge rates and indicates that the plate has the appropriate photoelectrical characteristics necessary for xerographic use. The residual plate voltage on light exposure varied from a few volts to zero potential.

Steady state dark and photocurrent measurements ( $\lambda$  5850 A.,  $2 \times 10^{12}$  hv./cm.<sup>2</sup>-sec.) were made in a comparable manner described by Busanovich on materials from Examples 1 through 5 and on the photoconductive CdS product prepared by the preferred Busanovich method. The results in all examples complemented the spectral photosensitivity noted in the xerographic mode by indicating the specific resistivity to be at least  $10^{12}$

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ohm-cm., a signal to noise ratio ranging from  $10^4$  to  $10^6$  and a photoresponse comparable to that observed from the Busanovich powder. These electrical properties satisfy the prerequisites for a useful photoconductor for general application rather than limited for specific use in the xerographic mode.

It has been frequently found in calcining at  $600^\circ$  C. in the upper region in flux concentration of 1% by weight that the preferred electrical properties in the xerographic mode are not fully realized due to low dark electrical resistivity, a reduction in signal to noise ratio and sluggish photoresponse. Sulfur treatment in accordance with the prior art (Busanovich, U.S. Pat. 2,876,202) has been shown to compensate for this behavior resulting in a material with the preferred electrical properties: dark electrical resistivity,  $10^{13}$  ohm-cm.; signal to noise level,  $10^4$ - $10^6$ ; response from dark to photoconditions within 1 to 2 seconds in the lateral conductivity analysis.

It is to be understood that in place of cadmium sulfide, cadmium selenide and mixtures of cadmium sulfide and cadmium selenide may be employed as the host crystal. In place of cadmium chloride, zinc chloride may be employed. While these materials can be employed in the range of from 0.01-1% by weight of the photoconductive powder, a preferred range is from 0.03-0.5%. A silver activator may be employed as the equivalent of copper. These may be introduced in the form of their salts, e.g. copper chloride, copper nitrate, silver nitrate, silver chloride, etc. The activator proportion of copper or silver and chlorine is introduced into the host crystal during firing. This amount is extremely small and generally is in the order of  $10^1$  to about  $10^2$  parts per million of the activator with respect to the weight of the host crystal.

The firing temperature while broadly in the range of from  $500^\circ$ - $700^\circ$  is preferably about  $600^\circ$  C. The time of firing should be at least long enough to incorporate the activator ions into the host crystal. At  $600^\circ$  C. this can usually be accomplished in from 1 to 10 minutes. Thus, by starting with photoconductive powder of less than 5  $\mu$ m. particle size, it can be activated by the present method without any meaningful grain growth.

It is to be understood that instead of employing cadmium sulfide, selenide or sulfoselenide as the starting

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material, up to 50% by weight of zinc may be present in these compounds.

What is claimed is:

1. A method of preparing a photoconductive powder consisting of particles having a surface mean diameter of less than about 5 microns consisting of; firing at a temperature of between about  $500^\circ$  to  $700^\circ$  C. a composition which consists essentially of a first particulate component selected from the group consisting of cadmium selenide, and cadmium sulfoselenide with a particle surface mean diameter of less than about 5 microns; an activating proportion of an activator selected from the group consisting of copper and silver, and a second component selected from the group consisting of zinc chloride and cadmium chloride in an amount of between about 0.1 to 1 percent by weight of said composition, said firing being carried out for a period of time sufficient to incorporate said activator in said first component without meaningful growth of said particles.

2. The method of claim 1 wherein said second component is present in an amount of from about .03 to 0.5 percent by weight of said composition.

3. The method of claim 2 wherein said powder is cadmium sulfide.

4. The method of claim 3 wherein said activator comprises copper and said second component is cadmium chloride.

5. The method of claim 4 wherein said composition is fired at about  $600^\circ$  C.

#### References Cited

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CHARLES E. VAN HORN, Primary Examiner

U.S. Cl. X.R.

252-501

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,694,201 Dated September 26, 1972

Inventor(s) A. J. Behringer

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

In Claim 1, column 6, line 9, after "of"  
please insert --cadmium sulfide,--.

In Claim 1, column 6, line 16, delete "0.1"  
and replace it with --.01--.

Signed and sealed this 17th day of December 1974.

(SEAL)  
Attest:

McCOY M. GIBSON JR.  
Attesting Officer

C. MARSHALL DANN  
Commissioner of Patents