United States Patent Office 2,918,437
Patented Dec. 22, 1959

2,918,437

METHODS FOR CONTROLLING LUMINESCENCE AND CONDUCTIVITY OF RADIANT ENERGY SENSITIVE MATERIALS

Immanuel J. Broser and Ruth E. Broser-Warminsky, Berlin, Germany, assignors, by mesne assignments, to Hupp Corporation, a corporation of Virginia

No Drawing. Application May 19, 1955, Serial No. 509,698. In Germany May 6, 1949

Public Law 619, August 23, 1954
Patent expires May 6, 1969

8 Claims. (Cl. 252—501)

This invention relates to improvements in methods for production and sensitization of radiant energy sensitive materials, and more particularly to new and improved methods for controlling luminescence and conductivity of such materials.

It is well known that a series of chemical compounds and especially the oxides, sulfides, selenides and tellurides of the metals zinc, cadmium and mercury, may be used as luminescent materials or as photoconductors if properly activated. If they are to be used as luminescent materials high efficiency of luminescence is required, if they are to be used as photoconductors high sensitivity to the stimulating radiation is required.

These materials as heretofore generally used or produced in the art are in the form of polycrystalline powders. For certain purposes large single crystals or coalescent non-particulate layers are preferred to polycrystalline powders because the grain structure of powders adversely affects image resolution in the case of luminescent materials and, due to high intergranular boundary resistances, it reduces photosensitivity in photoconductor materials. For these reasons, single crystals and grain-free layers are particularly advantageous for use in high sensitivity photoconductor applications, as fluorescent target screens with high resolving power, and as the luminescent material in scintillation type radiation counters.

Methods for manufacturing large crystals of the radiant energy sensitive materials listed above are disclosed in the literature and in our copending application Serial No. 509,697, filed on even date herewith. The present invention provides new and improved methods for obtaining predetermined desired luminescence and conductivity characteristics in single crystals and uniform layers produced by these and other manufacturing methods from the above listed compounds and mixtures thereof.

It is accordingly a primary object of the invention to provide new and improved methods for obtaining predetermined luminescence and conductivity characteristics in radiant energy sensitive materials such as the sulfides, selenides, tellurides and oxides of the metals cadmium, zinc and mercury.

It is also an important object of the invention to provide novel methods for activating and sensitizing or desensitizing such radiant energy sensitive materials either with or without introduction of activators, activation being either general or accurately localized dependent upon the particular application for which the material is intended.

Another object of the invention is the provision of novel methods for obtaining predetermined response characteristics in such radiant energy sensitive materials particularly in single crystal and non-granulate coalescent layer form.

These and other objects, features and advantages of the invention will become more fully apparent by reference to the appended claims and the following detailed description.

As stated above, this invention relates to methods for

treating single crystals and uniform coalescent layers of sulfides, selenides, tellurides and oxides of the metals zinc, cadmium and mercury, so as to obtain predetermined radiant energy response characteristics and particularly optimum luminescence power or maximum photoconductivity.

In one such method in accordance with the invention, maximum luminescence power is obtained by heating the material to at least 100° C. either during the final step of its manufacture or thereafter, and then quickly cooling the thus heated material to room temperature (about 20° C.), the cooling operation being carried out in an air or oxygen atmosphere. This method produces luminescent material which is very uniformly activated and provides extremely high luminescence power.

In one example, cadmium sulfide crystals immediately after manufacture and still at a temperature of 180° C. were exposed to atmospheric air and cooled to 20° C. in one minute. The CdS crystals thus treated were strongly luminescent in the red, with a uniform luminescence power of 23% when stimulated with alpha particles. This compares very favorably with the best ZnS—Cu, which is very difficult and costly to produce and has only slightly greater luminescence power, usually about 25%.

Luminescent materials manufactured by this method are free of the interference and high absorption characteristics which are found in polycrystalline powders because of their intergranular boundaries, in homogeneity and surface discontinuities. The materials of the invention therefore are very efficient for use as luminescent materials in scintillation counters especially when the counter is to count single particles, and also for general use wherever good sensitivity and high resolving power are desired.

Materials prepared by the method just described are only poorly photoconductive; i.e., their resistance changes but little on illumination with visible light. They have extremely low dark resistance, specific resistances of 1000 ohms/cm. being not unusual in crystals produced by this method, and this and their surface barrier characteristics well adapts these materials to photodiode and rectifier use.

In an alternative method also in accordance with the invention, materials having high photoconductivity are produced by a heating and cooling sequence similar to that described in the foregoing except that the maximum temperature reached is substantially reduced or the cooling period substantially extended. As before, the cooling process may if desired be carried out immediately after manufacture of the crystals or layers while still heated incident to the manufacturing process. Materials thus cooled in air either from a relatively low maximum temperature or over a relatively long period of time display only poor luminescence power, but they have high dark resistance and are highly sensitive as photoconductor materials particularly for use in detecting corpuscular and quantum radiation.

Thus, by the methods described it is possible to obtain materials which are either highly luminescent and poorly photoconductive, or highly photoconductive and poorly luminescent, depending on the starting temperature and the time of the cooling process. If desired, materials treated by the first of these methods may subsequently be treated by the second, in which case the poor luminescence and high photoconductivity which is characteristic of materials treated with lower starting temperature or longer cooling period will prevail.

Materials prepared according to the foregoing methods may be said to be self-activated, no foreign activator material being used. Since luminescence and photoconductivity are greatly influenced by activator metals, for

certain purposes it may be desirable to add them. To do so, the non-activated materials may in accordance with the invention be stored together with suitable amounts of the activator metal or metals in a hermetically sealed evacuated container maintained at a temperature above approximately 200° C. for a substantial period of time. Preferably, polycrystalline powder of the same material is stored beside the crystals or layers being treated, as this assures a more uniform activation of the material. The luminescence and conductivity of materials thus treated vary dependent on the amount and kind of activators used.

In an example, one gram of crystalline cadmium sulfide was placed together with silver nitrate (1 cc. of $AgNO_3$ containing 2×10^{-4} g. Ag) in an evacuated closed quartz tube for two hours with temperature being maintained at 300° C. This produced crystals having very good luminescence (efficiency of luminescence of about 18%) and excellent photoconductivity (high photosensitivity with low time constant).

For certain applications it may be desired that the entire sensitive layer not be uniformly luminescent. According to the invention, such non-uniform layers may be produced by exposing the parts thereof that are to have little or no luminescence to the effects of high energy particle bombardment, as for example alpha radiation. By this method the efficiency of luminescence of the irradiated portions of the layer may be reduced in controlled manner, which is useful for many purposes such as application of letters, numerals or other invisible marks capable of being made visible by stimulating the layer which is formed to luminescence.

For example, the efficiency of luminescence of a cadmium sulfide crystal approximately 1 sq. cm. in area may be halved by a 3-day exposure to alpha radiation of 1 mc. By this same method, the photosensitivity of material exposed to the high energy nuclear radiation is increased. For example, the specific resistance per sq. cm. surface area of a low activated cadmium sulfide crystal under illumination may be decreased to 0.01 megohm by a 3-day exposure to 1 mc. alpha radiation.

By concentrating the radiation, it is possible to obtain locally concentrated disturbance centers in the crystals or layers, which then are particularly useful as rectifiers and photoelements.

The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The present embodiments are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

What is claimed and desired to be secured by United States Letters Patent is:

1. A method of improving luminescence of grain-free coalescent layers of sufficient size to be used singly and of radiant energy sensitive materials selected from the group consisting of sulfides, selenides, tellurides and oxides of zinc, cadmium and mercury, and mixtures thereof, which includes during fabrication after the material has been produced as a coalescent layer, the steps of: placing the material at an elevated temperature of over 100° C. and less than that causing dissociation of said layer and thereafter quickly cooling the material to room temperature in the presence of oxygen in no more than a few minutes.

2. A method of improving luminescence of grain-free coalescent layers of sufficient size to be used singly and of radiant energy sensitive materials selected from the group consisting of sulfides, selenides, tellurides and oxides of zinc, cadmium and mercury, and mixtures thereof, which includes during fabrication after the material has been produced as a coalescent layer, the steps of: placing the material at an elevated temperature of over 100° C. and less than that causing dissociation of said layer and thereafter cooling the material to room temperature in the presence of oxygen in about one minute.

3. A method of controlling the luminescence and conductivity of grain-free coalescent layers of sufficient size to be used singly and of radiant energy sensitive materials selected from the group consisting of sulfides, selenides, tellurides and oxides of zinc, cadmium and mercury, and mixtures thereof, which includes during fabrication after the material has been produced as a coalescent layer, the steps of: placing the material at an elevated temperature of over 100° C. and less than that causing dissociation of said layer, cooling the material to room temperature in the presence of oxygen, and then storing the material with an activator metal at elevated temperature in a sealed chamber to activate said material.

4. A method of controlling the luminescence and conductivity of grain-free coalescent layers of sufficient size to be used singly and of radiant energy sensitive materials selected from the group consisting of sulfides, selenides, tellurides and oxides of zinc, cadmium and mercury, and mixtures thereof, which includes during fabrication after the material has been produced as a coalescent layer, the steps of: placing the material at an elevated temperature of over 100° C. and less than that causing dissociation of said layer, cooling the material to room temperature in the presence of oxygen, and then exposing at least part of the material to alpha particle bombardment to improve its photoconductivity.

5. The method of controlling the luminescence and conductivity of single crystals and coalescent layers of radiant energy sensitive material selected from the group consisting of sulfides, selenides, tellurides and oxides of zinc, cadmium and mercury, and mixtures thereof, which includes the steps of placing the material together with a substance which includes at least one activator metal in a closed container, at least partially evacuating the container and maintaining it at elevated temperature over a period of time.

6. The method defined in claim 5 wherein said elevated temperature is at least 200° C.

7. The method defined in claim 5 including the step of placing in the container with the radiant energy sensitive material, a polycrystalline powder of the same material for improved uniformity of activation of the non-powder material.

8. The method of increasing the conductivity in the fabrication of single crystals and coalescent layers of radiant energy sensitive photoconductive materials selected from the group consisting of sulfides, selenides, tellurides and oxides of zinc, cadminum and mercury, and mixtures thereof, which includes the step of exposing at least a portion of the material to high energy alpha particle bombardment effective to increase the photoconductivity of the material in controlled manner.

References Cited in the file of this patent

UNITED STATES PATENTS

2,298,948	Leverenz	Oct. 13, 1942
2,352,035	Strubig et al.	June 20, 1944
2,582,850	Rose	Jan. 15, 1952
2,600,579	Ruedy et al.	June 17, 1952
2,651,700	Gans	Sept. 8, 1953

FOREIGN PATENTS

748,627	Germany	Nov. 7, 1944
695,936	Great Britain	Aug. 19, 1953

OTHER REFERENCES

Physical Review, vol. 72, No. 7, October 1, 1947, pp. 594–601.

Smith: Influence of Atmosphere Firing, article in J. Electro Chem. Soc., vol. 93, pp. 324–333 (1948).