Dec. 20, 1955 S. M. THOMSEN 2,727,808

PANCHROMATICALLY-SENSITIVE ZINC OXIDE

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Fig. 1.

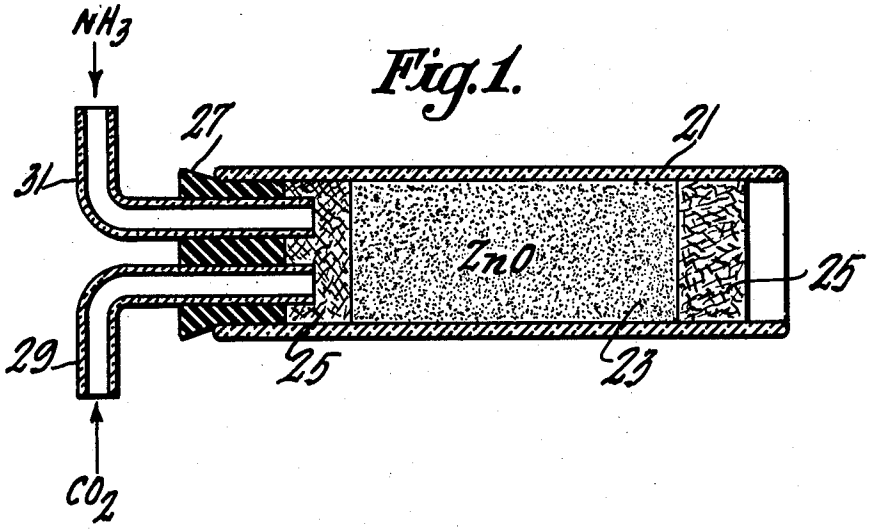
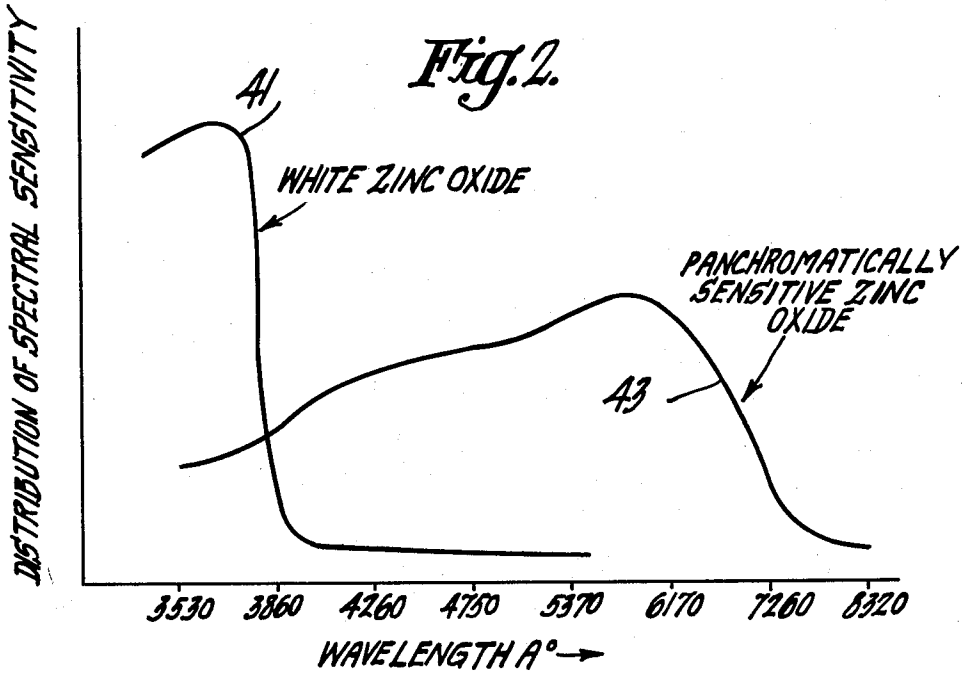


Fig. 2.



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PANCHROMATICALLY-SENSITIVE ZINC OXIDE

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2 Claims. (Cl. 23—147)

This invention relates to zinc oxide and more particularly to an improved method of preparing zinc oxide that is photosensitive over the entire range of the visible spectrum.

The zinc oxide made by the improved method of the present invention has been found to be particularly useful in electrostatic printing processes. Electrostatic printing is, generally, that type of process for producing a visible image, reproduction or copies which includes as an intermediate step converting a light image or signal into an electrostatic charge pattern on an insulating surface. H. G. Greig in U. S. patent application Serial No. 248,937, filed September 29, 1951, now abandoned but which is now embodied in U. S. continuation-in-part patent application Serial No. 383,677, filed October 1, 1953, describes a process wherein a sheet of paper or other conducting material is coated with a photoconductor such as zinc oxide in an insulating film-forming vehicle, then a blanket electrostatic charge is applied to the coated surface of the sheet. A light image is focused upon the charged surface whereby the elemental areas irradiated by the light rays are discharged, leaving a charge on the remainder of the surface forming an electrostatic image. The electrostatic image is rendered visible by the application of a developer powder which is held electrostatically to the charged areas of the sheet. The powder image thus formed may be fixed directly to the coated surface of the sheet.

White zinc oxide is known to have desirable photoconducting properties. A coating of white zinc oxide in an insulating film-forming vehicle also is known for its ability to hold a blanket electrostatic charge or an electrostatic image for considerable periods of time. Thus, electrostatic images may be formed on a sheet of a base material coated or impregnated with this type of composition. However, the spectral sensitivity of the white zinc oxide coating is limited to the ultraviolet and the blue end of the visible spectrum. Hence its use is limited to those processes where there is a radiation source within these spectral limits.

Pure zinc oxide also occurs in a second form which has been variously described as red, buff, salmon or brown in color. This material has a greater spectral sensitivity in the visible region of the spectrum than white zinc oxide. It is known that this second form of zinc oxide may be prepared by heating the hydrolytic products of an ammoniacal zinc nitrate solution, or by deflagrating white zinc oxide with ammonium nitrate or by fusing white zinc oxide with certain ammonium salts. These methods have the disadvantage that at least one wet process step is necessary. Ammoniacal zinc nitrate is prepared by a wet process. The other methods have a relatively low yield of the colored form of zinc oxide, which must be separated by elutriation. Furthermore, the colored oxide produced by previously known methods has a relatively low photosensitivity.

It is an object of this invention to provide a method

of preparing zinc oxide having improved photoconductive properties.

Another object is to provide a method of preparing zinc oxide that is photosensitive over the entire range of the visible spectrum.

A further object is to provide a method of preparing a zinc oxide that may be used to produce a panchromatically-sensitive coating on paper.

Another object is to provide an improved dry process method of preparing panchromatically-sensitive zinc oxide.

The foregoing objects and other advantages may be accomplished by one embodiment of the present invention which comprises reacting white zinc oxide with carbon dioxide gas and ammonia gas and then heating the reaction product at a temperature between 150° and 400° C.

A second embodiment comprises heating an intimate mixture of white zinc oxide and ammonium carbamate acid carbonate at a temperature between 150° and 400° C.

The invention will be described in greater detail by reference to the accompanying drawing in which:

Figure 1 is a sectional view of an apparatus which may be used to carry out the process of this invention, and

Figure 2 is a graph showing the distribution of spectral sensitivity in Angstrom units of ordinary white zinc oxide and a panchromatically-sensitive zinc oxide.

Example 1

Referring to Figure 1, a Pyrex tube **21** about 1" in diameter and 12" long is filled with about 50 grams of chemically pure dry process zinc oxide **23**. Glass wool plugs **25** are fitted at both ends of the zinc oxide to hold the zinc oxide in place. A rubber stopper **27** is fitted into one end of the tube **21**. A carbon dioxide inlet tube **29** and an ammonia inlet tube **31** extend through the rubber stopper **27** into the glass wool plug **25**.

About one hundred milliliters per minute of carbon dioxide and ammonia are passed through inlet tubes **29** and **31** into the zinc oxide **23** in the tube **21**. The gases react with the zinc oxide raising the temperature within the tube as high as 75° C. After about 30 minutes, the gas flow may be stopped and the stopper **27** with the inlet tubes **29** and **31** removed and placed in the opposite end of the tube. The gas flow is again continued for about one hour. The purpose of moving the stopper and inlet tubes to the opposite end of the tube is only to facilitate even distribution of gases through the zinc oxide **23**. The tube contents increase in weight by about 50 grams during this period. The rubber stopper **27** and the inlet tubes **29** and **31** are removed and the tube **21** with its contents is placed in an oven and baked at about 150° C. for about an hour, and then the temperature is raised to 250° C. for another hour. The color of the material in the tube **21** changes in color from white to brown during the last hour of baking. The tube and contents are then removed from the oven and allowed to cool.

Example 2

Another method for preparing the zinc oxide of the instant invention is to mix two parts by weight of ammonium carbamate acid carbonate with about one part of chemically pure dry process zinc oxide. The mixture is then placed in an oven and baked in the same manner as described in Example 1.

The products of the above methods are brown in color. Although the product is slightly caked, it is friable and therefore easily removed and powdered. If less than 50 grams of carbon dioxide and ammonia gas mixture is absorbed in Example 1, or less than 2 parts of ammonium carbamate acid carbonate is added in Example 2, lighter colored products result. The zinc oxide of this invention

may be prepared by heating the mixtures in Example 1 or 2, between about 150° and 400° C. for an hour or more. However, the higher the temperature and the longer the heating, the darker in color the resultant product will be. If the material is heated at a temperature above 400° C., it is converted from the panchromatically-sensitive variety to the ordinary white variety of zinc oxide. The products of the above two methods have an odor of ammonia which may be removed by further baking at about 250° C. in an oven having air circulation. Such removal may be either desirable or unnecessary depending upon the use for which the zinc oxide is intended.

Referring to Figure 2, ordinary white zinc oxide, such as the type used at the start of the instant process, is a photoconductor at ordinary temperatures with a spectral sensitivity in the ultraviolet and the blue end of the visible spectrum as indicated by curve **41**. The material produced by the instant process is also a photoconductor but exhibits a spectral sensitivity over the entire visible spectrum as indicated by curve **43**. In general, the spectral sensitivity of the zinc oxide is shifted to the longer wavelengths by the instant process. The curves **41** and **43** of Figure 2 are not to the same ordinate scale.

The zinc oxide of the instant invention may be mixed with an insulating film-forming resin, such as polyvinyl chloride, and coated on paper to produce a photosensitive sheet. The coating is photoconductive over the entire range of the visible spectrum. The zinc oxide of the instant invention may also be pressed into pellets and used as the active element of a photoconductive cell.

There has thus been described a dry process method for making a panchromatically-sensitive zinc oxide which is cheap, economical and simple to produce.

What is claimed is:

1. A dry process for making panchromatically-sensitive zinc oxide which comprises reacting white zinc oxide with carbon dioxide gas and ammonia gas and then heating the reaction product at a temperature between about 150° and 400° C.

2. A dry process for making panchromatically-sensitive zinc oxide which comprises reacting white zinc oxide with carbon dioxide gas and ammonia gas until there is a weight increase in the zinc oxide of about 100%, baking the reaction product at about 150° C. for about one hour and then heating the baked reaction product at about 250° C. for about one hour.

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