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PHOSPHORESCENT MATERIALS

Charles L. Graham and Herbert J. Dietz, Rochester, N. Y., assignors to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

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This invention relates to a method of preparing phosphorescent screens containing zinc sulfide.

While we have found our improved methods particularly useful in the making of phosphorescent screens to be used in a reflex copying process, such for instance as that disclosed in U. S. Patent Christensen, No. 1,565,256, granted December 15, 1925, they are by no means limited to that purpose. That process comprises exposing a phosphorescent screen to an exciting light and placing the glowing screen in contact with a document to be copied, at the same time exposing it through the back to red light which quenches the excitation except at the points opposite a black or non-reflecting portion of the document.

The screen may be made by dispersing the phosphorescent pigment in a vehicle such as a cellulose ester and coating the dispersion upon a suitable support. Such a screen should produce copies of good contrast and definition upon a sensitive material placed in contact with it, and we have found that this property is enhanced when the grain size of the pigment is relatively small, with an average diameter of from 10 to 15 mu. The grains must be thoroughly dispersed in the medium and the layer of phosphorescent material, and any transparent overcoating must be very thin.

However, prolonged grinding such as is usually necessary to disperse the pigment thoroughly and to reduce its grain size impairs its phosphorescent properties. The use of surface-active dispersing without grinding does not produce the desired fine grains, and the amount of active grain surface is relatively small.

It is to be understood that we use a zinc sulfide previously subjected to prolonged heat treatment at high temperature, say for two hours, at a temperature of the order of 1700° F., and which is in the form of relatively coarse grains having high phosphorescent properties. This product is obtainable on the market.

We have found that if the phosphorescent, large-grained, zinc sulfide is first dispersed in a solvent in the presence of a long-chain fatty acid, such as stearic acid, followed by the heating and removal of the solvent, its phosphorescent properties will be retained after a reasonable amount of grinding and its dispersibility increased by the

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heating operation, and the particles may be readily and uniformly dispersed by a final grinding operation in a coating composition which permits the formation of a very thin coating.

A detailed description of the entire process follows. The relatively coarse phosphorescent grains of zinc sulfide are included in the following dispersion:

	Grams
Zinc sulfide	910
Stearic acid	20
Butyl acetate	200

This mixture is ground in a pebble mill for 1 to 2 hours. After settling, the supernatant liquid is decanted and the remainder heated to 70° C. for several hours, at least three hours and preferably six hours or more, during which time the solvent evaporates completely.

At this point it should be pointed out that the purpose of this heating is not to remove the solvent, since the same solvent may be present in the coating composition in which the phosphorescent grains are later dispersed. There appears to be some chemical action, the mechanism of which is not clear, between the surface of the zinc sulfide grains and the higher fatty acid, which takes place as a result of the heating operation. Whatever the theory of the process, we have discovered and claim as an essential feature of our invention the surface treatment of the zinc sulfide grains with a higher fatty acid with heating. Presumably the stearic acid adsorbed to or reacted with the fresh surfaces, presumably forming zinc stearate.

It should also be pointed out that the temperature of heating is about the melting point of stearic acid. We contemplate the use of other higher fatty acids, and in such cases the temperature of heating should be at about the melting point of the acids used. In the specific example given the temperature mentioned is just above the melting point of stearic acid, and no useful results are obtained by using a higher temperature, but the action takes place to the required extent at temperatures above and somewhat below the melting point, the lower limit of usefulness being at about 62°, and the recommended lower limit being about 65° C. When in the claims we refer to a range of the order of the

melting point, we mean the useful range as here given. The length of heating time is not at all critical, but should be at least three hours to obtain markedly useful results.

The powder resulting from the above operations is then dispersed in the following composition:

	Grams
Cellulose nitrate (high viscosity)	36.3
Butyl acetate	418.0
Toluene (or benzene)	273.0
Butyl phthalate	18.0

Dispersion is accomplished by grinding for an hour or two in a pebble mill, and the screens are then coated from this composition.

The total time of grinding in the two operations is preferably not more than three hours under ordinary grinding conditions, since extended grinding reduces the phosphorescent properties. In that time the grains are reduced from an irregular grain size including grains as large as .040 mm. to a fairly uniform grain size of from 0.010 to 0.015 mm. The optimum grinding time cannot be categorically stated for all conditions, as it will depend on the size of the mill, size and number of pebbles, size of load, speed of mill, and other factors affecting the violence of the grinding operation, but in order to produce thin compact layers we find that the ratio of zinc sulfide to cellulose ester must be high, of the order of 25 to 1. A composition which will have a suitable coating viscosity should include solvents and diluents producing a high viscosity with a low solid content, the cellulose ester being about 5 per cent of the composition, exclusive of the phosphorescent pigment. The formula given above is by way of example, it being understood that other plastics and particularly other cellulose esters and derivatives such as ethyl cellulose may be used.

The screen may be made by first coating on a sheet of glass a very thin transparent layer over which the second or phosphorescent layer is formed, and over this in turn is formed a third or transparent supporting layer which may be colored with a dye transmitting red light. These three coatings are together stripped from the plate and form the complete screen, the first layer acting as a protective layer.

This first layer may be coated from a 10 per cent solution of cellulose acetate in acetone, the coating being 00.12 mm. thick when poured and drying to 00.01 mm. The screen should have the best possible contact with both the document to be copied and also with the sensitive material, and it is therefore important that the protective layer be very thin.

The phosphorescent composition is coated to a thickness of about .2 mm. and when dry, has a thickness from .08 mm. to .11 mm.

The thickness and composition of the support is relatively immaterial so far as the invention here disclosed is concerned. It has hitherto been impossible to obtain a fine grained zinc sulfide screen of high phosphorescent properties in a continuous layer as thin as 0.1 mm.

Since the luminescent light is emitted from one surface of the screen, and the quenching light enters from the other surface, the screens should be as thin and at the same time as uniformly luminescent as possible, and these desiderata are obtained by our process.

The phosphorescent screen so produced emits green light with a maximum at 530 millimicrons. It is excited by blue and violet light and quenched by red and infrared light. Ordinary tungsten filament lamps are satisfactory although they emit light over a wide range. The red rays should be filtered out, although this is not necessary if a longer exposure is given since the exciting action is more rapid than the quenching action. A blue fluorescent lamp is very efficient in its exciting action.

The quenching light should be of high intensity sufficient to give complete quenching in 15 seconds.

Having thus described our invention, we claim:

1. A method of preparing zinc sulfide for use in a phosphorescent screen that comprises grinding zinc sulfide in the form of coarse grains resulting from heat treatment and dispersing the grains in a coating composition, characterized by grinding the coarse grains in the presence of stearic acid in solution for at least an hour and until the grains are thoroughly dispersed, then removing the liquid and maintaining the grains at a temperature between 62° and 75° C. for at least three hours.

2. The method of preparing zinc sulfide for use in a phosphorescent screen that comprises grinding zinc sulfide, in the form of coarse grains resulting from heat treatment and having high phosphorescent properties, in an inert liquid containing stearic acid in solution until the grains are thoroughly dispersed, permitting the grains to settle, removing the supernatant liquid, and heating the residue at a temperature between 65° and 75° C. for at least three hours, whereby the solvent is evaporated, the particle size is reduced, and the stearic acid reacts with the surface of the particles.

3. The method of preparing a phosphorescent screen that comprises grinding zinc sulfide, in the form of coarse grains resulting from heat treatment and having high phosphorescent properties, in an inert liquid containing stearic acid in solution until the grains are thoroughly dispersed, permitting the grains to settle, removing the supernatant liquid, heating the residue at a temperature between 62° and 75° C. for at least three hours, and then grinding the particles in a coating composition, of which 5 per cent is a cellulose ester, and forming a coating from said composition.

4. The method of preparing a phosphorescent screen that comprises grinding zinc sulfide, in the form of coarse grains resulting from heat treatment and having high phosphorescent properties, in an inert liquid containing stearic acid in solution until the grains are thoroughly dispersed, permitting the grains to settle, removing the supernatant liquid, heating the residue at a temperature between 65° and 75° C. for at least three hours, and then grinding the particles in a coating composition, of which 5 per cent is cellulose ester, and the relative proportions of zinc sulfide to cellulose ester is of the order of 25 to 1, and forming a coating from said composition, the total time of grinding in both operations being not over three hours.

CHARLES L. GRAHAM.
HERBERT J. DIETZ.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,532,782	Shappard	Apr. 7, 1925

(Other references on following page)

UNITED STATES PATENTS

Number	Name	Date
1,569,484	Hall	Jan. 12, 1926
1,947,504	Starke	Feb. 20, 1934
1,954,462	Tainton	Apr. 10, 1934
1,985,076	Breyer	Dec. 18, 1934
2,002,891	Hall	May 28, 1935
2,103,032	Fritze	Dec. 21, 1937
2,177,691	Dawihl et al.	Oct. 31, 1939
2,181,305	Myers	Nov. 28, 1939
2,202,048	Einig et al.	May 28, 1940

Number	Name	Date
2,274,766	Ziehl	Mar. 3, 1942
2,310,424	Goodman	Feb. 9, 1943
2,317,977	Cassellini	May 4, 1943
2,366,270	Lemmers	Jan. 2, 1945
2,395,185	Isenberg	Feb. 19, 1946

OTHER REFERENCES

De Ment "Fluorochemistry," published 1945 by Chemical Publishing Co., pp. 202 and 359.