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2,929,708

PHOSPHOR SCREENS FOR COLOR TELEVISION AND METHOD OF PREPARING THE SAME WHILE USING DIAZOTYPE MATERIALS

Douglas Straw, Johnson City, N.Y., assignor to General Aniline & Film Corporation, New York, N.Y., a corporation of Delaware

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The present invention relates to the manufacture of phosphor screens for color television and more particularly to a method of accurately positioning the phosphor dots on such screens through the utilization of the light sensitive diazotype method.

Phosphor glass screens for color television tubes consist of finely discrete patterns of three different phosphors, each of which emits rays of a different primary color, to wit, red, green and blue. An apparatus employing such tubes and screens is illustrated on page 327 of the Proceedings of the I.R.E., January 1954, 42, No. 1, and it will be seen from this illustration that a short distance from the screen toward the gun end of the tube a thin perforated metal mask is mounted parallel to the screen. For each hole in the metal mask there is a corresponding trio of phosphor dots. Three electron guns are mounted symmetrically about the axis of the tube. The guns, mask and phosphor dotted screen are so positioned that the electron beam from each gun is directed through the holes in the mask so as to strike dots of one primary color only.

The advantages of this system speak for themselves, but its use has been considerably curtailed because of the difficulty experienced in accurately registering the phosphor dots on the glass screen. The art has bent its efforts to the solution of this problem and, to this end, it was recently suggested by Levy and Levine (Journal Electrochemical Society, 101, pages 99-103; 1954) that a negatively working photographic system be employed.

In the system thus suggested the photosensitive compound in a suitable solvent is blended with one of the phosphors and coated on the glass screen plate by whirling or spraying. After drying, the plate is located beneath the thin perforated metal mask and exposed by light from a suitable source. Where the light passes through the screen, tanning of the photosensitive layer ensues. The photosensitive layer and phosphor in the unexposed and hence untanned areas are washed away by a solvent which does not attack the tanned exposed areas. This results in the desired dot pattern of one phosphor bound by the tanned products in the exposed area.

The entire process is now repeated while utilizing the other phosphors, the screen and/or light source being changed so as to accurately position each particular phosphor with respect to the other two. When the entire dot pattern, consisting of the three colors, has been obtained the light-fixed or tanned binder is removed by baking at 400° C. and a permanent silicate binder is applied by spraying.

This type of negative working system presents a number of disadvantages. Thus, the light tanned products act as the sole binder for the phosphors until removed by baking. The dot pattern image so achieved is accordingly very sensitive to touch. Further, the tanned products must be gassed off in the subsequent baking. Finally, certain of these negative tanning agents markedly reduce the relative brightness of the luminescent

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output and also induce changes in the chromaticity values. The involved method, therefore, does not provide a satisfactory solution for the problem at hand.

It has now been discovered that the desired accurate positioning of the phosphor dots can be attained while avoiding the disadvantages of the prior procedures by using a positive working diazotype system employing high molecular weight, water-insoluble sulfonamides of naphthalene diazo oxides as the light sensitive medium and selectively removing by solvent action the photodecomposition products thereof from the irradiated areas to form open dots of exposed glass surrounded by undecomposed light sensitive diazo oxides. Phosphors applied to the glass plate from an aqueous silicate solution adhere more tenaciously to the open dots of the exposed glass than to the surrounding areas and, hence, may be confined to the exposed glass by solvent removal of the diazo oxide and silicate from the surrounding areas. Of equal significance is the fact that upon re-sensitization of the entire plate and re-exposure thereof to position the next series of phosphor dots, the unexposed diazo oxide layer, overlying the area occupied by the already applied phosphors, operates as a barrier or shield to prevent contact between said phosphors and those applied subsequent to removal of the photo-decomposition products of such re-exposure. Contamination of the various phosphors by one another is thus avoided.

Phosphor screens produced while resorting to this principle, and the method of their production, constitute the purposes and objects of the present invention.

My procedure, as is evident, involves as one of its main attributes the utilization of high molecular weight or resin-like, light sensitive, water-insoluble diazo oxides which are capable, when light struck, of yielding decomposition products having a different solubility in organic solvents than the diazo oxides per se. This permits, by use of a suitable solvent, the selective removal of the photodecomposition products to expose the glass in a dot pattern conforming to the exposure of the glass plate through the perforated metal mask. By confining one set of phosphors to the resulting dot pattern, accurate registering of this group of phosphors is attained.

The phosphors are applied to the exposed areas of the glass plate by way of an aqueous solution of an alkali metal silicate, such as of sodium or potassium. Such silicate I have determined has far greater adhesion for the glass than for the area defined by the light sensitive diazo oxide. It is, therefore, possible to remove the phosphors from the area surrounding the dots of exposed glass by resorting to a solvent which does not attack or dissolve the silicate in the area defined by the dots, but effects removal of the undecomposed diazo oxide and adhering silicate and phosphor.

In operating as prescribed, a glass plate destined to be the phosphor screen is coated by means of a whirler or other suitable apparatus with a solution of a water-insoluble, high molecular weight or resin-like sulfonamide of a naphthalene diazo oxide. The plate is then exposed under the perforated mask to be used in a television tube by a suitable light source for several minutes. It is then washed in a solvent which selectively removes the photodecomposition product but does not attack or dissolve the diazo oxide. There are thus obtained open dots of exposed glass surrounded by the undecomposed diazo oxide. After washing and drying, the plate is coated with a suspension of the selected phosphor in an aqueous solution of an alkali metal silicate. The plate is then dried and treated with a solvent which removes the diazo oxide, silicate and phosphor from the non-image areas but does not affect the silicate in the image areas. Brushing may be resorted to if necessary to facilitate removal.

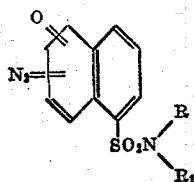
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The entire plate surface is then re-sensitized with the same diazo oxide and after adjustment of the light source and/or the plate it is re-exposed for registration of the next set of phosphors. After exposure, the plate is processed as before and this procedure is repeated until all three sets of phosphors have been accurately located on the plate.

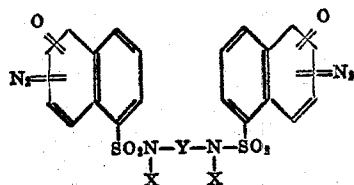
It has been determined that in re-sensitization the layer of diazo oxide coated on the plate adheres to the already applied phosphors and is not displaced from the area occupied by said phosphors when the photodecomposition products are removed. Consequently, the diazo oxide layer acts as a shield or barrier to prevent coating of the already positioned phosphors with the next application of silicate and phosphors. The layer of diazo oxide, in other words, prevents any intermingling of the various sets of phosphors. On the other hand, the bond between the applied phosphors and the layer of overcoated diazo oxide is not so strong as to prohibit ready removal of the diazo oxide layer by the solvent used to originally coat the diazo oxide.

Diazo oxides which have been found suitable for sensitization of the glass plates are those obtained by amidation of -2-diazo-1-naphthol-5-sulfonyl chloride or 2-naphthol-1-diazo-5-sulfonyl chloride with amines which may be aliphatic, such as methyl, ethyl, propyl, butyl, octyl, decyl, dodecyl, tetradecyl, benzyl and the like, aromatic, such as phenyl, toluyl, naphthyl and the like, or hydro-aromatic, such as a terpene, i.e., dehydroabietyl, dihydroabietyl, tetrahydroabietyl, dextroprimaryl and the like. The amines which are employed should be such that the nitrogen atom of the amide linkage is substituted by a group or groups, the sum of the carbon atoms of which totals at least 10.

Diazo oxides within the above broad category may be more precisely defined by the following formulae:



and



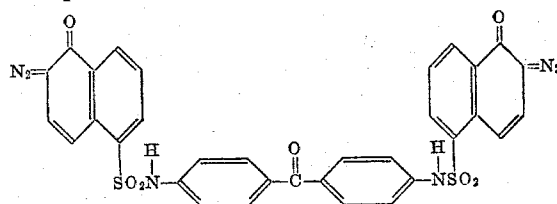
in which R may be hydrogen, alkyl, such as methyl, ethyl, propyl, butyl and the like; aryl, such as phenyl, toluyl and the like; aralkyl, such as benzyl and the like and R₁ is alkyl, such as methyl, ethyl, propyl, butyl, amyl, decyl, dodecyl, heptadecyl and the like; aromatic, such as phenyl, naphthyl, benzylphenyl, phenylacetylphenyl, phenoxyphenyl, or a hydro-aromatic radical such as a terpene, i.e., dehydroabietyl, dihydroabietyl, tetrahydroabietyl, dextroprimaryl and the like; X is hydrogen, alkyl, such as methyl, ethyl, propyl or the like, aryl, such as phenyl, toluyl or the like or aralkyl such as benzyl and the like and Y is an aromatic radical containing two

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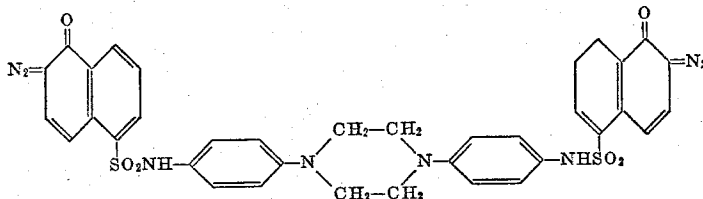
phenyl rings, the carbon atom of each ring being linked to an amide nitrogen atom, said ring being either directly linked or being linked through a grouping such as carbonyl, methylene, ethylidene, oxygen, piperazyl and the like, it being understood that the sum of the carbon atoms in R and R₁ must total at least 10.

Examples of such compounds which I have found to be suitable are:

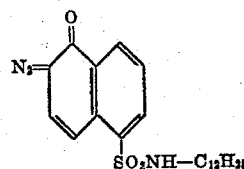
- (1) N-dehydroabietyl-6-diazo-5(6)-oxo-1-naphthalenesulfonamide
- (2) N - dehydroabietyl - N-2-hydroxyethyl-6-diazo-5(6)-oxo-1-naphthalenesulfonamide
- (3) N - dehydroabietyl-N-ethyl-6-diazo-5(6)-oxo-1-naphthalenesulfonamide
- (4) N,N' - didehydroabietyl - N,N'-ethylenebis-(6-diazo-5(6)-oxo-1-naphthalenesulfonamide)
- (5) N-dehydroabietyl-3-diazo-4(3)-oxo-1-naphthalenesulfonamide
- (6) N,N'-didehydroabietyl-3-diazo-4(3)-oxo-1,6-naphthalenedisulfonamide
- (7) N,N' - 4,4'-diphenylketonylbis-[6(5)-diazo-5(6)-oxo-1-naphthalenesulfonamide]



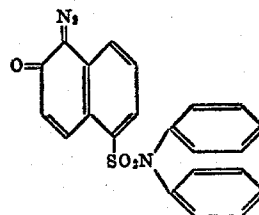
- (8) N,N'-4,4'-diphenyl-piperazylbis-6(5)-diazo-5(6)-oxo-1-naphthalenesulfonamide



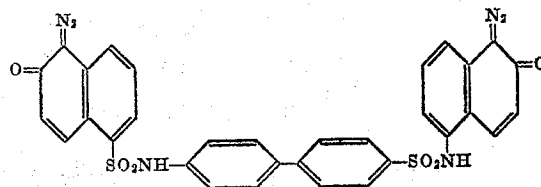
- (9) N-dodecyl-6-diazo-5(6)-oxo-1-naphthalenesulfonamide



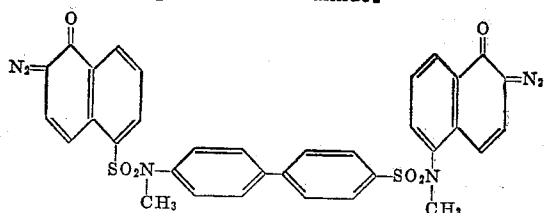
- (10) N,N-diphenyl-5-diazo-6(5)-oxo-1-sulfonamide



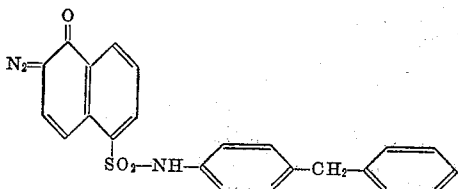
- (11) N,N' - 4,4'-diphenylenebis-[5(6)-diazo-6(5)-oxo-naphthalenesulfonamide]



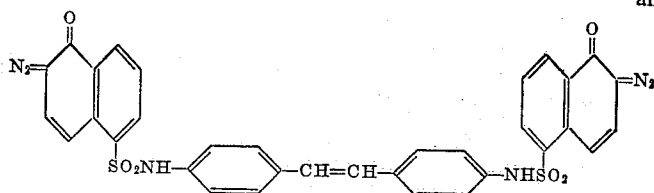
(12) N,N' - dimethyl - 4,4'-diphenylenebis-[6(5)-dialzo-5(6)-oxo-1-naphthalenesulfonamide]



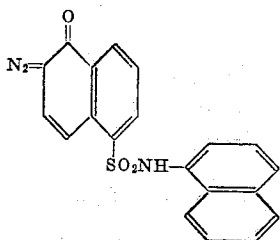
(13) N - fluorenyl-6-dialzo-5(6)-oxo-1-naphthalenesulfonamide



(14) N,N'-4,4'-stilbenylenebis[6-dialzo-5(6)-oxo-1-naphthalenesulfonamide]



(15) N - α-naphthyl-6-dialzo-5(6)-oxo-1-naphthalenesulfonamide



(16) N - dihydroabietyl-6-dialzo-5(6)-oxo-1-naphthalenesulfonamide

(17) N - tetrahydroabietyl - 6-dialzo-5(6)-oxo-1-naphthalenesulfonamide

(18) N-dextroprimaryl-6-dialzo-5(6)-oxo-1-naphthalenesulfonamide

The above compounds, with the exception of those containing a terpene radical, and their method of preparation are described in the literature. The terpene derivatives, on the other hand, and their method of preparation are described in U.S. Patent 2,797,213, granted to Ralph G. D. Moore on June 25, 1957.

The diazo oxides, despite their high molecular weight, resin-like structure, are soluble in normally liquid aliphatic solvents boiling above 75° C. to the extent of at least 1% and as such solvents reference may be made to methyl Cellosolve, dioxane, dimethyl acetamide, dimethylformamide, diethylketone, methylpropyl ketone, methylisobutyl ketone, methylethyl ketone and the like. The diazo oxides may, therefore, be laid down on the glass plate by the utilization of any of such solvents.

The photodecomposition products of the diazo oxides as aforesaid have a solubility which is different from the diazo oxides per se. Thus, I have discovered, and this is an important feature of my invention, that the photodecomposition products are soluble in and, hence, removable by normally liquid alkylol amines, on the one hand, and normally liquid aliphatic alcohols boiling at least as high as propyl alcohol, on the other hand. By resorting to the use of these solvents, which may be used alone or in admixture, it is possible after irradiation of

the sensitized glass plate to selectively remove the photodecomposition products while leaving the diazo oxides intact.

Examples of solvents within these categories and which I have found to be suitable are ethanolamine, butanolamine, ethanolpropanolamine, ethanolbutanolamine, triethanolamine, isopropyl alcohol, butyl alcohol, isobutyl alcohol, ethylene glycol, glycerine and the like. The solvents are preferably employed in aqueous solutions containing up to 50% of water, although this is not a necessary criterion to the successful removal of the photodecomposition products.

The selective removal of the phosphors applied with the silicate to the non-image areas is effected by utilization of any of the solvents for the diazo oxide. Preferably, the same solvent is used in this step as is used in coating the diazo oxide on the glass plate.

It is believed to be manifest that the layer of undecomposed diazo oxide must have a certain stability in order to withstand the mechanical action to which it is subjected in the removal of the photodecomposition products, on the one hand, and in the application of the phosphor and silicate solution, on the other hand. While the resin-

like diazo oxides enumerated above possess such stability, it is often preferable to provide increased stability by incorporating in the diazo oxide sensitizing solution a water-insoluble, alkali-resistant, adhesive resin which is soluble in any of the aforementioned solvents for the diazo oxide. In addition the resin should be resistant or impervious to the action of the solvents utilized for removing the photodecomposition products. The resin should thus withstand a contact time of ½ minute or longer with such reagents.

Many resins available on the open market manifestly fit these requirements and, in this connection, reference is made to polyvinyl resins, such as phenol modified coumarone-indene resins, polyvinyl acetate, polymethylacrylate, polymethylmethacrylate, cellulose derivatives, such as ethyl cellulose, cellulose acetate, cellulose propionate, mixed esters and the like.

It is a very simple test in any case, the solvents being identified, to determine a suitable resin having adhesive characteristics, which may be utilized for application with the light sensitive diazo compound.

The invention will be illustrated by the following examples, but it is to be understood that the invention is not restricted thereto.

Example I

A 10% solution of N-dehydroabietyl-6-dialzo-5(6)-oxo-1-naphthalenesulfonamide in methylethyl ketone was coated on a glass plate using a whirler and the plate dried. The plate was exposed under the thin perforated screen to be used in the television tube by an H-1 mercury arc at a distance of 11 inches for 10 minutes. The plate was then washed in a tray containing a 1:1 solution of diethanolamine and water, whereupon the photo-decomposition products are removed leaving the open, exposed glass dots surrounded by the unphotodecomposed photosensitive material. The plate was then washed in water and dried. The plate was then coated with a suspension of 2 parts of phosphor, 1 part of 40 to 42° Bé. sodium silicate solution (sold by J. T. Baker Chemical Co., as sodium silicate solution, technical) and 2 parts of water. After this coating had dried, the plate was placed in boiling methylethyl ketone and the removal of silicate and phosphor in non-image areas aided by

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brushing. Subsequent washings in acetone and water and drying results in the desired dot pattern of phosphor bound by silicate. The plate is then ready for resensitization and application of the other phosphors in the same manner while using the same diazo and solvents. 5

Example II

A 10% solution of N,N'-dimethyl-N,N'-4,4'-diphenylene-bis-[6(5)-diazo-5(6)-oxo-1-naphthalenesulfonamide] in dimethylformamide was coated on a glass plate and subsequently dried and exposed in a manner similar to that outlined in Example I. Removal of the photodecomposition product in this case was accomplished by washing in isopropanol. Application of the phosphor suspension was accomplished in the manner outlined in Example I. Removal of silicate and phosphor was accomplished by placing the dried plate in dimethylformamide and brushing. 10

Example III

The procedure is the same as in Example I, excepting that there is used a 6.5% solution of N-dehydroabietyl-6-diazo-5(6)-oxo-1-naphthalenesulfonamide in methylisobutyl ketone to sensitize the glass plate and the photodecomposition products are removed by the following solvent mixture: 15

- 1.5% monoethanolamine
- 10.0 triethanolamine
- 20.0% glycerine
- 68.5 ethylene glycol

The application of the phosphor by the outlined procedure has manifest advantages. Thus, the silicate acts as a strong binder for the phosphors, as a consequence of which, the image dots are not sensitive as are the tanned images in the reported procedure. Further, no photodecomposition products remain to be gassed off at highly elevated temperatures. Finally, the phosphors in the dot areas at no time contact the photodecomposition products so that the luminescent brightness or chromaticity values are not changed. 20

Various modifications of the invention will occur to persons skilled in the art. For example, in lieu of the diazo oxides of the examples, any of the aforementioned diazo oxides may be employed. Similarly, any of the solvents mentioned herein may be used in lieu of those of the examples. I, therefore, do not intend to be limited in the patent granted except as necessitated by the appended claims. 25

I claim:

1. In the process of producing phosphor glass plates for color television tubes, the improvement in the accurate positioning of the phosphor dots on such plates which comprises exposing beneath a perforated metal television mask a glass plate sensitized with a high molecular weight, water-insoluble sulfonamide of a naphthalene diazo oxide, selectively removing by solvent action 30

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the photodecomposition product of the diazo oxide to produce a dot pattern of exposed glass surrounded by the light sensitive diazo oxide, applying to the plate a suspension of a phosphor in an alkali metal silicate to cause adhesion of the silicate and phosphor to the exposed glass and removing by solvent action the undecomposed diazo oxide and the silicate and phosphor adhering to said undecomposed diazo oxide. 35

2. The process as defined in claim 1, wherein the nitrogen atom of the sulfonamide is substituted by a terpene radical.

3. The process as defined in claim 1, wherein the photodecomposition products are removed by means of a solvent selected from the class consisting of normally liquid alkylol amines and normally liquid aliphatic alcohols having a boiling point at least as high as propyl alcohol. 40

4. In the process of producing phosphor glass plates for color television tubes the improvement which comprises exposing beneath a perforated metal television mask a glass plate sensitized with a high molecular weight, water-insoluble sulfonamide of a naphthalene diazo oxide, developing an image by selectively removing by solvent action the photodecomposition product of the diazo oxide to produce a dot pattern of the exposed glass surrounded by the light-sensitive diazo oxide, applying to the plate a suspension of a phosphor in an alkali metal silicate to cause adhesion of the silicate and phosphor to the exposed glass, removing by solvent action the undecomposed diazo oxide and the silicate and phosphor adhering to said undecomposed diazo oxide, resensitizing the plate with the high molecular weight, water-insoluble sulfonamide of a naphthalene diazo oxide, adjusting the mask relative to the plate, re-exposing and redeveloping, applying to the plate a suspension of a different phosphor in alkali metal silicate to cause adhesion of the silicate and phosphor to the exposed glass and removing by solvent action the undecomposed diazo oxide and the silicate and phosphor adhering to said undecomposed diazo oxide. 45

References Cited in the file of this patent

UNITED STATES PATENTS

45	2,447,836	Beeber et al. -----	Aug. 24, 1948
	2,500,052	Yackel -----	Mar. 7, 1950
	2,544,903	Stahle -----	Mar. 13, 1951
	2,617,727	Slifkin -----	Nov. 11, 1952
	2,662,013	Sulich -----	Dec. 8, 1953
50	2,766,118	Sus et al. -----	Oct. 9, 1956
	2,747,997	Smith -----	May 29, 1956

FOREIGN PATENTS

713,908	Great Britain -----	Aug. 18, 1954
---------	---------------------	---------------

OTHER REFERENCES

Levy et al.: "The Sylvania Technologist," vol. VI, No. 3, July 1953 (copy in Scientific Library), pp. 60 to 63. 55