

1

3,824,099

**SENSITIVE ELECTROPHOTOGRAPHIC PLATES**  
Robert Bruce Champ and Meredith David Shattuck, San Jose, Calif., assignors to International Business Machines Corporation, Armonk, N.Y.  
No Drawing. Filed Jan. 15, 1973, Ser. No. 323,678  
Int. Cl. G03c 5/06

U.S. Cl. 96—1.5

4 Claims

## ABSTRACT OF THE DISCLOSURE

Very sensitive electrophotographic plates are provided having a charge generating layer comprising a squaric acid methine dye and a charge transport layer comprising a tri-aryl pyrazoline compound.

## FIELD OF THE INVENTION

The present invention is concerned with electrophotographic plates. In particular, it is concerned with layered plates having a charge generation layer and a separate charge transport layer. The charge generation layer comprises a squaric acid methine dye and the charge transport layer comprises a tri-aryl pyrazoline compound. Electrophotographic plates containing these layers have been found to be extremely sensitive to light.

## PRIOR ART

Squaric Acid methine dyes are known compounds which have been described in the literature. 1,3- and 1,2-squaric acid methine dyes, both of which are useful in the present invention, have been described, for example, in U.S. Pat. 3,617,270 where methods for their synthesis are also described. That patent discloses the use of squaric acid methine dyes for the optical sensitization of zinc oxide, in which use the squaric acid methine dye is used at a concentration of about 0.1 to 20 milligrams per square meter of finished photoconductive layer.

## SUMMARY OF THE INVENTION

The electrophotographic plates of the present invention comprise, in addition to a conductive substrate, a charge generating layer containing a squaric acid methine dye and a separate charge transport layer containing a tri-aryl pyrazoline compound. Electrophotographic plates having the structure recited above have been found to be extremely fast in their response to light. They are panchromatic out to about 7000 Angstrom units. They are also responsive to light having wave lengths up to 9000 Angstroms. A particularly suitable field for their use is with lasers having wave lengths of from about 8000 to about 9000 Angstroms.

To obtain the high sensitivities of the present invention it is necessary that the electrophotographic plates contain both squaric acid charge generating material and tri-aryl pyrazoline charge transporting material. Both are essential elements of the present invention. This result was totally unexpected and the theoretical explanation for it is not known.

The use of tri-aryl pyrazoline containing charge transport layers is disclosed in U.S. Patent Application Ser. No. 323,677, filed on even date herewith.

There are several well known electrophotographic reproduction processes in current use. They differ in the particular way in which they are carried out, particularly

2

in the sequence in which electric charging (usually with a corona) and illumination are carried out. All electrophotographic reproduction processes, however, involve the process step of selectively rendering portions of a photoconductor electrically conductive by selective exposure to light. The electrophotographic plates of the present invention are useful in all such processes.

In the electrophotographic plates of the present invention, the charge transport layer may be used either on top of the charge generating layer, or beneath the charge generating layer. For mechanical reasons, it is generally preferred that the charge transport layer be on top. The charge transport layer may vary considerably in thickness, in general being from about 10 to about 30 microns thick, preferably from about 15 to about 25. When the charge transport layer is on top of the charge generating layer, i.e. when the charge generating layer is between the charge transport layer and the conductive substrate, the electrophotographic plate should be charged negatively. In those instances where the charge transport layer is beneath the charge generating layer, that is, when the charge transport layer is between the charge generating layer and the conductive substrate, the electrophotographic plate should be charged positively.

In forming the charge generating layers of the present invention, the squaric acid methine dye may be used alone, but it is preferred to use a squaric acid methine dye in conjunction with a binder when the layer is formed by coating from a slurry. The optimum ratio of dye to binder, depending upon the particular dye, is generally from about 0.1 to about 0.9. Binderless layers may be formed by vacuum evaporation. Many types of binder materials, such as resins, are known to the prior art. Many polyesters are suitable materials. Sucrose benzoate may also be employed in many mixtures of the various binders. Particularly outstanding results have been obtained using polyvinyl butyral. In general, it is preferred that the charge generating layer be from about 0.1 to about 2 microns thick, most preferably about 0.5 microns. It is also preferred that the charge generating layer contain from approximately 50 to about 100 milligrams of the squaric acid methine dye per square meter of plate area.

The following examples are given solely for purposes of illustration and are not to be considered limitations on the invention, many variations of which are possible without departing from the spirit or scope thereof.

## EXAMPLES 1-8

The following squarylium pigments were all ground to a fine particle size in tetrahydrofuran and applied by a knife blade coater on aluminized Mylar substrate. (Mylar is a trade name for polyethyleneterephthalate film from Dupont.) The coating percent solids is 3% and the wet gap setting is one mil. Over this generation layer is then coated a transport layer of 2 parts Merlon 60 and 1 part DEASP by weight. Coating thickness is 13-15 microns thick. Merlon 60 is a trade name for a polycarbonate resin marketed by Mobay Chemicals. DEASP is a shortened abbreviation for 1-Phenyl-3-[p-diethylaminostyryl]-5 - [p-diethylamino phenyl]-pyrazoline. The coated films are then heated for 30 minutes in an electrometer. The illumination was from a tungsten halogen lamp, 75 watts, 28 volts at a distance of approximately .5 cm.

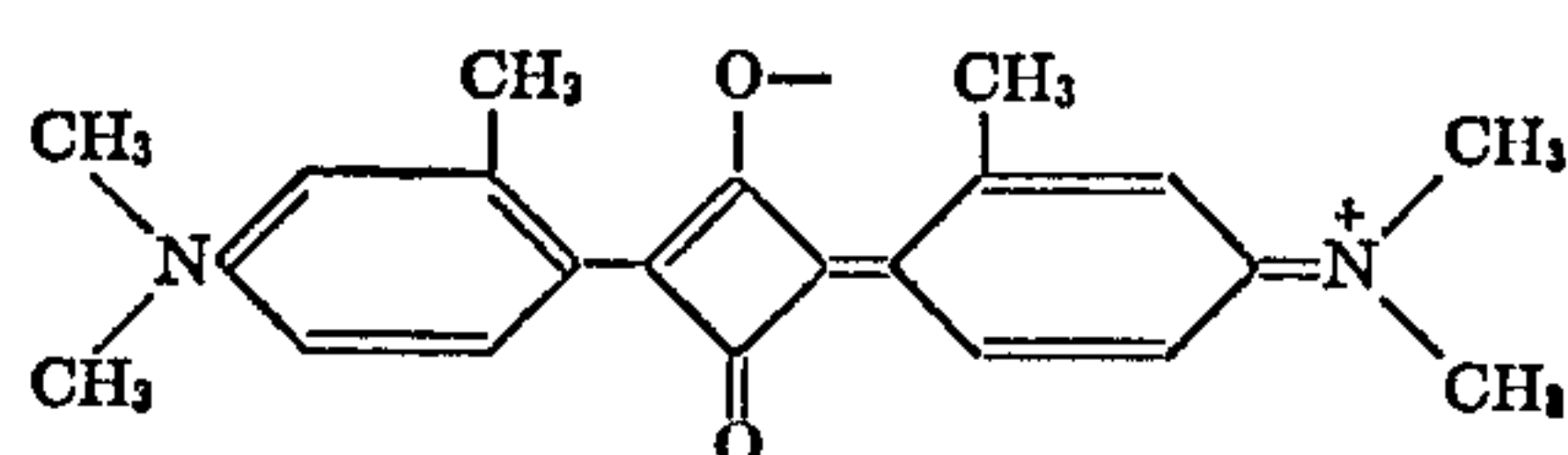


Example number	Pigment	Light decay $E-\frac{1}{2}$ * (-) (microjoules/ cm. <sup>2</sup> )	Charge acceptance (volts) (-)
1.....		60	400
2.....		115	420
3.....		30	580
4.....		0.84	1100
5.....		1.2	800
6.....		2.2	670
7.....		5.4	710
8.....		0.84	230

\* $E-\frac{1}{2}$  is the amount of energy required to decay the photoconductor by exposure to light to one-half its charge acceptance.

### EXAMPLE 9

One gram of the compound



is ground in a McCrone micronizing mill for 60 minutes whereupon 3 g. of 5% polyvinylbutyral (XYHL B-800 from Union Carbide) is added with 7 g. of tetrahydrofuran. The material is micronized for 20 minutes and then decanted into a jar. Seven grams of a 5% Elvacite

2010 (a methyl methacrylate polymer from Dupont) solution in THF is added with a gram of THF and the material is rolled in on a roller mill. The slurry is then coated on aluminized Mylar using a vertical meniscus coating apparatus. The optical density of this layer to green light should be 0.6 to 0.7.

Coated on this layer after it has air dried is a solution comprising

4.05 g. Merlon 60

2.7 g. DEASP.

8 d.p.s. 10% DC-200 (Dow Corning Silicon Oil) in tetrahydroforan.

5

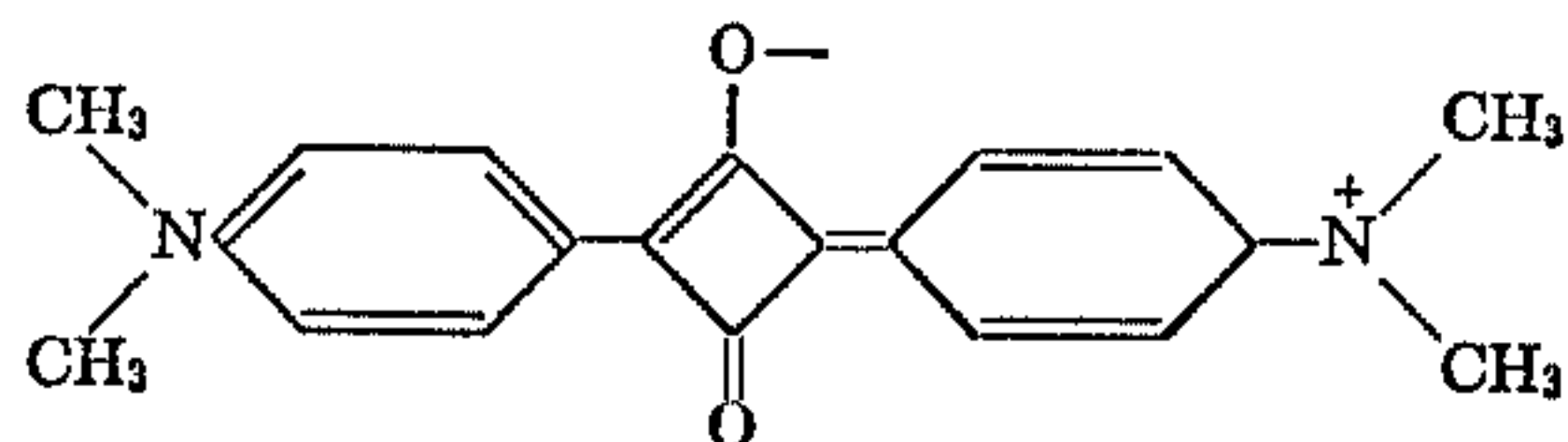
The percent solids is 15.5 and the coating speed is 8 f.p.m. The film is treated for 15 minutes at 115° C.

Sensitometry on the above film gave the following data:

Dark Decay v./Sec. ----- 40 volts/sec.  
 E<sub>200</sub> from 700 v. charge  
 [Photocopy green lamps  
 (PCG)] ----- 0.95 microjoules/cm.<sup>2</sup>.  
 Dark Charge with 650 Volts  
 on Screen ----- 780 v.

## EXAMPLE 10

When the compound

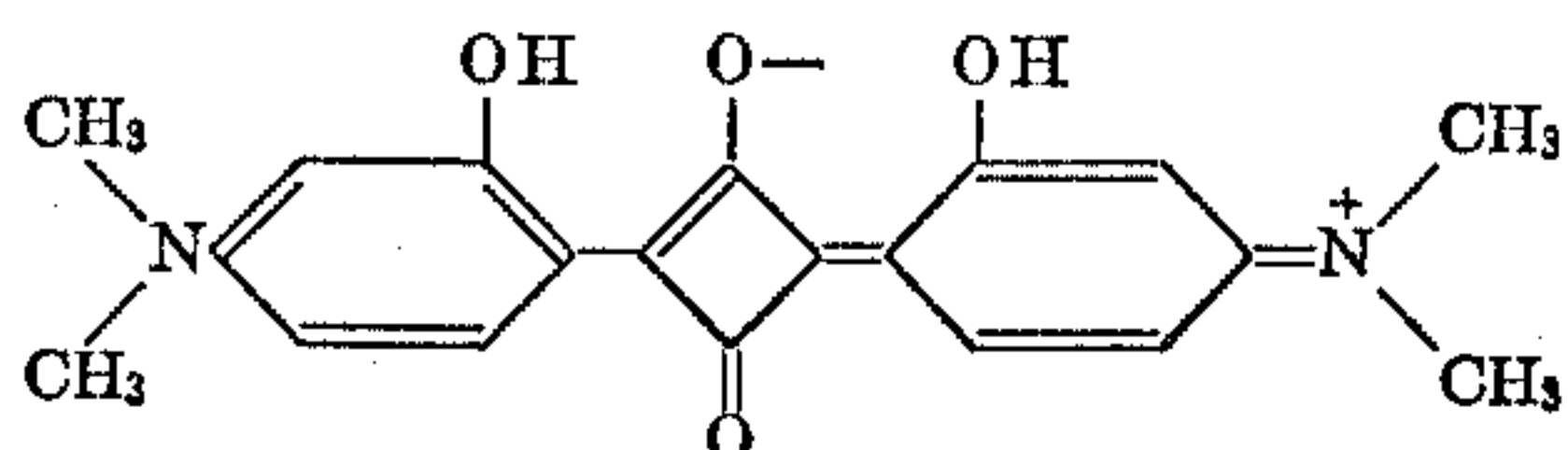


is employed in the above formulation and coated to an optical density of 0.2 to green light the following sensitometric results are obtained:

Dark Decay Volts/sec. ----- 220 volts/sec.  
 E<sub>200</sub> from 700 v. charge  
 (PCG) ----- 0.58 microjoules/cm.<sup>2</sup>.  
 Dark charge with 780 v. on  
 Screen ----- 800 v.

## EXAMPLE 11

When the compound



is employed in the formulation as described in Example 9 and coated to an optical density of 0.6 to green light the following sensitometric results are obtained:

Dark Decay Volts/sec. ----- 16 volts/sec.  
 E<sub>200</sub> from 700 v. charge  
 (PCG) ----- 0.74 microjoules/cm.<sup>2</sup>.  
 Dark charge with 720 v. on  
 screen ----- 780 v.

## EXAMPLE 12

When the formulation of Example 9 is coated on aluminized Mylar which has been subbed with a coating of 0.3μ of an acrylic resin (A-11 from Roehm and Haas) the following sensitometric data are noted:

6

Dark Decay v./sec. ----- 100 v./sec.  
 E<sub>200</sub> from 700 v. charge  
 PCG) ----- 1.1 microjoules/cm.<sup>2</sup>.  
 Dark charge with 680 v. on  
 screen ----- 750.

## EXAMPLE 13

The charge generating layer was prepared by evaporating the compound in Example 11 on an aluminized Mylar substrate to an optical density to green light of 0.4.

This was coated with a transport layer consisting of:

	Parts
Polyester (Vitel PE-200 from Goodyear) -----	2
DEASP -----	1

The percent solids is 20 in tetrahydrofuran and the coating speed is about 8 f.p.m. The film was dried to remove excess solvent at 115° C. for 30 minutes.

Sensitometry on the above film is as follows:

Dark Charge ----- 700 v.  
 Energy required to decay to  
 200 v. (Photocopy green  
 lamp) ----- 0.4 microjoules/cm.<sup>2</sup>.

What is claimed:

1. An electrophotographic plate comprising a conductive substrate having a layer comprising a squaric acid methine dye and a separate layer comprising a tri-aryl pyrazoline compound.
2. An electrophotographic plate as claimed in claim 1 wherein the pyrazoline compound containing layer is present as an overcoat to the other layer.
3. An electrophotographic plate as claimed in claim 1 wherein the pyrazoline compound containing layer comprises a binder.
4. An electrophotographic plate as claimed in claim 3 wherein the binder is polyvinyl butyral.

## References Cited

## UNITED STATES PATENTS

3,617,270	11/1971	Kampfer	96—1.7
3,527,602	9/1970	Fox	96—1.5
3,634,135	1/1972	Osaka	96—1.5

## FOREIGN PATENTS

4,326,710	11/1968	Japan	96—1.6
-----------	---------	-------	--------

RONALD H. SMITH, Primary Examiner

J. L. GOODROW, Assistant Examiner

U.S. Cl. X.R.

96—1.8, 1.6

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,824,099 Dated July 16, 1974

Inventor(s) Robert Bruce Champ et al

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

In the Claims, Claim 1 should read as follows:

1. An electrophotographic plate comprising a conductive substrate, a layer comprising a squaric acid methine dye and a separate layer comprising a tri-aryl pyrazoline compound.

Signed and sealed this 22nd day of October 1974.

(SEAL)

Attest:

McCOY M. GIBSON JR.  
Attesting Officer

C. MARSHALL DANN  
Commissioner of Patents