

[54] **PHOTOSENSITIVE MATERIAL
COMPRISING BENZOPYRYLIUM DYE
SENSITIZER**

3,600,179 8/1971 Yamada et al..... 96/90 R
3,607,266 9/1971 Yamada et al..... 96/90 R
3,300,314 1/1967 Rauner et al. 96/90 R

[75] Inventors: **Takamiti Enomoto; Toshiyuki
Kawanishi; Akiyoshi Yasumori;
Tsuyoshi Shiga; Yujiro Hirose;
Tomio Kubota**, all of Tokyo, Japan

Primary Examiner—Ronald H. Smith
Attorney—Henry T. Burke et al.

[73] Assignee: **Ricoh, Co., Ltd.**, Tokyo, Japan

[22] Filed: **Dec. 23, 1971**

[21] Appl. No.: **211,743**

[30] **Foreign Application Priority Data**

Dec. 28, 1970 Japan..... 45/125987

[52] **U.S. Cl.** **96/90 R, 96/115 P, 204/159.23**

[51] **Int. Cl.**..... **G03c 1/70**

[58] **Field of Search**..... **96/115 P, 90 R;
204/159.23**

[56] **References Cited**

UNITED STATES PATENTS

3,503,745 3/1970 Yamada et al..... 96/90 R

[57] **ABSTRACT**

A photosensitive material for producing a photographic recording material, comprising a resinous binder solution containing dispersed therein a photo-polymerizable N-vinyl monomer, a photo-active agent and a dye sensitizer, said dye sensitizer consisting essentially of a salt selected from the group consisting of (1) a benzopyrylium salt and (2) a double complex salt consisting essentially of said benzopyrylium salt and a decolorized derivative of said benzopyrylium salt.

6 Claims, No Drawings

PHOTOSENSITIVE MATERIAL COMPRISING BENZOPYRYLIUM DYE SENSITIZER

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a photosensitive material for producing a photographic recording material useful in the reproduction of an original image thereon by photopolymerization.

2. Description of the Prior Art

It is widely known to form photographic images by reactions caused by the effect of a light. Particularly a research on photo polymerization has of late been conducted wherein free radicals are produced by means of irradiation by the light and these free radicals cause the polymerization of certain kinds of monomers. Based upon such research, applications in the field of image forming have been developed, for instance, an application in the preparation of a relief image. In these applications a number of photographic recording materials are known. Such photographic recording materials are obtained by forming a photosensitive layer on one of the surfaces of a support. The photosensitive layer is prepared by dispersing a photo-active agent, which produces free radicals by means of an action of a light, a photo-polymerizable monomer, which is polymerized in the presence of aforementioned free radicals, and a dye sensitizer, which promotes the photopolymerization, in a proper resinous binder solution. Either a positive or negative image can be formed on thus prepared photographic recording material by exposure to a mercury lamp as a light after having been fixed with a desired proper original image laid thereon, and then by being subjected to the heat treatment. According to the U.S. Pat. No. 3,503,745 specification and the Japanese Patent Publication No. 45-13258, for instance, photographic recording materials are specified, wherein, as for the monomer used in the preparation of photosensitive layer, a vinyl monomer (for instance, vinyl-carbazole and vinylindole) comprising a heterocyclic ring which has at least one nitrogen atom in its composing molecules is used; as for the photo-active agent, an aliphatic hydrocarbon halide (for instance, carbon tetrabromide, ethane hexabromide, bromoform, iodoform, etc.) is used; and as for the binder, such natural water soluble high polymeric substances as gelatin, casein, gum arabic, etc., such synthetic water soluble high polymeric substances as polyvinyl alcohol, polyacrylic acid, polyamide, etc., and copolymer of styrene-acrylic nitrile. The dye sensitizers which have hitherto been suggested to be used in the photosensitive layer of such photographic recording materials as mentioned above are generally obtainable on the market and include the following dyes: triphenylmethyl dyes (such as Malachite Green, Crystal Violet, etc.), Rhodamine B, Eosine B, Cyanin dyes (such as pinacyanol, Ethyl Red, Quinaldine Red, etc.), Styryl dyes [4-(p-dimethylaminostyryl)quinoline, etc.], Acridine dyes, Thiazine dyes, etc. Rhodamine B and Styryl dyes are said to be most satisfactory. However, the performance of the aforementioned dye sensitizers are not completely satisfactory in meeting the requirements of photographic recording materials.

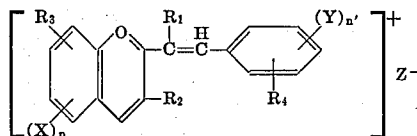
SUMMARY OF THE INVENTION

The present invention provides photosensitive materials for producing photographic recording materials

having improved properties due to the use of novel dye sensitizers.

The dye sensitizers utilized in the photosensitive products of the present invention are salts selected from the group consisting benzopyrylium salts having a chemical structure expressed by formula-(I) and double complex salts formed as reaction products of said benzopyrylium salts and decolorized derivatives thereof having a chemical structure expressed by the formula-(II).

Formula-(I)



wherein

X is a radical selected from the group consisting of hydrogen, halogen, nitro radical and nitrile radical;

Y is a radical selected from the group consisting of hydrogen, halogen, nitro radical, nitrile radical and carboxyl radical;

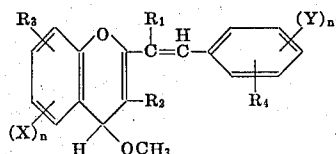
R₁ is a radical selected from the group consisting of hydrogen and alkyl radicals having 1 to 4 carbon atoms;

R₂ is a radical selected from the group consisting of hydrogen and phenyl radical;

R₃ and R₄ each is a radical selected from the group consisting of hydrogen, alkyl radicals having 1 to 2 carbon atoms and alkoxy radicals having 1 to 2 carbon atoms;

n and n' each is an integer of 1 to 2; and Z⁻ is an anionic functional group.

Formula-(II)



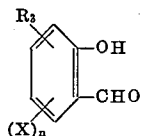
wherein X, Y, R₁, R₂, R₃, R₄, n and n' each is identical with that of the aforesaid formula-(I).

These dye sensitizers comprising a benzopyrylium salt or a double complex salt consisting essentially of said benzopyrylium salt and its decolorized derivative have properties which remarkably contribute to the improvement of photo sensitivity of the photosensitive layer extending over a very wide region of wave length ranging approximately from 400 mμ to 800 mμ. They are crystalline substances which are violet — bluish violet — blue in color when dissolved in an organic solvent.

A benzopyrylium salt having a chemical structure expressed by the formula-(I), which can be used as a dye sensitizer by itself and a partner component of a complex dye sensitizer as well, is synthetically prepared as described below:

The benzopyrylium salt having the formula-(I) is prepared by reacting a substituted 2-hydroxybenzaldehyde having the formula-(II')

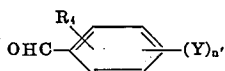
3



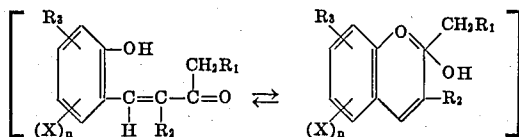
where R_3 , X and n are as defined above with an acetone derivative having the formula-(III)



where R_1 and R_2 are the same radicals as R_1 and R_2 in the formula-(I), in an acid reaction solvent at $-10^\circ - 30^\circ\text{C}$, preferably at $0^\circ - 20^\circ\text{C}$, and thereafter reacting the reaction product in the same reaction system with an aldehyde having the formula . . . (IV)



where R_4 , Y and n' are as defined above and then by adding an acid having the desired anion functional group to the same reaction system. Of the aforementioned series of reactions, the reaction which takes place between the compounds having respectively the formula-(II') and (III) forms an aldehyde acetone derivative having the formula resonance structure with the formula-(V)



where R_1 , R_2 , R_3 , X and n are as defined above. By adding aldehyde having the formula-(IV) to the previous product, a condensation cyclic reaction takes place. As for the mineral acid, hydrochloric acid is used; and for the solvent, such organic acids as formic acid, acetic acid, etc., are used. The quantity of the mineral acid added in this reaction is from 2 to 6 moles per mole of substituted 2-hydroxybenzaldehyde.

The anionic functional group which corresponds to Z^- in the formula-(I) can be obtained either by selecting the acid which is introduced at the time of the condensation cyclic reaction or by reacting an acid or a salt having the desired functional group with the product mentioned above. Typical acids or salts for this reaction include perchloric acid, periodic acid, phosphoric acid, hydrochloric acid, sulfuric acid, oxalic acid, sodium borofluoride, potassium iodide, sodium iodide, potassium bromide, sodium bromide, dimethylphosphate, diphenylphosphate, etc.

Compounds within the scope of formulas (II), (III) and (IV) are obtained by known methods and are also available commercially. For instance, the substituted 2-hydroxybenzaldehyde having the formula-(II') can be readily prepared, either by chlorinating or brominating the corresponding aldehyde or by formylating phenols. The substituted 2-hydroxybenzaldehyde thus prepared may be reacted with the acetone derivative having the formula-(III) in a mixed acid consisting of acetic acid and formic acid, or with the addition of any of the aforementioned acids, in the presence of a mineral acid or acids. The over-all reaction required for the preparation of the benzopyrylium salts can be con-

4

ducted in succession in one reactor at room temperature.

The decolorized derivatives which form the double complex salts of the present invention are prepared by refluxing a benzopyrylium salt of formula-(I), in an alkaline solvent, for instance, a mixed solvent of methanol-benzene containing sodium bicarbonate. The solution is then concentrated and the reaction product is poured into a mixture of crashed ice and water to precipitate the crystals. The amount of alkali such as sodium bicarbonate and sodium carbonate employed is from 60 to 80 wt. percent based on the weight of the reactants.

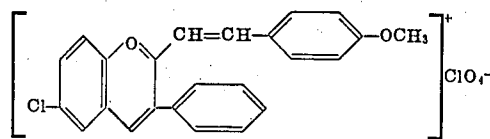
Since more than 1 liter of methanol is required to dissolve about 10 g of the benzopyrylium salt having the formula-(I), the subsequent reactions are necessarily conducted in a large reactor and the method presents many difficulties in separating the reaction product from the solvent. However, with the use of the aforementioned mixed solvent, the reaction of form the decolorized derivative can be readily conducted in a small quantity of reaction solvent thus avoiding many of the difficulties.

The double complex salt consisting essentially of the benzopyrylium salt and its decolorized derivative is prepared by means of a chemical reaction wherein the decolorized derivative obtained according to the aforementioned method and indicated by the formula-(II) is admixed with the benzopyrylium salt having the formula-(I) and reacted in a suitable solvent. The resultant double complex salt demonstrates excellent sensitivity when used in the photosensitive materials. Reaction solvents utilized in combining a decolorized derivative having the formula-(II) with a benzopyrylium salt having the formula-(I), may be selected from the group consisting of dichloroethane, toluene, xylene and tetrahydrofuran. The reaction takes place under reflux conditions at a temperature from 50° to 150°C , preferably at $50^\circ - 60^\circ\text{C}$. After completion of the reaction, the solvent is removed by distillation under reduced pressure and the reaction product is added to ether to precipitate the desired crystalline product.

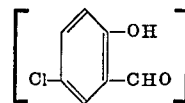
The following detailed explanation illustrates the synthesis of benzopyrylium salts and their decolorized derivatives.

EXAMPLES OF SYNTHESIZING THE BENZOPYRYLIUM SALTS

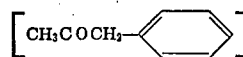
A. Synthesis of 2-p-methoxystyryl-3-phenyl-6-chlorobenzopyrylium perchlorate having the formula:



12 g of 2-hydroxy-5-chlorobenzaldehyde

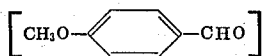


was added to 11 g of phenylacetone



5

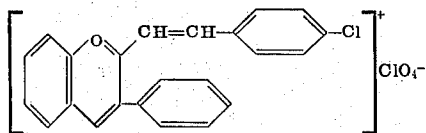
and was dissolved with the use of 45 ml of formic acid. 30 ml of 35 percent hydrochloric acid was added to this solution with swirling at a room temperature over a period of 20 - 30 minutes. After the completion of the addition, the stirring was continued for another two hours and then 12 g of p-anisaldehyde



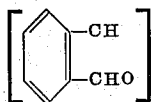
and 50 ml of formic acid were added. 10 ml of 35 percent hydrochloric acid was added dropwise over a period of about 20 minutes. The mixture was stirred for an hour and was left standing overnight. The reaction mixture thus prepared was added dropwise to 180 ml of 15 percent HClO_4 which had been cooled to 10°C or below with stirring during a period of about 2 hours. The resultant precipitate was filtered by suction and was washed with 300 - 400 ml of ethyl ether. Recrystallization was effected with acetic acid to obtain 15 g of desired crystalline product. The melting point of this product ranged between 214° and 216°C .

The absorption maximum wave length (λ max) measured with the product in dichloroethane solution was 577 $\text{m}\mu$.

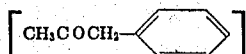
B. Synthesis of 2-p-chlorostyryl-3-phenyl benzopyrylium perchlorate having the formula:



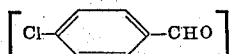
A mixture of 10 g of 2-hydroxybenzaldehyde



and 11 g of phenylacetone



was dissolved in 45 ml of formic acid, into which solution 30 ml of 35 percent hydrochloric acid was added with stirring at room temperature over a period of 20 - 30 minutes. After the addition was completed, the stirring was continued for another two hours. 11.5 g of p-chlorobenzaldehyde

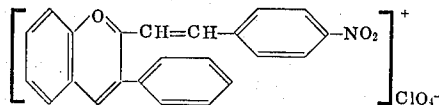


and 50 ml of formic acid were added to the preceding solution, and 10 ml of 35 percent hydrochloric acid was added at room temperature over a period of about 20 minutes. The stirring was then continued for one hour and the solution was left standing overnight. The reaction mixture was added to 180 ml of 15 percent HClO_4 which had been cooled to 10°C or below with stirring over a period of approximately two hours. The precipitate was filtered with suction and washed with 300 - 400 ml of ethyl ether. The desired crystalline product weighing 6 g in weight was obtained. The melting point

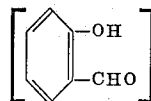
6

of this product was 211°C and the measurement of its maximum wave length (λ max) in dichloroethane solution showed the value of 510 $\text{m}\mu$.

C. Synthesis of 2-p-nitrostyryl-3-phenyl benzopyrylium perchlorate having the formula:



A mixture of 10 g of 2-hydroxybenzaldehyde

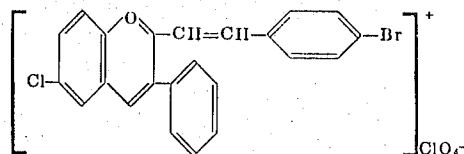


and 11 g of phenyl acetone was dissolved in 45 ml of formic acid, into which solution 30 ml of 35 percent hydrochloric acid was added with stirring at room temperature over a period of 20 - 30 minutes. When the addition was complete, stirring was continued for an additional two hours. 12.4 g of p-nitrobenzaldehyde

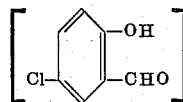


and 50 ml of formic acid were added, followed by the addition of, 10 ml of 35 percent hydrochloric acid at room temperature over 20 minutes. The stirring was continued for one hour and the mixture was left standing overnight. The reaction mixture thus obtained was added to 180 ml of 15 percent HClO_4 which had been cooled to 10°C or below with stirring during a period of approximately for two hours. The precipitate was filtered with suction and was washed with 300 - 400 ml of ethyl ether. 11 g of the desired crystalline product having the melting point of $159^\circ - 160^\circ\text{C}$ was obtained. 0.453 mg of the product thus prepared was dissolved in 100 ml of dichloroethane and a maximum wave length (λ max) of 480 $\text{m}\mu$ was observed.

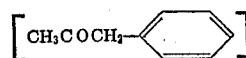
D. Synthesis of 2-p-bromostyryl-3-phenyl-6-chlorobenzopyrylium perchlorate having the formula:



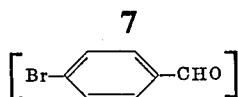
A mixture of 12 g of 2-hydroxy-5-chlorobenzaldehyde



and 11 g of phenylacetone



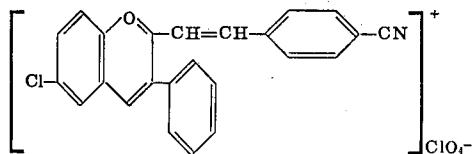
was dissolved in 45 ml of formic acid, and 30 ml of 35 percent hydrochloric acid was added at room temperature over a period of 20 - 30 minutes. After the addition was completed, stirring was continued for an additional two hours. Then 16 g of p-bromobenzaldehyde



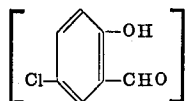
and 50 ml of formic acid were added, and 10 ml of 35 percent hydrochloric acid was dropped into the mixture at room temperature over a period of approximately for 20 minutes. Another one-hour stirring followed and the mixture was left standing for one night. The reaction mixture thus prepared was added to 180 ml of 15 percent HClO_4 , which had been cooled to 10°C or below with stirring for nearly two hours. The precipitate formed in the mixture and was recovered by suction. It was washed with 300 - 400 ml of ethyl ether. 4 g of the desired crystalline product having a melting point of $228^\circ - 230^\circ\text{C}$ was obtained.

Its absorption maximum wave length (λ_{max}) was $525 \text{ m}\mu$.

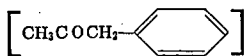
E. Synthesis of 2-p-cyanostyryl-3-phenyl-6-chlorobenzopyrylium perchlorate having the formula:



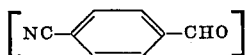
A mixture of 12 g of 2-phdroxy-5-chlorobenzaldehyde



and 11 g of phenylacetone



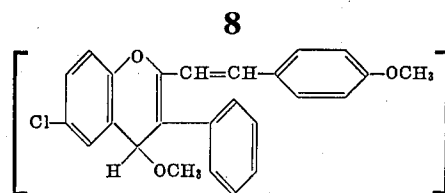
was dissolved in 45 ml of formic acid, to which solution 30 ml of 35 percent hydrochloric acid was added at room temperature with stirring over a period of 20 - 30 minutes. After the addition was complete, the stirring was continued for another two hours and 11.5 g of p-cyanobenzaldehyde



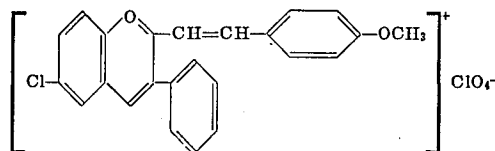
and 100 ml of formic acid were added. 10 ml of 35 percent hydrochloric acid was added dropwise at room temperature. This was followed by the one-hour stirring and the mixture was left standing overnight. The reaction mixture thus prepared was added to 180 ml of 15% HClO_4 , which had been cooled to 10°C or below, with stirring over a period of about two hours. The precipitate thus formed was recovered by suction and 3.5 g of the desired crystalline product with a melting point of $212^\circ - 214^\circ\text{C}$ was obtained. The product was dissolved in dichloroethane to measure its absorption maximum wave length (λ_{max}) which was $532 \text{ m}\mu$.

EXAMPLES OF SYNTHESIZING THE DECOLORIZED DERIVATIVES FROM THE BENZOPYRYLIUM SALTS

A. Synthesis of 2-p-methoxystyryl-3-phenyl-4-methoxy-6-chloro-1.4-benzopyran having the formula:



10.8 g of 2-p-methoxystyryl-3-phenyl-6-chlorobenzopyrylium perchlorate having the formula



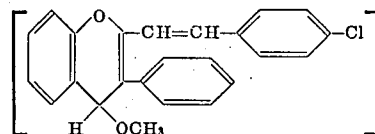
and 15 g of sodium hydrogencarbonate were mixed with 50 ml of methanol and 100 ml of benzene and the mixture was heated for about one hour, during which time the color of the reaction mixture turned from purple to yellow. After the reaction matter was cooled, it was subjected to the filtration by means of suction. The mother liquor was concentrated under reduced pressure. The residue was dissolved and extracted with methanol and was then poured into the mixture of crashed ice and water to separate the desired product as light yellow crystals which were recovered by suction and dried under reduced pressure after washing with water. The crystals thus obtained melted at $74^\circ - 76^\circ\text{C}$. The results of its elemental analysis were as follows:

theoretical values: H 5.19%, C 74.41%, Cl 8.78%

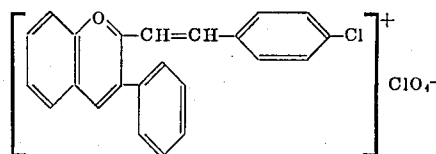
experimental values: H 5.32%, C 74.56%, Cl 8.50%

Its absorption maximum wave length (λ_{max}) in dichloroethane solution was $420 \text{ m}\mu$ and the molar extinction coefficient was found to be 3.47×10^4 . The desired product was obtained almost quantitatively.

B. Synthesis of 2-p-chlorostyryl-3-phenyl-4-methoxy-1.4-benzopyran having the formula:



10 g of 2-p-chlorostyryl-3-phenylbenzopyrylium perchlorate,



and 15 g of sodium carbonate was added to 50 ml of methanol and 100 ml of benzene and the mixture was heated for about one hour. The reaction mixture was cooled and filtered by suction. The filtrate was concentrated under decreased pressure. The residue was dissolved and extracted with methanol and was poured into a mixture of crashed ice and water, to separate the product as light yellow crystals. It was recovered by suction, washed thoroughly, and dried under decreased pressure to obtain 7.5 g of the desired product. The melting point of the crystals

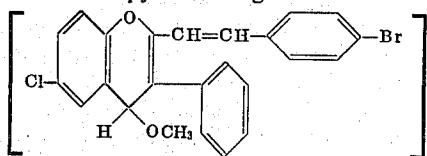
thus obtained was 70.5°C. The results of elemental analysis were as follows:

theoretical values: H 5.07%, C 76.90%, Cl 9.48%

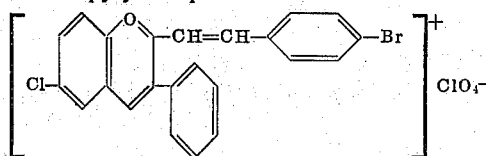
experimental values: H 5.21%, C 76.83%, Cl 9.67%

The absorption maximum wave length (λ_{max}) measured in dichloroethane solution was 310 $m\mu$ and the molar extinction coefficient was 1.02×10^4 .

C. Synthesis of 2-p-bromostyryl-3-phenyl-4-methoxy-6-chloro-1,4-benzopyran having the formula:



10 g. of 2-p-bromostyryl-3-phenyl-6-chlorobenzopyrylium perchlorate



and 15 g of sodium bicarbonate were added to 50 ml of methanol and 100 ml of benzene and the mixture was heated for one hour. The reaction mixture was cooled, filtrated by suction, and the filtered was concentrated under reduced pressure. The residue was dissolved in methanol and poured into a mixture of crashed ice and water to separate light yellow crystals. The mixture containing the crystals was filtered with suction. The precipitate was thoroughly washed, and dried under reduced pressure to obtain the desired crystalline product quantitatively, with a melting point of 80° - 82°C. As the result of elemental analysis, the following values were obtained:

theoretical values: H 3.97%, C 63.51%, Br 17.86%, Cl 7.82%

experimental value: H 3.75%, C 63.32%, Br 17.60%, Cl 8.06%

The measurement made with the product dissolved in dichloroethane showed that the absorption maximum wave length (λ_{max}) was 324 $m\mu$ and the molar extinction coefficient 1.57×10^4 .

EXAMPLES OF SYNTHESIZING THE DOUBLE COMPLEX SALTS

A decolorized derivative was prepared from 10.8 g of 2-p-methoxystyryl-3-phenyl-6-chlorobenzopyrylium-

perchlorate according to the method explained in the foregoing examples. To the yellow viscous liquid obtained by concentration under reduced pressure was added 4.2 g of 2-p-methoxystyryl-3-phenyl-6-methoxybenzopyrylium perchlorate and 150 ml of dichloroethane. The mixture was refluxed at 50° to 60°C for the period of five hours. About 100 ml of dichloroethane was then removed by reduced pressure distillation and the residual liquid (about 50 ml) was cooled to room temperature. It was then mixed in small portions with approximately 300 ml of ether to separate crystals of the desired complex dye. The mixture was left standing for about 30 minutes and was filtered with suction. The crystals were then dried under reduced pressure.

The crystals thus obtained had a melting point of 208° - 210°C and its dichloroethane solution was blue. When the spectral absorption spectrum was measured in dichloroethane solution of 1×10^{-8} mol/ml concentration, the absorption maximum wave length (λ_{max}) was in the range between 581 $m\mu$ and 657 $m\mu$.

A number of the benzopyrylium salts having the formula-(I) as indicated in Table-1 and a number of the decolorized derivatives having the formula-(II) as indicated in Table-1 were prepared according to the aforesaid procedures. Additionally, a number of the double complex salts as indicated with No. 1 to No. 16 in Table-1 were prepared by the following procedure.

To the benzopyrylium salts were added each of the concentrates (yellow viscous liquid substances) obtained in the syntheses of the decolorized derivatives in the ratio of from 1.7 to 2.5 parts by weight per one part by weight of said benzopyrylium salt. The resultant mixtures were each added to 150 ml of dichloroethane and then refluxed at the temperature between 50° and 60°C for 5 hours. About 100 ml of dichloroethane contained in the respective reaction products were removed with reduced pressure distillation and the residual liquids (about 50 ml) were each cooled to room temperature and then mixed in small portions with approximately 300 ml of ether to separate crystals of the desired double complex salts. The mixtures were left standing for about 30 minutes and then filtered with suction. The crystals were then dried under reduced pressure.

The double complex salts thus obtained and their properties are summarized in Table-1. The colors indicated in Table-1 are colors of the dichloroethane solutions containing the aforesaid double complex salts.

TABLE 1

| Complex dye | Compound structure | | λ_{max} ($m\mu$) | $\epsilon/10^4$ | Color of solution |
|-------------|--|---|----------------------------|-----------------|-------------------|
| | Compounds belonging to Formula (I) | Compounds belonging to Formula (II) | | | |
| 1..... | 2-p-methoxystyryl-3-phenyl-6-chlorobenzopyrylium perchlorate. | Discolored 2-p-methoxystyryl-3-phenyl-6-methoxybenzopyrylium perchlorate. | 538 | 2.34 | Blue. |
| 2..... | 2-p-methoxystyryl-3-phenyl-6-methoxybenzopyrylium perchlorate. | Discolored 2-p-methoxystyryl-3-phenyl-6-chlorobenzopyrylium perchlorate. | 668 | 5.82 | |
| 3..... | 2-p-methoxystyryl-3-phenyl-6-chlorobenzopyrylium perchlorate. | Discolored 2-p-methoxystyryl-3-phenylmethylbenzopyrylium perchlorate. | 581 | 8.98 | Do. |
| | | | 657 | 2.98 | |
| 4..... | 2-p-methoxystyryl-3-phenyl-6-methylbenzopyrylium perchlorate. | Discolored 2-p-methoxystyryl-3-phenyl-6-chlorobenzopyrylium perchlorate. | 516 | 2.97 | Do. |
| | | | 606 | 5.03 | |
| 5..... | 2-p-methoxystyryl-3-phenyl-6-methoxybenzopyrylium perchlorate. | Discolored 2-p-nitrostyryl-3-phenylbenzopyrylium perchlorate. | 652 | 8.67 | Do. |
| | | | 528 | 2.90 | |
| 6..... | 2-p-nitrostyryl-3-phenylbenzopyrylium perchlorate. | Discolored 2-p-methoxystyryl-3-phenyl-6-methoxybenzopyrylium perchlorate. | 658 | 6.81 | Do. |
| | | | 450 | 9.28 | |
| 7..... | 2-p-nitrostyryl-3-phenylbenzopyrylium perchlorate. | Discolored 2-p-methoxystyryl-3-phenyl-6-methoxybenzopyrylium perchlorate. | 576 | 6.86 | Violet. |
| | | | 448 | 0.95 | |
| 8..... | 2-p-nitrostyryl-3-phenylbenzopyrylium perchlorate. | Discolored 2-p-nitrostyryl-3-phenylbenzopyrylium perchlorate. | 579 | 8.48 | Do. |
| | | | 567 | 6.13 | |
| 9..... | 2-p-nitrostyryl-3-phenylbenzopyrylium perchlorate. | Discolored 2-p-methoxystyryl-3-phenyl-6-methylbenzopyrylium perchlorate. | 640 | 8.38 | Reddish violet. |
| | | | 567 | 7.56 | |
| 10..... | 2-p-chlorostyryl-3-phenylbenzopyrylium perchlorate. | Discolored 2-p-methoxystyryl-3-phenyl-6-methoxybenzopyrylium perchlorate. | 648 | 1.22 | Violet. |
| | | | 581 | 4.62 | |
| | 2-p-chlorostyryl-3-phenylbenzopyrylium perchlorate. | Discolored 2-p-chlorostyryl-3-phenylbenzopyrylium perchlorate. | 643 | 2.65 | Bluish violet. |
| | | | 580 | 5.68 | |
| | | | 650 | 2.85 | Do. |

TABLE 1—Continued

| Complex dye | Compound structure | | λ max. (m μ) | Color of solution |
|-------------|--|---|---------------------------|----------------------|
| | Compounds belonging to Formula (I) | Compounds belonging to Formula (II) | | |
| 11..... | 2-p-methoxystyryl-3-phenyl-6-methylbenzopyrylium perchlorate. | Discolored 2-p-chlorostyryl-3-phenylbenzopyrylium perchlorate. | 485 571 643 | 2.63 5.61 3.80 |
| 12..... | 2-p-chlorostyryl-3-phenylbenzopyrylium perchlorate. | Discolored 2-p-methoxystyryl-3-phenyl-6-methylbenzopyrylium perchlorate. | 589 647 | 7.59 3.81 |
| 13..... | 2-p-carboxystyryl-3-phenylbenzopyrylium perchlorate. | Discolored 2-p-methoxystyryl-3-phenyl-6-methoxybenzopyrylium perchlorate. | 514 654 | 2.46 8.60 |
| 14..... | 2-p-methoxystyryl-3-phenyl-6-methoxybenzopyrylium perchlorate. | Discolored 2-p-carboxystyryl-3-phenylbenzopyrylium perchlorate. | 510 654 | 2.36 8.26 |
| 15..... | 2-p-carboxystyryl-3-phenylbenzopyrylium perchlorate. | Discolored 2-p-methoxystyryl-3-phenyl-6-methylbenzopyrylium perchlorate. | 536 661 | 3.11 7.46 |
| 16..... | 2-p-methoxystyryl-3-phenyl-6-methylbenzopyrylium perchlorate. | Discolored 2-p-carboxystyryl-3-phenylbenzopyrylium perchlorate. | 524 656 | 2.88 7.61 |

The present invention provides photosensitive materials comprising a resinous binder solution for producing a photographic recording material wherein a dye sensitizer comprising either a benzopyrylium salt which is obtained according to the aforementioned synthetic method or its double complex salt dye sensitizer is utilized in the place of previously known dye sensitizers such as Rhodamine B or Styryl dye which have been used in conventional photographic recording materials. The supports, photo-active agents, vinyl monomers, and other materials such as solvents utilized in this invention are which have been conventionally employed. Binders utilized in this invention are not necessarily limited to water soluble resins, but include various kinds of resins and natural high polymeric substances. Typical examples include, cellulose acetate, cellulose acetate propionate, ethylcellulose, cellulose nitrate, polyvinylchloride, polyvinylidene chloride, polyvinylacetate, polyvinyl acetal, polyvinyl alcohol, polymethyl methacrylate, polystyrene, rubber hydrochloride, gelatin, casein, carboxymethyl cellulose gum arabic, etc. Useful photo-active agents (radical generators) include, in addition to the conventional aliphatic halides, such alicyclic compounds as benzene hexachloride, etc., and an aromatic halides such as polychlorobiphenyl, etc. Typical photo-active halides include those selected from the group consisting of chloroform, carbon tetrachloride, carbon tetrabromide, iodoform, hexachloroethane, hexachlorobenzene, tetrabromobutane, tetrachlorotetrahydronaphthalene and polychlorobiphenyl.

With respect to a photo-polymerizable N-vinyl monomer, any of monomers such as N-vinylindole, N-vinylcarbazole, N-vinyl-phenyl- α -naphthylamine, N-vinylpyrrole, N-vinylpyrrolidone, N-vinyldiphenylamine, N-vinylsuccinimide, N-vinylphthalimide, N-vinyl-N-phenylacetamide, N-vinyl-N-methylacetamide, N-vinyl-diglycollylimide and 3,6-dibromo-N-vinylcarbazole, can be used in the present invention.

Typical liquids which serve as solvents or dispersion media for use in the invention include water, methyl-ethylketone, ethylacetate, acetone, toluene, trichloroethylene and methylalcohol.

According to the present invention, when a photosensitive material comprising a resinous binder solution containing the aforementioned resinous binder and photosensitive materials is applied to the surface of a support, made of film or paper to form a photosensitive layer, a transparent photosensitive film or photosensitive recording paper of light yellow — light bluish violet color is obtained and its sensitivity is much better than conventional ones as seen from the examples.

The color tone of the image developed on the photographic recording material made of the photosensitive material of the present invention wherein the photosensitive material prepared according to the present invention varies depending upon the kind of the resinous binder admixed with the aforementioned photosensitive materials. For instance, in case where gelatin is used as a resinous binder, the developed image takes on a color tone of deep reddish purple; in case where polystyrene, ethyl cellulose, cellulose nitrate, rubber hydrochloride, cellulose acetate, polyvinylchloride, cellulose acetate propionate and polyvinylidene chloride are used, the developed image develops the color tone of greenish brown or blackish green. When polyvinyl acetate is used, the developed image presents the light brown color tone; and when polymethylmethacrylate is used, the developed image shows the color tone of light grey.

As for the composition of the photosensitive material according to the present invention, it is preferable to employ the resinous binder in the range between 50 and 100 parts by weight in a proper solvent, a photo-active agent between 5 and 100 parts by weight, and a dye sensitizer between 0.001 and 1.0 part by weight respectively per 100 parts by weight of N-vinyl monomer contained in said proper solvent.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A number of Examples of the invention will now be described: Example 1.

10 g of gelatin were dissolved uniformly in 50 ml of water at approximately 50°C, to which 5 g of N-vinylcarbazole monomer (manufactured by Nippon Shokubai Kabushiki Kaisha or Japan Catalyst Mfg. Co., Ltd.) and 0.1 g of complex dye sensitizer No. 1 in Table 1 were added little by little and the mixture was stirred. After this solution was heated up to approximately 70°C, 1 g of carbon tetrabromide was added to the solution and then it was stirred about two minutes. The suspension thus prepared was applied to the surface of a polyester film to form a light-yellow photosensitive layer of a thickness of 5 μ — 10 μ , and dried in the darkness to obtain a photographic recording material.

An original image was placed on this photographic recording material, and was exposed to the high voltage mercury lamp of 300 W for 30 seconds. It was then heated at a temperature between 60° and 70°C for one minute. A deep reddish-purple image was formed thereon exactly opposite to those of the original image.

For comparison, a control photosensitive recording material was prepared according to the same method except for the use of Rhodamine B in the place of the dye sensitizer No. 1. It required about five minutes ex-

posure to the light source to obtain the same density of the reproduced image as was obtained with the photosensitive recording material according to the present invention.

When any of bromoform, chloroform and iodoform were utilized in the place of carbon tetrabromide in the preparation of the aforementioned photographic recording material according to this invention, the said

spective materials were processed to prepare the photographic recording materials with the same process described in Example 1. Table-II shows the results of the color-tone observations obtained from the respective photographic recording materials operated for copying in the same copying procedure used in Example, except that exposing times shown in Table-II were employed.

TABLE II

| Example | Composition of photosensitive material | | | | | Exposing time (sec.) | Color tone of image area | Color tone nonimage area |
|---------|--|-------------------------------------|---------------------------|------------------------------------|--------------------------|----------------------|--------------------------|--------------------------|
| | Resinous binder (g.) | N-vinyl monomer (g.) | Photo-active agent (g.) | Dye sensitizer (mg.) | Solvent (ml.) | | | |
| 5 | Gelatin (10) | 3,6-dibromo-N-vinyl carbazole (5.0) | Carbon tetrabromide (1.0) | No. 6 sensitizer in Table 1 (0.1) | Water (50) | 25 | Light yellow. | Deep reddish purple. |
| 6 | Polyvinylidene chloride (5.0) | 3,6-dibromo-N-vinyl carbazole (5.0) | Chloroform (1.0) | No. 12 sensitizer in Table 1 (20) | Methyl ethyl ketone (20) | 30 | do | Greenish brown. |
| 7 | Cellulose acetate propionate (1.0) | 3,6-dibromo-N-vinyl carbazole (1.0) | Iodoform (0.2) | No. 13 sensitizer in Table 1 (5.0) | Ethyl acetate (9.0) | 30 | Light yellowish green. | Blackish green. |

result was obtained. When a sheet of baryta paper was used as a support instead of the polyester film, a similar result was obtained. Example 2.

5 g of polyvinylidene chloride were dissolved in 20 ml of methylethylketone, to which 5 g of N-vinyl carbazole monomer and 20 mg of the complex dye sensitizer No. 4 shown in Table-1. The same procedures were used as in Example 1 to obtain a photographic recording material. A greenish-brown image was produced in the photosensitive layer of the resultant photographic recording material when developed by the same method as that of Example 1.

Example 3.

1 g of N-vinylcarbazole, 0.2 g of iodoform and 5 mg of the complex dye sensitizer No. 5 shown in Table-1 were added to 10 g of 10 percent ethyl acetate solution of cellulose acetate propionate. The succeeding procedures were as described in Example 1 to obtain a photographic recording material having a light yellowish green photosensitive layer. Another photographic recording material was also prepared by using the same quantity of bromoform instead of the aforementioned iodoform. These photographic recording materials respectively reproduced a blackish green image thereon whose density was the same as the one reproduced on the conventional photographic recording material in which Rhodamine B was used, despite the fact that the exposure was reduced by 1/5 to 1/10.

Example 4.

The photographic recording materials were prepared by using the respective benzopyrylium salts obtained according to the aforementioned examples (A) through (E) for preparing the benzopyrylium salts in the place of the respective complex dye sensitizers which were used as a dye sensitizer in Examples 1 - 3 with similar conditions and procedures. The photographic recording materials thus prepared showed substantially the same developed image color tones and performances as those obtained in the Example 1 - 3 respectively.

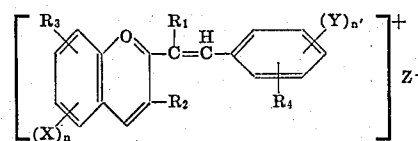
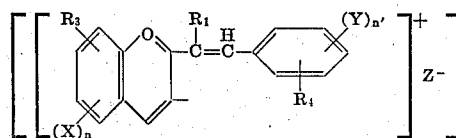
Examples 5, 6 and 7

Examples of 3 kinds of photographic recording materials according to the present invention are shown in the following Table-II.

The photosensitive materials having the compositions shown in Table-II were prepared and then the re-

We claim:

1. A photosensitive material for producing a photographic recording material, comprising a resinous binder solution containing dispersed therein a photo-polymerizable N-vinyl monomer, a photo-active halide which produces free halogen radicals when exposed to light and a dye sensitizer, said dye sensitizer consisting essentially of a salt selected from the group consisting of (1) benzopyrylium salts having a chemical structure expressed by the formula-(1)



wherein

X is a radical selected from the group consisting of hydrogen, halogen, nitro radical and nitrile radical;
Y is a radical selected from the group consisting of hydrogen, halogen, nitro radical, nitrile radical and carboxyl radical;

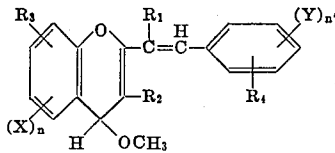
R₁ is a radical selected from the group consisting of hydrogen and alkyl radicals having 1 to 4 carbon atoms;

R₂ is a radical selected from the group consisting of hydrogen and phenyl radical;

R₃ and R₄ each is a radical selected from the group consisting of hydrogen, alkyl radicals having 1 to 2 carbon atoms and alkoxy radicals having 1 to 2 carbon atoms; n and n' each is an integer of 1 to 2; and Z⁻ is an anionic functional group; and

(2) double complex salts consisting essentially of said benzopyrylium salt and a decolorized derivative having a chemical structure expressed by the formula-(II)

15



wherein X, Y, R₁, R₂, R₃, R₄, n and n' are as defined above.

2. A photosensitive material according to claim 1, in which said photo-polymerizable N-vinyl monomer is a member selected from the group consisting of N-vinylindole, N-vinylcarbazole, N-vinyl-phenyl- α -naphthylamine, N-vinylpyrrole, N-vinylpyrrolidone, N-vinyldiphenylamine, N-vinylsuccinimide, N-vinylphthalimide, N-vinyl-N-phenylacetamide, N-vinyl-N-methylacetamide, N-vinyldiglycolylimide and 3,6-dibromo-N-vinylcarbazole.

3. A photosensitive material according to claim 1, in which said photo-active halide is selected from the group consisting of chloroform, carbon tetrachloride, carbon tetrabromide, iodoform, hexachloroethane, hexachlorobenzene, tetrabromobutane, tetrachlorotetrahydronaphthalene and polychlorobiphenyl, and the amount of said photo-active halide contained in said resinous binder solution is in the range of from 5 to 100 parts by weight per 100 parts by weight of said N-vinyl

16

monomer contained in said resinous binder solution.

4. A photosensitive material according to claim 1, in which a resinous binder dissolved in said resinous binder solutions is a member selected from the group consisting of cellulose acetate, cellulose acetate propionate, ethylcellulose, cellulose nitrate, polyvinylchloride, polyvinylidene chloride, polyvinylacetate, polyvinyl acetal, polyvinyl alcohol, polymethyl methacrylate, polystyrene, rubber hydrochloride, gelatine, casein, carboxymethyl cellulose and gum arabi, and a mixing ratio of said resinous binder against said N-vinyl monomer contained in said resinous binder solution is in the range of from 50 to 500 parts by weight per 100 parts by weight of said N-vinyl monomer.

5. A photosensitive material according to claim 1, in which the amount of said salt dye sensitizer contained in said resinous binder solution is in the range of from 0.001 to 1.0 part by weight per 100 parts by weight of said N-vinyl monomer contained in said resinous binder solution.

6. A photosensitive material according to claim 1, in which a solvent used in said resinous binder solution is a member selected from the group consisting of water, methylethylketone, ethylacetate, acetone, toluene, trichloroethylene and methyl-alcohol.

* * * * *

30

35

40

45

50

55

60

65

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,775,130 Dated 11/27/73

Inventor(s) Takamiti Enomoto et al.

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

Column 14, the first formula should be deleted.

Signed and sealed this 16th day of April 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents