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Zographos et al.

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[45] **May 21, 1974**

[54] **PHOTOELECTROPHORETIC IMAGING PROCESS EMPLOYING NAPTHOFURANEDIONES**

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[73] Assignee: **Ciba-Geigy AG**, Basel, Switzerland

[22] Filed: **Dec. 13, 1971**

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[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** ..... **96/1.3**, 96/1 PE, 96/1 PC, 96/1.2, 96/1.5, 204/181 PE

[51] **Int. Cl.** **G03g 17/00**, G03g 5/00

[58] **Field of Search** ..... 96/1.5, 1.3, 1 PE, 1 PC; 252/501

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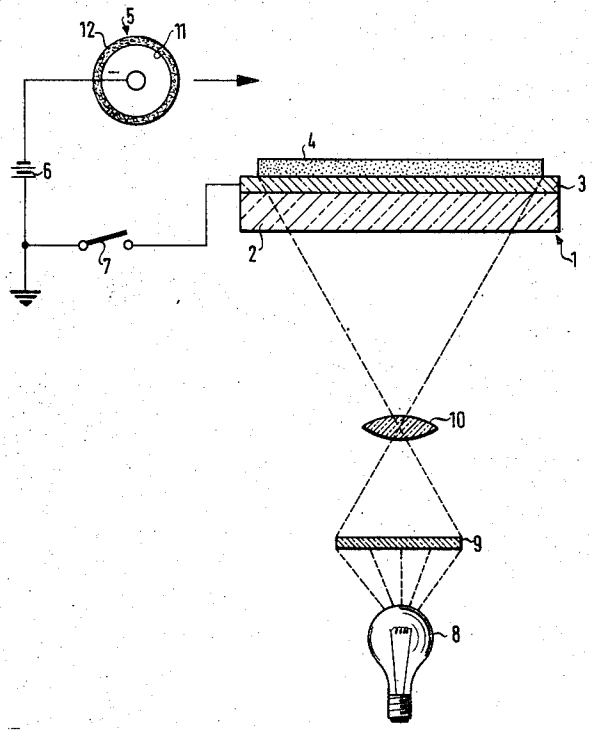
Primary Examiner—Norman G. Torchin

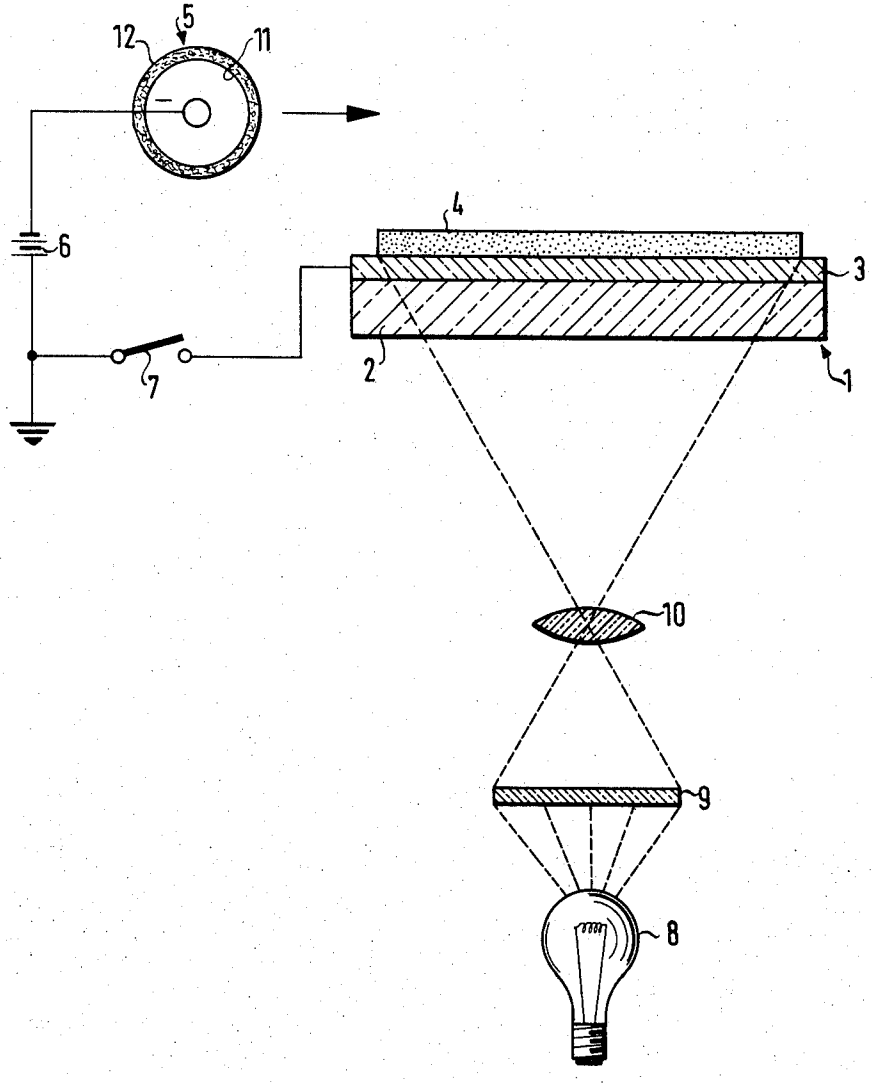
Assistant Examiner—John R. Miller

[57] **ABSTRACT**

Use of 4,4'-diamino-1,1'-dianthraquinonyl, naphthofuran-diones, quinophthalones and phthalimidopyrazolones in the photoelectrophoretic production of images.

4 Claims, 1 Drawing Figure

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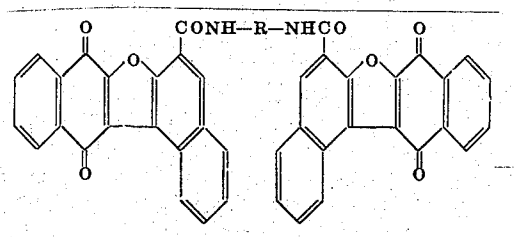
PHOTOELECTROPHORETIC IMAGING PROCESS EMPLOYING NAPTHOFURANEDIONES

It is known that single-colour and multi-colour reproductions can be produced electrophoretically by the use of photoconducting organic pigments. This system employs photoconducting particles and is described, for example, in U.S. Pat. Nos. 3,384,565, 3,384,566 and 3,385,480. In such a system for producing images, light-absorbing particles of different colours are suspended in a non-conducting liquid carrier. The suspension is introduced between electrodes, after which a potential is applied and an image is projected. Thereafter, an image is produced on one or both electrodes through migration of dyestuff particles in the electric field.

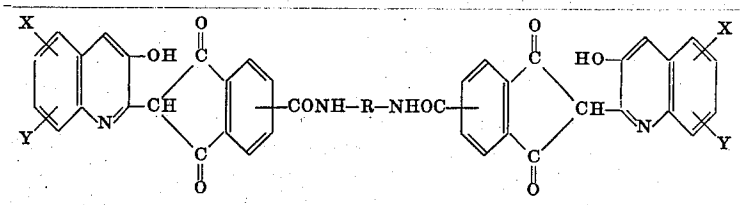
An essential component of the system are the suspended particles which must be electrically photosensitive. These particles evidently undergo a change in charge during irradiation with an activating electromagnet radiation, and in particular do so through interaction with one of the electrodes. In a monochromatic system, particles of a single colour are used, whereby a single-colour image is produced which is equivalent to a customary black and white image. In a polychromatic system, the images are produced in a natural colour, since mixtures of particles of two or more different colours each sensitive to light of a specific wavelength or of a narrow wavelength range, are used.

Hitherto, only few pigments are known which meet the high demands of the electrophoretic reproduction technique. This is because the dyestuffs in question must be distinguished by the following properties: pure colour shade, high colour strength and fastness to light, insolubility in water and organic solvents and high photosensitivity. Furthermore it is important that the maximum of the photosensitivity should lie as nearly as possible in the same wavelength range as the maximum of the light absorption. The dyestuffs must also be sufficiently transparent so that when three toners are superposed an intense, deep black is produced.

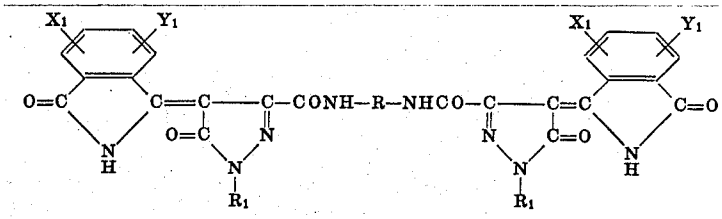
It has now been found that excellent results are obtained if the following dyestuffs are used: 4,4'-diamino-1,1'-dianthraquinonyl, as well as naphthofuranediones of the formula



wherein R denotes an arylene radical, or the quinophthalones of the formula

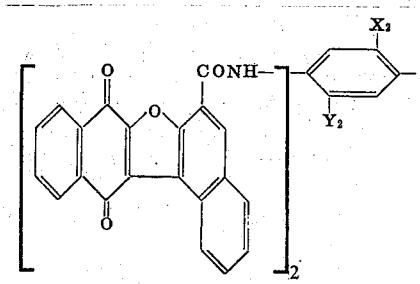


wherein R denotes an arylene radical, X and Y denote hydrogen or halogen atoms or alkyl or alkoxy groups, or X and Y together with two adjacent C atoms of the base substance can form a benzene ring, or phthalimidopyrazolones of the formula

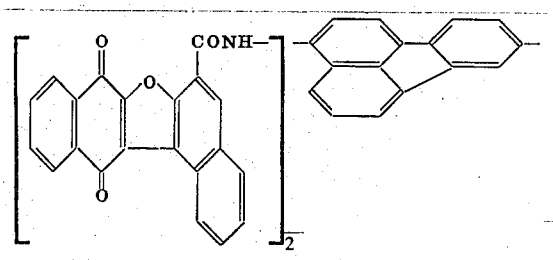


wherein R denotes an arylene radical, X_1 and Y_1 denote hydrogen or halogen atoms or alkoxy, carbonamide or nitro groups and R_1 denotes a benzene radical.

The 4,4'-diaminodianthraquinonyl is known amongst the series of the naphthofuranediones, the dyestuffs of the formula

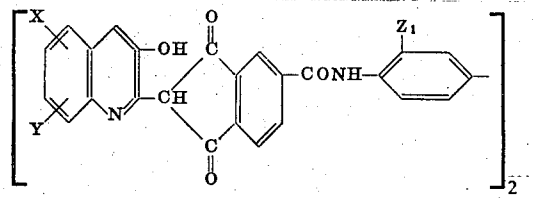


wherein X_2 and Y_2 denote chlorine atoms or alkyl groups, or the dyestuff of the formula



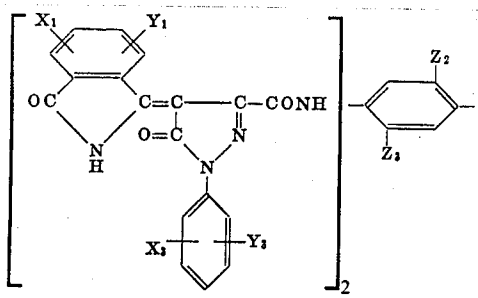
may especially be mentioned. These dyestuffs are known. Their manufacture is described in German Pat. No. 1,209,683.

Amongst the series of the quinophthalone dyestuffs, those of the formula



wherein X and Y denote hydrogen or halogen atoms or alkyl or alkoxy groups and Z_1 denotes a chlorine atom or an alkoxy group, may especially be mentioned. These dyestuffs are known. Their manufacture is described in German Patent No. 1,279,258.

Finally, amongst the series of the phthalimidopyrazolones, those of the formula



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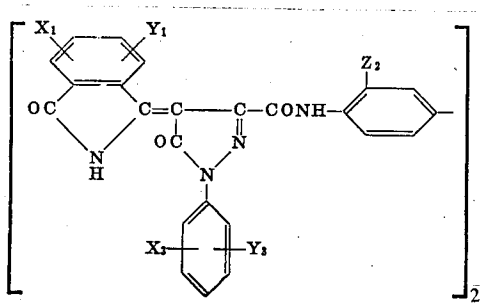


wherein, in the formulae shown, X_1 and Y_2 denote hydrogen or halogen atoms or nitro or alkoxy groups and X_3 and Y_3, Z_2 and Z_3 denote hydrogen or halogen atoms or alkyl or alkoxy groups may especially be mentioned. These dyestuffs are known. Their manufacture is described in U.S. Pat. application Ser. No. 65332.

The dyestuffs are preferably in a finely divided form, the average particle size appropriately being less than 10 μ and advantageously between 0.1 and 5 μ. It is advantageous if the particles are of uniform size.

The toners appropriately contain a binder which permits the pigment particles to be fixed to the final image carrier. The specific resistance of the binder should be greater than 10^{10} Ohm.cm, and appropriately greater than 10^{12} Ohm.cm. Natural, semi-synthetic or synthetic resins, such as abietic acid esters, tetrahydroabietic acid esters, cellulose esters, cellulose ethers, chlorinated rubber, vinyl resins, such as, for example, polyvinyl chloride, polyvinyl acetate, copolymers of vinyl chloride and vinyl acetate, polyvinyl acetals, polyvinyl alcohols, polyvinyl ethers, polyvinylcarbazole, polyisobutylene, polybutadiene, polyacrylic esters or polymethacrylic esters, polystyrene, polyacrylonitrile or silicone resins are suitable for this purpose. Amongst the series of the condensation resins, phenol-formaldehyde resins, urea-formaldehyde resins, melamine-formaldehyde resins, aldehyde or ketone resins, polyamides, polyurethanes or epoxy resins may be mentioned as examples. The proportion of binder in the toner is appropriately between 10 and 60 percent. It proves to be advantageous to achieve as intimate a mixing of the toner with the binder as possible, for example, on grinding or kneading the two materials together. In doing so, the desired reduction in particle size can be achieved simultaneously if a crude pigment is employed.

The use of the dyestuffs according to the invention in photoelectrophoretic systems for producing images is presented in more detail in the subsequent text, with reference to the attached drawing which shows an example of such a system.

The drawing shows a transparent electrode **1** which in this case consists of a layer of an optically transparent glass **2** which is coated with a thin optically transparent layer **3** of tin oxide. This material is commercially available under the description "NESA-glass." This electrode is subsequently described as the "injector electrode." A thin layer **4** of finely divided, light-sensitive particles, dispersed in an insulating liquid carrier, is coated onto the surface of the injector electrode **1.** The term "light-sensitive" is to be understood, according to the invention, as indicating the property of a particle that, once it has been attracted by the injector electrode, it migrates away from the electrode under the influence of an applied electrical field if an irradiation with an actinic electromagnetic radiation is carried out. A more detailed theoretical explanation of the mechanism which probably occurs is to be found in U.S. Pat. Nos. 3,384,565, 3,384,566 and 3,385,488. The liquid suspension **4** can furthermore contain a sensitising agent and/or a binder for the pigment particles, these agents being at least partially soluble in the suspending liquid or carrier liquid, as will still be described in more detail below. Adjoining the liquid suspension there is a second electrode **5** subsequently described as the "blocking electrode." This electrode is connected via a switch **7** to one side of the potential source **6.** The opposite side of the potential source **6** is connected to the injector electrode **1** so that if the switch **7** is closed an electrical field is applied between the electrodes **1** and **5** at right angles to the liquid suspension **4.** A projector consisting of a light source **8,** a diapositive **9** and a lens **10** irradiates the dispersion **4** with a light image of the diapositive **9** which is to be reproduced. The electrode **5** is constructed in the form of a roller with a conducting central core **11** connected to the potential source **6.** The core is covered with a layer of a blocking electrode material **12,** which can be baryte paper. The pigment suspension is irradiated with the image to be reproduced, whilst applying a potential at right angles to the blocking electrode and injector electrode by closing the switch **7.** The roller **5** is rolled over the upper surface of the injector electrode **1** during the image irradiation, whilst the switch **7** is closed. The consequence of the irradiation with light is that exposed pigment particles, which have originally been attracted by the electrode **1,** migrate through the liquid and adhere to the surfaces of the blocking electrode, leaving, on the injector electrode surface, a pigment image which is a duplicate of the diapositive **9.** After the irradiation, the relatively volatile carrier liquid evaporates, leaving the pigment image. This pigment image can subsequently be fixed in situ, for example by applying a coating layer to the upper surface, or by means of a binder, such as, for example, paraffin wax, dissolved in the carrier liquid. Other suitable binders

which are obtained from the solution when the carrier liquid evaporates can also be used. About 3 – 6 per cent by weight of the paraffin binder in the carrier give good results. The carrier liquid itself can be a liquid paraffin wax or some other suitable binder. According to another embodiment, the pigment image which is left on the injector electrode can be transferred to another surface and fixed thereon. As will still be explained in more detail below, this system can produce either monochromatic or polychromatic images, depending on the type and number of the pigments which are suspended in the carrier liquid and depending on the colour of the light with which this suspension is irradiated when carrying out the process.

Any suitable insulating liquid can be used as a carrier for the pigment particles in this system. Typical carrier liquids are decane, dodecane, N-tetradecane, paraffin, wax or other thermoplastic materials, Sohio Odorless Solvent 3440 (a kerosene fraction marketed by Standard Oil Company, Ohio) and Isopar-E (a branched saturated aliphatic hydrocarbon marketed by Esso Oil Company, New Jersey). Images of good quality are obtained at voltages of between 300 and 5,000 volt, which are applied when using the device described in the attached drawing. The proportion of pigment in the solvent is appropriately 2 – 10 percent. The addition of smaller amounts, for example 0.5 – 5 mol percent, of electron donors or electron acceptors to the suspensions results in a marked improvement of the light sensitivity of the system.

In a monochromatic system, particles of the same composition are dispersed in the carrier liquid and irradiated with a black and white image. Thereby, a single colour is obtained, analogous to a customary black and white image. In a polychromatic system the particles are so chosen that the particles with different colours respond to the various wavelengths in the visible spectrum, in accordance with their main absorption bands. Furthermore, the pigments should be so chosen that their spectral response curves do not significantly overlap, so that a colour separation and a subtractive multi-colour image production is possible. In a typical multi-colour system, the dispersion of particles should contain particles of cyan colour, which are mainly sensitive to red light, particles of magenta colour, which are mainly sensitive to green light, and particles of yellow colour, which are mainly sensitive to blue light. On mixing in a carrier liquid, these particles produce a liquid of black appearance. If one or more of these particles migrate from the electrode 11 in the direction of the upper electrode, particles are left which produce a colour which is equivalent to the colour of the incident light. For example, the result of an irradiation with red light is that the pigments of cyan colour migrate, leaving the pigments of magenta colour and the pigments of yellow colour. The combination of these colours gives a final red image. In the same way, blue and green colours are reproduced by removal of pigments of yellow and magenta colour, respectively. If white light is incident on the mixture, all pigments migrate, so that the transparent substrate remains. If no irradiation takes place, all pigments remain and together give a black colour. This is an ideal method of subtractive colour production, since the particles in each case not only consist of a single component but additionally also fulfil the double function of an image dyestuff and of a light-sensitive medium.

The dyestuffs according to the invention are outstandingly suitable for an electrophoretic system for single-colour or multi-colour image production. Their good spectral response and their high light sensitivity result in the formation of dense and brilliant images.

The examples which follow illustrate the invention. The parts and percentages indicated are by weight, unless otherwise stated. These examples illustrate various embodiments of the electrophoretic image production process, without however restricting the invention thereto.

The examples which follow are carried out in a device which corresponds to the type illustrated by the attached drawing. The image production mixture 4 is applied to an NESA-glass substrate. The irradiation takes place through this glass. The NESA-glass surface is wired in series with a switch, a potential source and the conducting core of a roller which has a baryte paper covering on its surface. The roller has a diameter of about 63 mm (2½ inches) and is moved over the surface of the plate at a speed of about 1.45 cm per second. The plate used is about 19.3 cm^2 (3 square inches) in size and is irradiated with a light intensity of 8,000 foot candles, measured on the uncoated NESA-glass surface. The magnitude of the potential applied is 2,500 volt. The irradiation is carried out with a 3,200 K lamp through a neutral dense wedge filter to measure the sensitivity of the suspensions to white light, and through Wratten filters **29**, **61** and **47***b*, each placed by themselves in front of the light source, in order to measure the sensitivity of the suspensions to red, green and blue light, respectively, in separate tests.

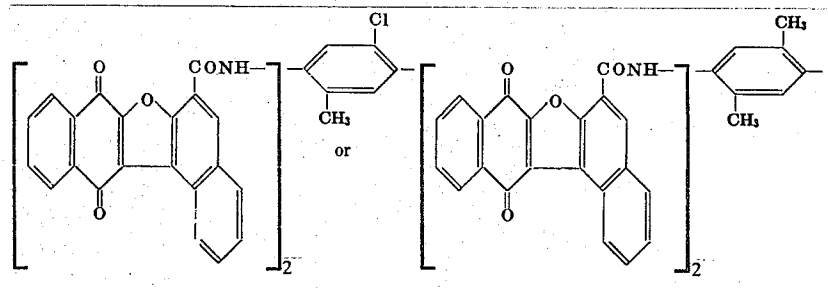
The dyestuffs according to the invention are also suitable for other photoelectrophoretic reproduction processes.

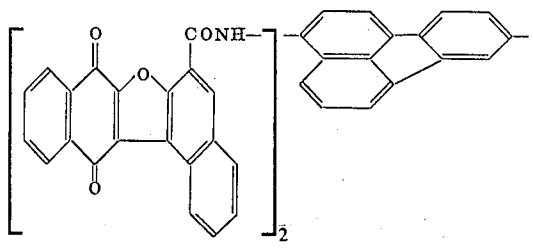
EXAMPLE 1

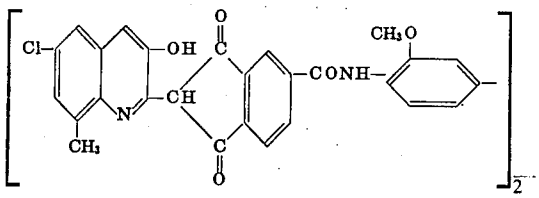
10 g of 4,4'-diamino-1,1'-dianthraquinonyl of average particle size maximally 1 μ are suspended in 90 g of Isopar E, a saturated aliphatic hydrocarbon obtainable from ESSO Standard. The resulting paste is employed, either as such or diluted with further Isopar E, for the process described above. Brilliant, red images of excellent transparency and fastness to light are obtained.

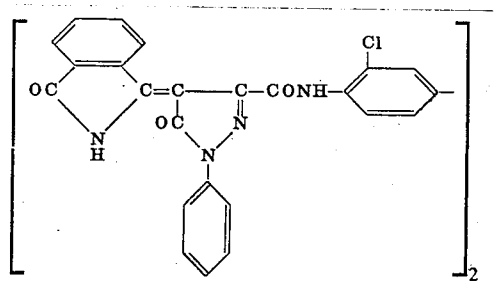
EXAMPLE 2

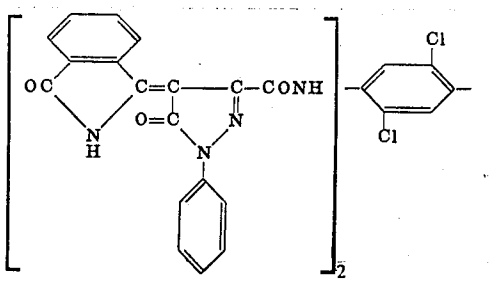
The procedure in Example 1 is followed, but the dyestuffs of the formula







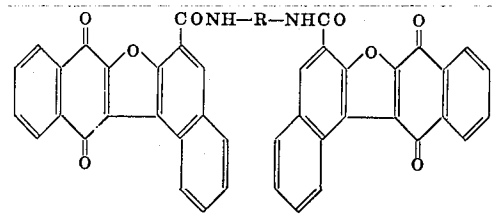




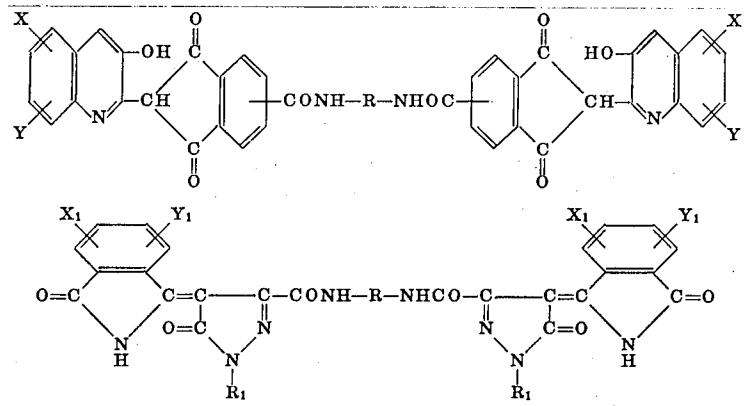
are used as toners, thus yielding brilliant yellow images of high fastness to light.

What we claim is:

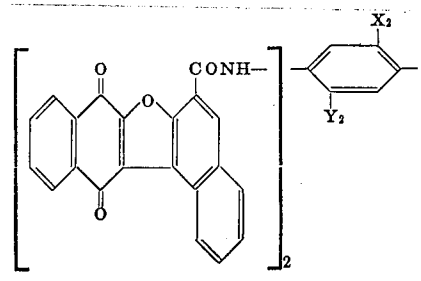
1. Method for the photoelectrophoretic production of images comprising subjecting a layer of a suspension to an electric field between two electrodes, at least one of which is partially transparent and simultaneously exposing said suspension to an image through said transparent electrode to actinic radiation whereby a pigment image is formed on at least one of said electrodes, said suspension comprising a plurality of finely divided particles of at least one color dispersed in an electrically insulating liquid carrier, said particles comprising a photosensitive pigment selected from the group consisting of naphthofuranediones of the formula



wherein R denotes an arylene radical,

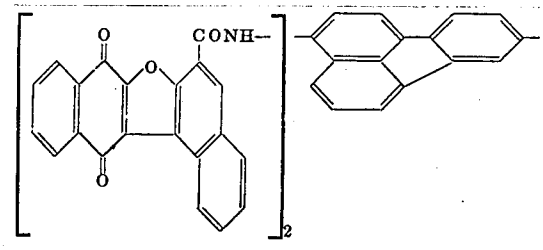


2. Method according to claim **1** in which a naphthofuranedione of the formula



wherein X_2 and Y_2 denote chlorine atoms or lower alkyl groups, is used as photosensitive pigment.

3. Method according to claim **1** in which the naphthofuranedione of the formula



is used as photosensitive pigment.

4. Method according to claim **1**, characterised in that the pigments have a particle size of 0.1 to 5 μ.

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