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[54] A PHOTOELECTROPHORETIC IMAGING COMPOSITION CONTAINING B-CAROTENE
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[56] References Cited

UNITED STATES PATENTS

3,384,488	5/1968	Tulagin et al.	252/501 X
3,384,565	5/1968	Tulagin et al.	96/1.3 X
3,384,566	5/1968	Clark	204/181

OTHER REFERENCES

Cherry et al., " Photoconductivity of Carotenoids," 1967, Vol. 3, Molecular Crystals, pp. 251–259

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ABSTRACT: There is disclosed a photoelectrophoretic imaging system wherein the imaging suspension utilized contains a photomigratory pigment dispersed in an insulating carrier liquid. The imaging suspension contains a vitamin precursor, beta carotene, in conjunction with the other components of the vehicle. The suspension is interpositioned between at least two electrodes and subjected to a potential difference while substantially simultaneously being selectively exposed to a reproducible image by a source of electromagnetic radiation. As a result of the suspension of the present invention it is now possible by regulating the polarities of the electrodes in the system to produce both negative and positive images from a single sense input.

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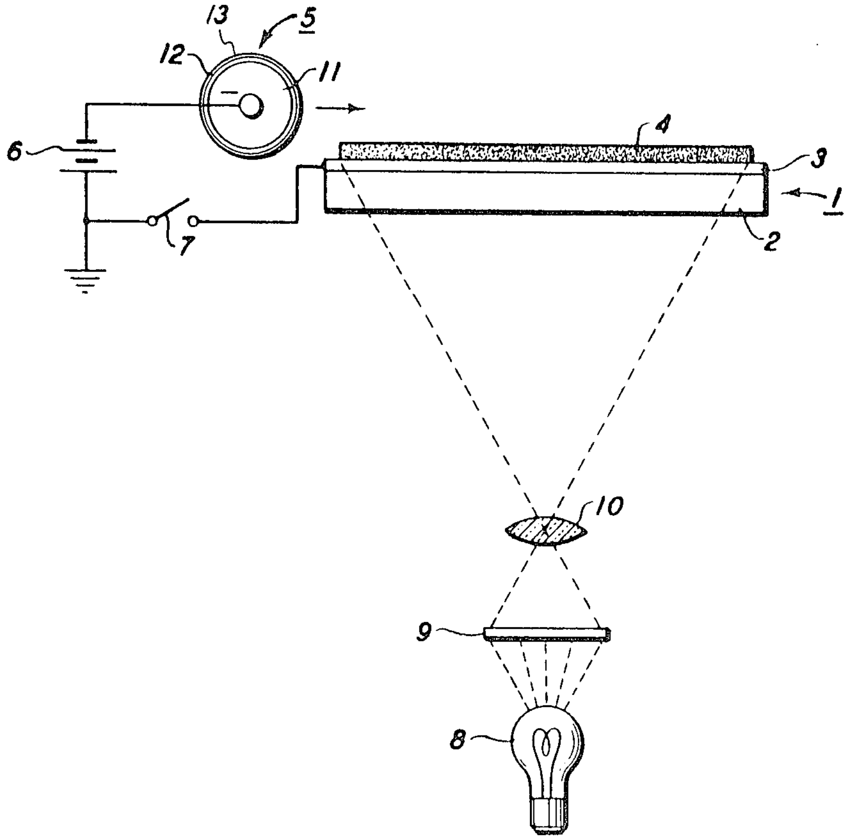

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A PHOTOELECTROPHORETIC IMAGING COMPOSITION CONTAINING B-CAROTENE

This application is a continuation-in-part of U.S. Pat. application Ser. No. 642,005 filed May 29, 1967, now abandoned and relates to an imaging system and more specifically to a photoelectrophoretic imaging system.

BACKGROUND OF THE INVENTION

In photoelectrophoretic imaging colored photosensitive particles are suspended in an insulating carrier liquid. This suspension is then placed between at least two electrodes, subjected to a potential difference and exposed to a light image. Ordinarily, in carrying out the process, the suspension is placed on a transparent electrically conductive member in the form of a thin film, and exposure is made through this member while a second generally cylindrically shaped biased electrode is rolled across the suspension. The particles are believed to bear an initial charge when suspended in the liquid which causes them to be attracted to the transparent base electrode and upon exposure, to change polarity so that the exposed particles migrate to the second or roller electrode thereby forming complementary images on each of the electrodes by particle subtraction. The process may be used to produce both polychromatic and monochromatic images. In the latter instance a single color photoresponsive particle may be used in the suspension or a number of differently colored particles may be used all of which respond to the exposure radiation. An extensive and detailed description of the photoelectrophoretic imaging techniques as described above may be found in U.S. Pat. Nos. 3,383,993; 3,384,488; 3,384,565; and 3,384,566, and are hereby incorporated by reference.

Although it has been found that good quality images can be produced, especially when a relatively insulating "blocking electrode" surface is used, due to the nature of the process the photoresponsive particles tend to respond in one particular imaging mode. Thus, in a monochromatic system, acceptable imaging has been found to be generally restricted to a single sense process so that with positive input a negative image may be reproduce. In order to obtain a positive output the image input must be a negative image.

It is, therefore, an object of this invention to provide an imaging system which will overcome the above-noted disadvantages.

It is a further object of this invention to provide a novel imaging system capable of a high degree of flexibility.

Another object of this invention is to provide a novel imaging system capable of producing high-contrast, background-free images in a one step process.

Yet, still a further object of this invention is to provide a novel photoelectrophoretic monochromatic imaging system.

Still a further object of the present invention is to provide a novel monochromatic imaging composition.

Yet, still another object of the present invention is to provide a one-step imaging system capable of producing high-contrast images of either optical sense regardless of the sense of the input information.

SUMMARY OF THE INVENTION

The foregoing objects and others are accomplished in accordance with this invention, generally speaking, by providing a suspension of photoelectrophoretic imaging particles in an insulating carrier liquid. The suspension utilized in the process of the present invention contains β-carotene, a vitamin precursor additive, which makes it possible upon proper orientation of the electrode polarities to readily produce high-contrast, background-free images in both a positive and negative imaging sense. The suspension is interpositioned between at least two electrodes and subjected to an electrical field. The suspension is selectively exposed to a reproducible image by a source of electromagnetic radiation. Generally speaking, the imaging suspension is placed on a transparent electrically conductive member of first electrode in the form of a thin film, and exposure is made through the transparent member while in contact with a second imaging electrode which is placed or roller over the top of the imaging suspension. The photomigratory particles present in this suspension respond to the electromagnetic radiation to form a visible image pattern at one or both of the electrodes, the images being complementary in nature. The imaging suspension employs intensely colored pigment particles the photosensitive pigment portion of which serves both as the colorant and as the photosensitive material. Additional photosensitive materials are not required thus providing a very expedient imaging process.

It has been determined that upon introducing β-carotene, a vitamin precursor, into the photomigratory imaging suspension of the present invention it is possible, upon proper orientation of the electrode polarities, to produce high-contrast, background-free images in either a positive to negative or positive to positive imaging mode. Heretonow, the materials used as components of the imaging suspension have substantially restricted the imaging capabilities of the photoelectrophoretic monochromatic imaging system. It has now been demonstrated that upon introducing into the imaging suspension the β-carotene additive, it is now possible to produce images of either sense by changing the polarity of the bias on the electrodes in the system.

DESCRIPTION OF THE DRAWINGS

The invention is more specifically defined in the accompanying drawing in which there is seen a transparent electrode generally designated 1 which, in this instance, is made up of a layer of optically transparent glass 2 overcoated with a thin optically transparent layer 3 of tin oxide. Tin oxide coated glass of this nature is commercially available under the trade name "NESA glass." This electrode shall hereafter be referred to as the injecting electrode. Coated on the surface of the injecting electrode 1 is a thin layer 4 of finely divided photosensitive pigment particles dispersed in an insulating carrier liquid. The term "photosensitive," for the purposes of this application, refers to the properties of a particle which, once attracted to the injecting electrode, will migrate away from this electrode under the influence of an applied electric filed when it is exposed to actinic radiation. A further detailed explanation of the apparent mechanism of the operation is disclosed in the above U.S. Pat. Nos. 3,384,565 and 3,384,566.

The imaging suspension will consist of specifically colored, finely divided photosensitive particles dispersed in an insulating carrier liquid or vehicle. Any suitable photosensitive pigment particle may be used such as disclosed in U.S. Pat. Nos. 3,384,565 and 3,384,566. As above stated, the pigment portion of the photomigratory particle provides both the photosensitivity and coloration for the respective particle. Any suitable insulating carrier liquid may be used in the course of the present invention. Typical insulating carrier liquids include long chain saturated aliphatic hydrocarbons such as decane, dodecane and tetradecane, kerosene fractions such as Sohio Odorless Solvents available from Standard Oil Co. of Ohio, Isopar G commercially available from Humble Oil Co. of New Jersey and paraffin wax, molten beeswax and other molten thermoplastic materials, mineral oil, corn oil, linseed oil, olive oil, marine oils such as sperm oil and cod liver oil, silicone oils such as dimethyl polysiloxane (Dow Corning Co.), fluorinated hydrocarbons such as Freon and mixtures thereof. The imaging suspension may also contain a sensitizer and/or binder for the pigment particles. To the imaging suspension of the present invention is added a vitamin precursor ingredient, beta carotene, generally in amounts ranging from about 0.0025 to about 1.0 gram per gram of photoresponsive or photomigratory pigment. Preferred amounts fall in the range of from about 0.0125 to 0.5 grams with optimum results being obtained in a range of from about 0.02 to about 0.1 gram.

Above the liquid suspension is passed a second or imaging electrode 5 which, in this illustration is represented as a roller having a conductive central core 11 connected to a power source 6. The core in this instance is covered with a layer 12 of blocking material which may, for example, be polyurethane, capable of blocking DC current and referred to as a blocking layer. A transfer sheet 13 or ordinary bond paper is attached to the outer surface of the roller. The blocking or imaging electrode is connected to one side of potential source 6 through switch 7. The opposite side of potential source 6 is connected to the injecting electrode 1 so that when switch 7 is closed an electric filed is applied across the liquid suspension 4 between electrode 1 and 5. The pigment suspension is exposed by way of the projector mechanism made up of a light source 8, a transparency 9, and a lens system 10. For purposes of this illustration a microfilm positive is used during the process. A detailed description of the types of materials which may be employed as the blocking layer may be found in U.S. Pat. No. 3,383,993. The blocking electrode 5, having a cylindrical configuration in the present illustration, is rolled across the top surface of the injecting electrode 1 supporting the suspension 4 containing the photomigratory particles. Switch 7 is closed during the period of image exposure. Upon proper orientation of the electrode polarities, the light exposure causes the exposed pigment particles suspended in the carrier to migrate to the surface of electrode 5 leaving behind a complementary image on the surface of the injecting electrode 1 of the unexposed particles. Upon reversing the polarities at which the filed is applied the image sense is reversed while maintaining the same input information. It should be noted at this point of the discussion that although the blocking electrode in the present illustration is represented as a cylinder it may also take the form of a flat-plate electrode, as in the case of the illustrated injecting electrode, and the blocking electrode could be the optically transparent electrode and exposure made through it. Thus, it is to be understood that it is not intended that the structural arrangement of the apparatus represented by the illustration be restricted to the design as set out herein and all similar configurations which will satisfy the requirements of the present invention are contemplated. For example, all electrodes utilized may be cylindrically shaped thus providing for an expedient continuous process.

The pigment image produced need not necessarily be formed on the surface of an electrode but may in fact be formed on a removable paper substrate or sleeve superimposed on or wrapped around the blocking electrode or otherwise interpositioned between the electrodes at the site of imaging. The pigment image may then be fixed in place as for example by placing a lamination over its top surface such as by spraying with a thermoplastic composition, or by solvent evaporation. The image may also be transferred to the surface of a receiver substrate to which it may in turn be fixed. This would especially be desirable in the case where the image is formed directly on the electrode surface. Such a transfer step may be carried out by adhesive pickoff techniques or preferably by electrostatic filed transfer while the image is still wet. The blocking layer itself may be in the form of a removable sleeve in which instance it is simply replaced following imaging with a similar material. When the image is formed on a substrate wrapped about or superimposed on the electrode itself it is only necessary to disengage the substrate from the electrode surface. The system herein described produces a high-contrast monochromatic image with little or no background degradation in either a positive or negative or positive to positive imaging mode by a simple reversing of the polarities within the system.

Any suitable material may be used as the receiving or transfer substrate for the image produced such as paper or various transparent plastics such as Mylar (polyethylene terephthalate), Tedlar (polyvinylfluoride) or cellulose acetate sheets, the latter particularly if it is desirable to produce a transparency suitable for image projection.

When used in the course of the present invention, the term injecting electrode should be understood to mean that it is an electrode which will preferably be capable of exchanging charge with the photosensitive particles of the imaging suspension hen the suspension is exposed to light so as to allow for a net change in the charge polarity on the particle. By the term blocking electrode is meant one which is substantially incapable of injecting charge carriers into the above mentioned photosensitive particles thus substantially blocking DC current. The use of the blocking electrode serves to minimize particle oscillation in the system.

It is preferred that the injecting electrode be composed of an optically transparent material, such as glass, overcoated with a conductive material such as tin oxide, copper, copper iodide, gold or the like; however, other suitable materials including many semiconductive materials such as raw cellophane, which are ordinarily not thought of as being conductors but which are still capable of accepting injected charge carriers of the proper polarity under the influence of an applied electric field may be used within the course of the present invention. The use of more conductive materials allows for cleaner charge separation and prevents possible charge buildup on the respective electrode, the latter tending to diminish the interior electrode field. The blocking layer of the imaging electrode, on the other hand, is selected so as to prevent or greatly retard the injection of charge carrier into the photosensitive pigment particles when the particles reach the surface of this electrode. Although a blocking electrode material need not necessarily be used in the system, the use of such a layer is preferred because of the markedly improved results which it is capable of producing. It is preferred that the blocking layer, when used, be either an insulator or a semiconductor which will not allow for the passage of sufficient charge carriers, under the influence of the applied field, to discharge the particles finely bound to its surface thereby preventing particle oscillation in the system. The result is enchanced image density and resolution. Even if the blocking layer does allow for the passage of some charge carriers to the photosensitive particles it still will be considered to fall within the class of preferred materials if it does not allow for the passage of sufficient charge so as to recharge the particles to the opposite polarity. Exemplary of the preferred blocking materials used are baryta paper, Tedlar, Mylar and polyurethane. Any other suitable materials having a resistivity of from about 10^7 ohm-cm. or greater may be employed. Typical materials in this resistivity range include cellulose acetate coated papers, cellophane, polystyrene and polytetrafluoroethylene. The core of the blocking electrode generally will consist of a material which is fairly high in electrical conductivity. Typical conductive materials including conductive rubber, and metal foils of steel, aluminum, copper and brass have been found suitable. Preferably, the core of the electrode will have a high electrical conductivity in order to establish the required field differential in the system; however, if a material having a low conductivity is used a separate electrical connection may be made to the back of the blocking layer of the blocking electrode. For example, the blocking layer or sleeve may be semiconductive polyurethane material having a conductivity of from about 10^{18} to 10^{19} ohms-cm. If a hard rubber nonconductive core is used then a metal foil may be employed as a backing for the blocking sleeve. Other materials that may be used in conjunction with the injecting and blocking electrodes and other photosensitive particles which may be used as the photomigratory pigments and the various conditions under which the process operates may be found in the above-cited issued patents U.S. Pat. Nos. 3,384,565 and 3,384,566 as well as U.S. Pat. Nos. 3,384,488 and 3,383,993.

It is to be understood that any suitable photosensitive pigment particle such as identified in the above-cited patents may be employed within the course of the present invention with the selection depending largely upon the photosensitivity and the spectral sensitivity desired. Typical photoresponsive organic materials include substituted and unsubstituted organic pigments such as phthalocyanines, for example, copper phthalocyanine; beta form of metal-free phthalocyanine; tetrachlorophthalocyanine; and x-form of metal-free phthalocyanine; quinacridones as for example 2,9-demethyl quinacridone; 4,11-dimethyl quinacridone; 3,10-dichloro-6,13-dihydro-quinacridone; 2,9-dimethoxy-6,13-dihydro-quinacridone and 2,4,9,11-tetrachloro-quinacridone; anthraquinones such as 1,5-bis-(betaphenylethylamino) anthraquinone; 1,5-bis-(3′-methoxypropylamine) anthraquinone; 1,2,5,6-di-(C,C′-diphenyl)-thiazole-anthraquinone; 4-(2′-hydroxyphenyl-methoxyamino) anthraquinone; triazines such as 2,4-diaminotriazine; 2,4-di-(1′-anthraquinonyl-amino)-6-(1″ pyrenyl)-triazine; 32,4,6 tri-(1′, 1″, 1‴-pyrenyl)-triazine; azo compounds such as 2,4,6-tris-(N-ethyl-N hydroxy-ethyl-p-aminophenylazo) phloroglucinol; 1,3,5,7-tetrahydroxy-2,4,6,8-tetra (N-methyl-N-hydroxy-ethyl-p-amino-phenylazo) naphthalene; 1,3,5-tri-hydroxy-2,4,6-tri-(3′-nitro-N-methyl-N-hydroxy-methyl-4′-aminophenylazo) benzene; metal salts and lakes of azo dyes such as calcium lake of 6-bromo-1 (1′-sulfo-2-naphthylazo)-2-naphthol; barium salt of 6-cyano-1 (1′-sulfo-2-naphthylazo)-2-naphthol; calcium lake of 1′(2′-azonaphthaliene-1′-sulfonic acid)-2-naphthol; calcium lake of 1-(4′5-chloroazo-benzene-2′-sulfonic acid)-2-hydroxy-3-naphthoic acid; and mixtures thereof. Other organic pigments include polyvinylcarbazole; tri-sodium salt of 2-carboxyl phenyl azo (2-naphthiol-3,6-disulfonic acid; N-isopropylcarbazole; 3-benzylidene aminocarbazole; 3-aminocarbazole; 1-(4′-methyl-5′-chloro-2′-sulfonic acid) azobenzene-2-hydroxy-3-naphthoic acid; N-2″ pyridyl-8,13-dioxodinaphtho-(2,1-b; 2′, 3′-d)furan-6-carboxamide; 2-amino-5-chloro-p-toluene sulfonic acid and the like.

Typical inorganic photosensitive compositions include cadmium sulfide, cadmium selenide, cadmium sulfoselenide, zinc oxide, zinc sulfide, sulfur, selenium, antimony sulfide, lead oxide lead sulfide, arsenic sulfide, arsenic-selenium, sulfur-selenium and mixtures thereof. The imaging suspension may contain one or more different photosensitive particles each having various ranges of spectral response.

A wide range of voltages may be applied between the electrodes in the system. For good image resolution, high-image density and low background it is preferred that the potential applied to such as to create an electric filed of at least about 300 volts per mil across the imaging suspension. For example, when the imaging suspension is coated to a thickness of about 1 mil the electrode spacing will be such that an applied potential of about 300 volts produces a field across the suspension of about 300 volts per mil. Potentials as high as 8,000 volts have been applied to produce images of high quality. As is apparent the applied potential necessary to obtain the desired filed of strength will vary depending upon the interelectrode gap as well as the type and thickness of the blocking material utilized. The upper limit of the field strength appears to be limited primarily by the breakdown potential of the suspension. The imaging suspension is generally coated to a thickness of up to about 1 mil or 25 microns, with a preferred operational thickness being in the range of from about 3–5 microns.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

To further define the specifics of the present invention, the following examples are intended to illustrate but not limit the particulars of the present system. Parts and percentages are by weight unless otherwise indicated.

In the following examples, the injecting first electrode consists of NESA glass as described above. The imaging or blocking electrode consists of a conductive steel core coated with a layer of polyurethane, unless otherwise indicated. A potential of about 7,000 volts is applied across the imaging suspension.

EXAMPLE I

A commercial, metal-free phthalocyanine is purified by acetone extraction to remove organic impurities. Since this extraction step yields the less sensitive beta crystalline form, the desired alpha form is obtained by dissolving 100 grams of the beta form in 600 cc. of sulfuric acid, precipitating it by pouring the solution into 3,000 cc. of ice water and washing with water to neutrality. The thus purified alpha phthalocyanine is then salt milled for 6 days and desalted by slurrying in distilled water, vacuum filtering, water washing, and finally, methanol washing until the the initial filtrate is clear, thus, producing x-form phthalocyanine. After vacuum drying to remove residual methanol, the x-form phthalocyanine produced is used to prepare an imaging suspension according to the following formulation:

phthalocyanine (x-form)	10 g.
beta carotene (β)	0.3 g.
sperm oil (ADM 38 BW)	250 cc.
tricresyl phosphate	18 g.

The phthalocyanine is ground in a mortar, placed in a Waring blender with the other ingredients and dispersed for about 10 minutes at high speed. The resulting suspension is coated on the surface of a NESA glass electrode. As the blocking electrode with paper sleeve is passed across the surface of the suspension liquid at a rate of about 4 inches per second, the potential is established as stated above and the suspension is selectively exposed to a light intensity of about 12 foot-candles through a positive transparency with a General Electric visible light source. The blocking electrode is maintained as the positive pole and the NESA glass electrode the negative pole. By a single material transfer a high-quality negative image with little or no background is formed on the surface of the paper sleeve.

EXAMPLE II

The process of example I is repeated with the exception that the polarities on the blocking electrode and the NESA glass electrode are reversed. There results a high-quality positive image on the surface of the paper sleeve thereby demonstrating the capability of the present system to image in a direct manner in a positive to positive imaging mode. Comparing the results of example I and example II, there is demonstrated the claimed capabilities of the present invention, that is, the capability of imaging in either a positive to negative or positive to positive imaging mode, obtaining images in a single-pass system of high-quality, high-contrast, low-background characteristics.

EXAMPLE III

An imaging suspension of the following formulation is prepared:

phthalocyanine (x-form)	4 g.
olive oil	20 cc.
mineral oil	56 cc.
tricresyl phosphate	4 g.
beta carotene	0.1 g.

The phthalocyanine, prepared according to the process of example I, is ground in a mortar, placed in a Waring blender with the other ingredients and dispersed for about 10 minutes at high speed. The resulting suspension is coated on the surface of the NESA glass electrode and imaged through a positive transparency as in example I with the blocking electrode with paper sleeve having a positive polarity and the NESA glass injecting electrode a negative polarity. The resulting image produced on the paper sleeve is similar to that obtained in example I.

EXAMPLE IV

The process of example III is repeated with the exception that the polarities on the two electrodes are reversed. The resulting high-quality positive image obtained on the paper sleeve further demonstrates the high-quality positive to positive image capable of the present system.

EXAMPLES V & VI

Two separate imaging suspensions are prepared according to the process of example I. However, in the present examples, the beta carotene component is excluded from each formulation. The imaging suspension prepared is coated on the NESA electrode. The polarity of the blocking electrode is made positive and the polarity on the injecting electrode negative. The resulting image produced on the paper sleeve of example V according to the process described in example I is of a high-quality, low-background nature. Next, the polarities of the two electrodes are reversed with the blocking electrodes made negative and the injecting electrode positive. The resulting image produced from this arrangement, example VI, is of a low-quality, low-contrast nature. In comparing these two examples, that is, examples V and VI, it is evident that the elimination of the beta carotene component from the imaging formulation restricts the image capability of the system, to a positive to negative or negative to positive imaging system.

EXAMPLE VII

The process of example I is repeated with the exception that the following formulation is utilized:

Watchung Red B	1 g.
phthalocyanine (x-form)	4 g.
mineral oil	80 cc.
tricresyl phosphate	20 g.
beta carotene	0.05 g.

Utilizing a positive transparency at the input end with the blocking electrode having a negative polarity and the injecting electrode a positive polarity a high-quality positive image is produced on the paper sleeve of the blocking electrode.

EXAMPLE VIII

The process of example I is repeated with the exception that the following formulation is utilized:

Algol Yellow	1 g.
phthalocyanine (x-form)	4 g.
tricresyl phosphate	2 g.
linseed oil	106 cc.
styrene	20 g.
beta carotene	0.05 g.

With a negative transparency at the input end and with the blocking electrode having a negative polarity and the injecting electrode a positive polarity, a high-quality negative image is produced on the surface of the paper sleeve of the blocking electrode.

Although the present examples were specific in terms of conditions and materials used, any of the above-listed typical materials may be substituted when suitable in the above examples with similar results. In addition to the steps used to carry out the process of the present invention, other steps or modifications may be used, if desirable. For example, the process may be readily adapted to be used in a continuous imaging system. In addition, other materials may be incorporated in the imaging suspension, injecting electrode or blocking electrode to enhance, synergize or otherwise desirably effect the properties of this system for their present use. For example, the imaging suspension may contain sensitizers for the photoconductive particles which are dissolved or suspended in the carrier liquid.

Anyone skilled in the art will have other modifications occur to him based on the teachings of the present invention. These modifications are intended to be encompassed within the scope of this invention.

What is claimed is:

1. A photoelectrophoretic imaging composition comprising a vitamin precursor, beta carotene, and a plurality of photoelectrophoretic imaging particles dispersed in an insulating carrier liquid each of said particles comprising an electrically photosensitive pigment which is both the primary electrically photosensitive ingredient and the primary colorant for said particle.

2. The composition as disclosed in claim 1 wherein said beta carotene is present in an amount about 0.0025 to about 1.0 gram per gram of said photosensitive pigment.

3. A photoelectrophoretic imaging composition comprising a plurality of photoelectrophoretic imaging particles and beta carotene dispersed in an insulating carrier liquid, each of said particles comprising an electrically photosensitive pigment which is both the primary electrically photosensitive ingredient and the primary colorant for said particle, said carrier liquid comprising at least one member of the group consisting of mineral oil, olive oil, sperm oil, and linseed oil.

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