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(54) A RECORDING PROCESS AND IMAGING APPARATUS

(71) We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America, of 343 State Street, Rochester, New York 14650, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to migration imaging.

As disclosed in the migration imaging process set forth in U.S. Patent 2,758,939 and subsequently a layer of photoconductive particles, that is electrically photosensitive particles, is subjected to the influence of an electric field between two spaced electrodes, at least one of which is transparent, and is imagewise exposed to illumination. As a result, those particles which are in electrical contact with an electrode during light exposure undergo a net change in charge polarity and migrate or are attracted to the adjacent spaced electrode having the opposite polarity, whereas the particles which are not exposed to light retain their original charge polarity. Thus, by producing an imagewise change in the charge polarity of the exposed photoconductive particles, photoconductive particle images may be formed at or near the surfaces of one or both of the two spaced electrodes, which images correspond to the original light image.

Such electrophoretic migration imaging processes of the type described are often referred to as *Photo*E*lectro*P*horetic* processes or by the acronym PEP, wherein there is described an imaging system in which one or more types of photosensitive radiant energy absorbing particles which are believed to bear a charge when suspended in a non-conductive liquid carrier are suspended in such a liquid placed in an electrode system employing a blocking electrode and exposed to an image. When these steps are completed, particle migration takes place in image configuration providing a visible image at one or both of the electrodes. The system employs particles which are photosensitive and which apparently undergo a net change in charge polarity upon exposure to activating radiation, by interaction with one of the electrodes.

In the PEP process it is the exposed photosensitive particles which undergo a net change in charge polarity. In many situations, however, it would be desirable to cause the unexposed particles to undergo a net change in charge polarity. This would produce images having a reverse image sense in comparison to the images typically formed in known PEP processes. In conventional PEP monochrome and multicolour processes, imaging has been found to be generally restricted to a single sense process so that with positive input a negative image is produced and vice versa.

It is known by the addition of either beta-carotene, a vitamin precursor, or a halogen to the admixture of photosensitive particles used in a PEP process to produce a change in charge polarity in exposed photosensitive particles, while the unexposed particles retain their original charge polarity.

According to the present invention there is provided a recording process, wherein electrically photosensitive particles, having a positive polarity electrostatic charge, are disposed between two spaced electrodes and are caused to migrate by application of an electric field and imagewise exposure to "activating radiation", as hereinafter defined, to form a corresponding image comprising the particles, one of the electrodes being at least partally transparent to the radiation, one of the electrodes having on the surface thereof adjacent the particles, a layer comprising a "dark charge exchange material", as hereinafter defined.

There is also provided a recording process wherein electrically photosensitive particles, at least some of which bear a positive polarity electrostatic charge, are disposed between two spaced electrodes, subjected to an electric field, and imagewise exposed to activating radiation, one of the electrodes having as an overcoat for the surface thereof adjacent to the particles a uniform layer comprising an amount of a dark charge exchance material sufficient to provide a net change in charge polarity of at least a portion of the positive polarity particles

upon electrical contact therewith in the presence of the field and in the absence of activating radiation, the process comprising, substantially simultaneously, establishing a potential difference between the electrodes to create the field such that at least a portion of the positive polarity particles move into electrical contact with the layer of "dark charge exchange material", and imagewise exposing the particles to activating radiation such that at least a portion of the exposed, positive polarity particles are immobilized at the surface of the layer of "dark charge exchange material" and at least a portion of the unexposed positive polarity particles, upon electrical contact with the layer of "dark charge exchange material", undergo a net change in charge polarity and are repelled therefrom, whereby an image is formed.

There is further provided an imaging apparatus comprising two spaced electrodes arranged to receive electrically photosensitive particles disposed therebetween, at least one of the electrodes being at least partially transparent to "activating radiation", as hereinafter defined, means for applying an electric field between the electrodes whereby the electrically photosensitive particles may be caused to migrate, and means for exposing the photosensitive particles to "activating radiation", as hereinafter defined, one of the electrodes bearing on the surface thereof, a layer comprising a "dark charge exchange material", as hereinafter defined.

The recording process and the imaging apparatus have been described and claimed in Patent Specification No. 1,482,019, with the additional requirement that the electrode has on the surface thereof adjacent to the particles a blocking layer as therein defined.

The recording process will be referred to herein, for convenience, by the acronym PIER, that is *P*hoto*I*mmobilized *E*lectrophoretic *R*ecording.

A "dark charge exchange material", hereinafter referred to as "as hereinbefore defined", where electrically photosensitive particles are subjected to an electric field and exposed to "activating radiation", as hereinafter defined, prevents the imagewise exposed electrically photosensitive particles from undergoing a change in charge polarity upon electrical contact, or such close approach to contact as would otherwise cause charge transfer with the "dark charge exchange material", while where electrically photosensitive particles are subjected to an electric field and not exposed to "activating radiation" as hereinafter defined, a proportion of the unexposed particles undergo a change in charge polarity upon electrically contacting the "dark charge exchange material".

The term "activating radiation" as used herein, and henceforth referred to as "as herein before defined", is defined as electromagnetic radiation such as visible light, to which the electrically photosensitive particles used exhibit an electrically photosensitive response, for example, the generation of electron-hole pairs, the radiation being of such an intensity that the electrically photosensitive response occurs.

As used herein the field strength is defined as the voltage drop per unit length separation of the electrodes excluding voltage drops occurring across the "dark charge exchange material" layer and the "blocking layer" (if one is used) coated on the opposing surfaces of the spaced electrodes.

The term "blocking electrode", and "blocking layer", are well known in photoelectrophoretic processes and are described in, for example, U.S. Patent No. 3,384,566 wherein the "blocking electrode" is selected so as to prevent or greatly retard the injection of electrons (or holes depending upon the initial polarity of charge on the particle) into the particle when it reaches the surface of this electrode. Accordingly, the surface of the other electrode may have thereon 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 finally bound to it thereby preventing particle oscillation in the system. Even if this "blocking electrode" will allow for the passage of some charge carriers through it to the particles, it will still be considered to come within the class of preferred materials if it does not allow for the passage of sufficient carriers to recharge the particle to the opposite polarity because even a discharged particle will tend to adhere to this "blocking electrode" by Van Der Waals forces.

In carrying out the present invention, the exposed photosensitive particles typically are immobilized at or near the surface of the layer of "dark charge exchange material" and form a negative appearing image of the original image; while the unexposed particles, upon electrical contact with the "dark charge exchange layer", undergo a net change in charge polarity and are repelled from the "dark charge exchange layer" toward the adjacent electrode surface where they may form a positive appearing image of the original image.

The electrically photosensitive particles may be disposed between the two spaced electrodes in a liquid imaging suspension comprising an electrically insulating liquid. Upon being dispersed in such a liquid, the particles acquire an electrostatic charge. Many particles as a result of incorporation in such a liquid vehicle tend to acquire a positive polarity electrostatic charge although it is not uncommon for the imaging suspension to contain a mixture of both positive and negative polarity particles. Advantageously, to improve the charge and dispersion stability of the liquid imaging suspension, various charge control agents, may

also be incorporated in the imaging suspension.

It has been found that PIER is especially effective in providing a multicolour image using a mixture of at least two differently coloured photosensitive particles, each of which is primarily responsive to "activating radiation" of a different wavelength. In this record, it has been found that multicolour images produced by PIER using subtractive colour formation advantageously exhibit good to excellent reproduction of neutral colour tones. Furthermore, to date it has been found that PIER generally provides multicolour images exhibiting higher colour density and better colour separation than comparable PEP multicolour imaging processes, and, for reasons not yet fully understood, the electrically photosensitive particles employed in multicolour imaging suspensions in both PIER and PEP multicolour processes are found advantageously to tend to exhibit less deleterious particle interaction in PIER than in PEP.

In contrast to PEP imaging processes, in the PIER imaging process it is the unexposed electrically photosensitive particles which exchange charge. This is by use of a "dark charge exchange material" on an electrode whereby a net change in particle charge polarity occurs.

The invention will now be described by way of example, with reference to the accompanying drawings, in which:—

Fig. 1a—1d and 2a—2d are diagrammatic representations illustrating certain of the differences between a typical PIER process and a conventional PEP process, respectively;

Fig. 3a—3c illustrates a typical colour image-forming PIER process;

Fig. 4 represents diagrammatically the individual components of the total voltage differences between the spaced electrodes used in PIER.

Fig. 5 illustrates a typical imaging apparatus for use in a PIER process wherein the exposure is effected through an electrode at least partially transparent to the activating radiation.

Fig. 6 illustrates an alternative imaging apparatus for use in PIER wherein the exposure to "activating radiation" is effected without exposing through an electrode.

Fig. 7a is a top view of an interdigitated electrode system and Fig. 7b illustrates diagrammatically a side view of an interdigitated electrode configuration useful in evaluating various imaging suspensions which may be employed to test the "dark charge exchange properties" of a particular material.

The PIER-process may be varied depending upon the ultimate result desired, the specific materials which may be preferred to obtain a particular result, the particular processing conditions used. It is not possible to catalogue all conceivable variations of the present invention in the present application and, therefore, the description set forth herein is illustrative and should not be regarded as limiting the present invention.

To illustrate diagrammatically the imaging sequence which occurs in PIER as opposed to the imaging sequence of a typical PEP imaging process, reference will now be made to Figs. 1a—1d and 2a—2d.

Referring to Fig. 1a and Fig. 2a, there is illustrated a typical spaced electrode configuration for use in PIER and a PEP process, respectively. Both PIER and the PEP process use two spaced electrodes 50 and 51 between which is sandwiched a plurality of electrically photosensitive particles illustrated in Fig. 1a and Fig. 2a, as a liquid imaging suspension 61 generally comprising an electrically insulating liquid 53 having dispersed therein electrically photosensitive particles 56 bearing an electrostatic charge. At least one of the electrodes in both the PIER and the PEP process illustrated in Figs. 1a—1d and 2a—2d is at least partially transparent to "activating radiation", for example, a conductive tin oxide coated glass electrode such as NESA (Trade Mark) glass may be used where the radiation is visible light. In this case, electrode 51 of Fig. 1a and Fig. 2a is partially transparent.

At least one of the electrodes in PIER, generally the transparent electrode if one is used, has coated on its interior surface adjacent the imaging suspension a layer of a "dark charge exchange material" 54 as hereinbefore defined. No such layer is present in the PEP process. If, as is shown in Fig. 1a, the "dark charge exchange layer" 54 is coated on the partially transparent electrode 51 it is advantageous that the "dark charge exchange layer" also be at least partially transparent to the "activating radiation". In contrast, the partially transparent electrode of a typical PEP electrode configuration consists merely of a transparent conducting electrode such as NESA glass. In conventional PEP processes, electrode 51 is sometimes referred to as an "injecting" electrode. The electrode 50 bears a "blocking layer" 59 exhibiting minimal charge exchange capability with the electrically photosensitive particles under normal process imaging conditions, for example, an electrically insulating material.

Referring to Figs. 1b and 2b, imaging may be initiated in both the PIER and the PEP processes by closing switch 60 to establish an electric field between electrodes 50 and 51 from a voltage source 52. For convenience, in Fig. 1b and 2b it is assumed that the charge-bearing electrically photosensitive particles 56 have associated with them a positive charge. It should be recognized, however, that imaging suspensions containing mixtures of both positively and negatively charge-bearing electrically photosensitive particles may be employed in the process of the present invention.

It is necessary that at least a portion of the particles bear a positive polarity electrostatic charge. In general, however, it is advantageous in PIER to use imaging suspensions which contain a substantial proportion of positively charged particles (i.e., greater than 40 percent) and preferably a majority of positively charged particles (i.e. 80 to 100 percent of positively charged particles) in the imaging suspensions. This results in better defined images and a more efficient image-forming process. Assuming that the electric field applied between electrodes 50 and 51 by the closing of switch 60 provides a negative potential on the "dark charge exchange surface" 54 or electrode 51 and a negative potential on electrode 51 of the PEP process, it is apparent that, upon application of this field, the positively charged photosensitive particles suspended in the carrier liquid will begin to electrophoretically migrate toward electrode 51 due to the forces of electrostatic attraction existing between the positively charged particles and the electrode 51.

In a typical imaging operation in both the PIER and PEP imaging processes, an electric field is created between the electrode 50 and 51, and during application of the field imagewise activating radiation 64 is applied through transparent electrode 51 as shown in Fig. 1c and 2c. Advantageously, the creation of the electric field and the imagewise exposure in PIER occur simultaneously.

It should be understood that the phrase "substantially simultaneously" as used herein to describe the sequence of the electrical field application and exposure events between the spaced electrodes used in PIER includes any sequence of field application and exposure events wherein the time of exposure coincides with a time in which the electrical field is present. As indicated above, to date, it has generally been found advantageous to apply the field and effect exposure simultaneously, at least insofar as this is technically possible. It will be appreciated, however, that, for example, with respect to a particular combination of electrode shapes and field application techniques or where it is desired to alter somewhat the normal response of the photosensitive particles in PIER, it may be desirable to create the field at some small, but finite, time before effecting imagewise exposure.

In PIER, referring now to Fig. 1c, as a result of the radiation 64, a positively charged electrically photosensitive particle 57 which comes into electrical contact with the "dark charge exchange layer" 54 is immobilized and retained at the surface of "dark charge exchange layer" 54. On the other hand, a positively charged electrically photosensitive particle 58 which is not exposed to "activating radiation" undergoes a net change in charge polarity upon electrical contact with the "dark charge exchange layer" 54 to become negatively charged. Particle 58 is then repelled from the "dark charge exchange layer" and begins to migrate toward electrode 50 due to the electrostatic attraction existing between the now negatively charged electrically photosensitive particle 58 and the positive polarity of electrode 50.

In contrast to PIER, the PEP process as illustrated in Fig. 2c appears to involve the following mechanism upon exposure to "activating radiation": In the PEP process, a positively charged electrically photosensitive particle 58 which is not exposed to "activating radiation" retains its original charge polarity upon electrical contact with transparent injecting electrode 51. As a result, unexposed particle 58 remains attracted to electrode 51 due to the electrostatic forces of attraction existing between positively charged particle 58 and the negative polarity of electrode 51. On the other hand, in the exposed areas, "activating radiation" 64 is transmitted through the transparent injecting electrode 51 and as positively charged electrically photosensitive particle 57 makes electrical contact therewith a net change in charge polarity of particle 57 does occur. Thus, in PEP the initially positively charged photosensitive particle 57 when subjected to exposure by "activating radiation" 64 undergoes a net change in charge polarity upon electrical contact with charge injecting surface 51 to become negatively charged and, as a result, is repelled from negative polarity injecting electrode 51 and migrates toward positive polarity electrode 50.

Based on the foregoing, as shown in Fig. 1d, PIER produces an image on electrode 50 corresponding to the original image. In contrast, as shown in Fig. 2d, the PEP process produces a reversal image on electrode 50 corresponding to the original image.

As is apparent, the essential feature of the present invention is the use of a "dark charge exchange layer" 54. It is this layer which enables charge exchange with the electrically photosensitive particles to occur in the absence of "activating radiation". Materials which can be used as the "dark charge exchange materal" as hereinbefore defined, in this layer are selectable from a variety of crystalline and amorphous materials, including, inorganic materals such as certain metals, organic materials, and organo-metallic materials.

Regardless of the specific composition of the "dark charge exchange layer", the layer must be capable of exchanging charge with the electrically photosensitive particles used in the present invention in the absence of "activating radiation" in order to reverse the polarity of the unexposed particles.

One aid which is considered to be a useful guide for the selection of crystalline "dark charge exchange materials", particularly inorganic materials having utility in PIER,

may be illustrated with reference to Table 1. Table 1 lists representative "reported" work function values of various inorganic crystalline materials, i.e., those materials exhibiting crystallinity detectable by conventional X-ray diffraction techniques. It is believed that these inorganic crystalline materials which have an "effective" work function which is lower than the "effective" work function of the electrically photosensitive particles used in PIER provide useful "dark charge exchange materials" for these particular electrically photosensitive particles. The terms "effective" work function and "reported" work function are used herein because as is well-known many of the methods for determining work functions of various materials are difficult to carry out and may be affected by numerous factors such as the purity of the material being measured, the physical treatment of a material, e.g., milling can alter the work function of a material, the physical and chemical surface properties of the material, e.g., whether the surface is clean, contaminated with impurities, or has a surface film such as an oxide film, or polymer film. It should be further noted that not all of the methods of evaluating the work function are of equivalent precision or accuracy, nor are they all equally suited for use for each different type of material or material surface. Thus, it will be appreciated that the "reported" work functions and energy levels of a given electrically photosensitive particle and inorganic crystalline material may differ markedly from their actual "effective" work functions when subjected to the environmental operating conditions of a specific PIER process. In fact, as is known, reported literature values of the work functions for the same material vary.

As suggested above, the relative values, not the absolute values, of the effective work function of the "dark charge exchange material" and the effective work function of the electrically photosensitive particle material are of primary concern. That is, of inorganic crystalline materials, one of which has a lower effective work function than the effective work function associated with the particular photosensitive particles intended for use would be selected as an inorganic crystalline "dark charge exchange material".

With respect to specific inorganic crystalline materials which may be employed in "dark charge exchange layers" it is believed that of crystalline materials, those such as metals, having an effective work function of less than about 4 ev. are preferable for use in the invention. (See Table 1). These materials are believed useful because many of the known electrically photosensitive particles for example, phthalocyanine pigment particles, useful in the present invention appear to have a reported work function greater than about 4 ev. (See Table 1). As will be appreciated, the greater the difference between the effective work functions of an inorganic crystalline "dark charge exchange material" and a particular electrically photosensitive particle, the more efficient PIER should become.

TABLE 1.

Material	Reported Work Function[1]
	ev.
Rb	2.05
K	2.1
Na	2.20
Ba	2.25
Sr	2.30
Li	2.35
Pr	2.60
Ce	2.60
Ca	2.70
Sm	3.1
Nd	3.2
La	3.2
Be	3.25
Th	3.30
Mg	3.40
Hf	3.50
Zn	3.60
Tl	3.70
Zr	3.75
Cd	3.80
In	3.80[2]
Cb	3.85
Ga	3.90
Pb	4.0
Si	4.05
Sn	4.10
Sb	4.10
Ti	4.15
Co	4.2
Al	4.2[2]
Ag	4.25
Bi	4.25
Fe	4.30
Cu	4.50
a phthalocyanine pigment	4.50[3]
B	4.55
Ru	4.55
Hg	4.60
Ge	4.65
Os	4.65
Pd	4.75
Au	4.8[2]
Ni	4.80
ZnO	4.84[4]
As	5.1
Pt	5.3[5]

[1] The work function values in Table 1 are the values reported in the indicated literature sources. As explained previously the "effective" work function of a material used in PIER is, in large part, dependent on the various milling procedures and other surface treatments such as various

contaminants to which it is subjected. Accordingly, it should be recognized that the reported work function value of Table I may differ fairly substantially from the "effective" work function of the same material used in PIER. All reported work function values are taken from Gordy and Thomas, *J. Chem. Phys.*, Vol. 24, page 439 (1956), except where otherwise indicated.

[2] J. P. Mitchell and D. G. Denure, "Electrical Contacts on Photoconductive Sb_2S_3 Films", *Thin Solid Films*, Vol. 16, page 295, Fig. 7, (1973).

[3] Taken from H. Meier, *Spectral Sensitization*, The Focal Press, page 174, Table 19 (1968).

[4] Taken from H. Meier, *Spectral Sensitization*, The Focal Press, Page 175, Table 19A 19A (1968).

In addition to the various inorganic crystalline "dark charge exchange materals" described above, various organic, including organo-metallic, materials also may be employed as "dark charge exchange materials". Organic materials have not, to date been extensively reported in the literature in terms of work function or relevant energy level measurements. However, one criterion which appears to provide a useful guide for the selection of organic "dark charge exchange materials" is that many electron acceptor materials, sometimes referred to as Lewis acid materials, provide useful "dark charge exchange materials". For example, 2,4,7-trinitro-9-fluorenone, which is conventionally referred to as a Lewis acid material has been found especially useful in forming the "dark charge exchange layers" used in PIER.

Typical useful electron acceptor materials are substituted aromatic compounds containing one or more substituted aromatic rings. These substituted mono- and poly-cyclic aromatic materials may typically contain from 4 to 40 or more carbon ring atoms and, of a heterocyclic ring is, or heterocyclic rings are present, from 1 to 8 or more atoms other than carbon, for example oxygen, sulphur, selenium and nitrogen may be included in the heterocyclic ring or rings. The aforementioned materials are monomers. It will be appreciated however, that polymers having repeating units containing such monomers may also be used.

Electron acceptor materials which have been found especially useful as "dark charge exchange materials" may be characterized as follows: (a) the material contains at least one substituted aromatic ring, including substituted heterocyclic rings which possess conjugated aromatic unsaturation in the heterocyclic ring; and (b) the material has an electron acceptor strength, χ, which is greater than -0.35, i.e. the material has a χ value more positive than -0.35. The term "electron acceptor strength" as used herein, sometimes referred to in the literature simply as "acceptor strength" has reference to acceptor strength values of materials as determined by the method described by Dewar and coworkers in (1) M. . S. Dewar and A. R. Lepley, *J. Amer. Chem. Soc.*, Vol. 83, pg. 4650 (1961) and (2) M. J. S. Dewar and H. Rogers, ibid., Vol. 84, pg. 395 (1962). A further explanation of this method and a partial listing of acceptor strengths of compounds, certain of which compounds have been found to be useful as "dark charge exchange materials" in PIER, may be found in T. Sulzberg and R. T. Cotter, *J. Org. Chem.*, Vol. 35, No. 8, p. 2762 (1970), (Table III thereof).

The electron acceptor materials useful as "dark charge exchange materials" in PIER typically have as substituents on an aromatic thereof one or more strong electron withdrawing groups, i.e. a substituent which is an electron accepting (electronegative) group. Typical of strong electron withdrawing groups nitro groups, cyano groups, dicyanoalkylene groups such as dicyanomethylene, cationic amino groups, i.e., $NR_3^{\oplus}$ wherein R represents hydrogen or an organo group such as an alkyl, e.g., methyl and sulphones such as $-SO_2R$ wherein R is as defined above.

It has been found that strong electron withdrawing groups especially useful in the invention are groups having positive Hammett sigma values greater than 0.35, electron withdrawing groups having positive sigma values greater than 0.70, such as nitro groups, have been found particularly effective in the invention. Hammett sigma values for a variety of substituents for an aromatic nucleus can be determined by reference to the published literature or can be determined directly using procedures described in the literature. In accord with conventional practice, electron withdrawing groups are assigned positive sigma values while electron donating (electropositive) groups are assigned negative sigma values.

Sigma values for a given substituent of an aromatic nucleus may vary as a function of ring position. For example, a given substituent to a phenyl ring can exhibit one sigma value in the *meta* position and another when in the *para* position. Exemplary *meta* and *para* sigma values and procedures for their determination are set forth by H. Van Bekkum, P. E. Verkade and B. M. Webster in *Rec. Trav. Chim.*, Volume 78, page 815, published 1959; by P. R. Wells in *Chem. Revs.*, volume 63, page 171, published 1963; by H. H. Jaffe, *Chem. Revs.*, volume 53, page 191, published 1953; by M. J. S. Dewar and P. J. Grisdale in *J. Amer. Chem. Soc.*, volume 84, page 3548, published 1962; and by Barlin and Perrin in *Quart. Rev.*, volume 20, page 75

et seq, published 1966. A partial list of common substituents of aromatic rings is given illustrative Hammett sigma values for various in Table 2.

TABLE 2

Hammett Sigma Values (δ_m and δ_p) for Substituents Attached to Aromatic Ring

Substituent Group	σm	σp
$-CH_3$	-0.07	-0.17
$-C_2H_5$	-0.04	-0.15
$-C_6H_5$	+0.06	+0.01
$-CF_3$	+0.42	+0.55
-OH	0.00	-0.46
$-O^{\ominus}$	-0.71	-0.52
$-OCH_3$	+0.12	-0.27
-F	+0.34	+0.06
-Cl	+0.37	+0.23
-Br	+0.39	+0.23
-I	+0.35	+0.28
$-NO_2$	+0.71	+0.78
$-NH_2$	-0.16	-0.66
$-N(CH_3)_3^{\oplus}$	+0.91	+0.86
$-NH-\overset{\overset{O}{\|}}{C}-Ph$	+0.22	+0.08
-COOH	+0.36	+0.27
$-\overset{\overset{O}{\|}}{C}-O^{\ominus}$	+0.10	+0.13
-CHO	+0.38	+0.22
$-\overset{\overset{O}{\|}}{C}-CH_3$	+0.31	+0.52
-CN	+0.68	+0.63
$-SO_2CH_3$	+1.0	+1.2[1]

All reported sigma values are taken from E.S. Gould, Mechanism & Structure in Organic Chemistry, Published by Holt, Rinehart and Winston, page 221 (1959), except where otherwise indicated.

[1]Estimated Value.

(17)

Electron acceptor materials especially useful as "dark charge exchange materials" in the present invention include those aromatic compounds which contain two or more fused aromatic rings. A partial list representative of such compound includes 2,4,7-trinitro-9-fluorenone; 9 - (dicyanomethylene) - 2,4,7-trinitrofluorene; 2,4,5,7 - tetranitro - 9 - fluorenone; methyl - 2,7 - dinitro - 9 - fluorenone carboxylate; 2 - dicyanomethylene-1,3-indandione. The aforementioned "dark charge exchange materials" may also contain one or more substituents in addition to the desired strong electron withdrawing groups. Such additional substituents may be selected from a wide variety of known substituent groups for aromatic molecules.

Because of the diverse materials which have been found useful as "dark charge exchange materials", the following simple "dark test" is presented for the selection and identification of "dark charge exchange materials", the test being carried out in the dark.

1. The particular material to be tested as a "dark charge exchange material" is applied on a conductive, at least partially transparent support, such as the conductive tin oxide surface of a NESA glass plate, over a surface area, such as a square having dimensions of 80 mm. by 80 mm. The material to be tested should be applied on the conducting support to form a uniform smooth layer of the material. If the material to be tested is an inorganic material, it may be conveniently applied by vacuum evaporation. If the material to be tested for "dark charge exchange properties" is not easily applied by itself, such as many of the above-noted organic materials; it may advantageously be admixed with a suitable film-forming polymeric binder for example, a bisphenol polycarbonate such as 'Lexan' (Trade Mark) 145, and a suitable liquid vehicle, preferably a liquid which is a solvent for both the binder and the material to be tested. The resultant dope may then be uniformly coated on the tin oxide surface of the NESA glass plate. After coating, the liquid vehicle may be removed by evaporation to form a smooth uniform layer suitable for testing. If the solvent coating method described immediately above is used, it should be recognised that the material to be tested for "dark charge exchange properties" and binder may be admixed in the coating vehicle in varying amounts depending upon the compatibility of the particular binder and material to be tested. In this regard, it is noted that many materials when admixed in relatively small amounts with a binder are unsuitable for use as a "dark charge exchange material"; however, certain of these materials are quite effective "dark charge exchange mtaerials" when larger amounts thereof are combined with the binder material.

2. A liquid imaging suspension composed of the particular kind of photosensitive particles which are desired to be used in combination with the material to be tested for "dark charge exchange properties" is formulated. This may be done simply by forming a suspension of the desired electrically photosensitive particles in an electrically insulating liquid such as an isoparaffinic hydrocarbon which is chemically inert with respect to the photosensitive particles. For example, the solvent sold under the name 'Isopar G' (Trade Mark) by the Exxon Corporation, an isoparaffinic hydrocarbon having a boiling point within the range of from 145°C. to 185°C, may be used as the electrically insulating liquid. The electrically photosensitive particles used in the suspension may be selected from a wide variety of known materials which are electrically photosensitive. (Greater detail concerning specific electrically photosensitive particles is given below). In any practical PIER imaging application, the particular photosensitive particles selected for use would be dependent on the particular wavelength of "activating radiation" used. For purposes of the present test, which is carried out in the dark, it is necessary only to be certain that the particular electrically photosensitive particles selected are substantially insensitive to any extraneous radiation which may be present in the test environment other than visible light radiation. For example, electrically photosensitive particles composed of the beta form of copper phthalocyanine, C.I. 74160 (available from American Cyanamid under the Trade Mark of 'Cyan Blue GTNF') have been found especially useful for testing the "dark charge exchange properties" of materials. In preparing the suspension of the electrically photosensitive particles in the electrically insulating liquid, it has generally been found that a liquid imaging suspension containing 0.1 to 1.0 percent by weight of the electrically photosensitive particles dispersed therein may be used the average particle size being typically from 0.1 to 3 microns. In addition, it has been found desirable to admix a charge control agent in the liquid imaging suspension to assist in stabilizing the suspension of the electrically photosensitive particles and to maximize the number of photosensitive particles having a positive polarity electrostatic charge. 'Piccotex 100', the Trade Mark of a copolymer of styrene and vinyl toluene sold by Pennsylvania Industrial Chemical Corporation has been found useful as the charge control agent with 'Cyan Blue GTNF' particles and many other electrically photosensitive particles responsive to visible light. Because it is desirable to have a "standard" suspension of electrically photosensitive particles to use in evaluating a series of materials to be tested for "dark charge exchange properties" and to optimize the total number of particles in the liquid imaging suspension which have a positive polarity, it is suggested that the test imaging suspension be prepared as follows:

Ballmill at 180 r.p.m. for 4 weeks in 250 millilitre brown glass bottles filled to ½ volume with stainless steel balls having a diameter of 3 mm. a composition of 0.5 g. of 'Cyan Blue GTNF' as the electrically photosensitive material selected for use and 150 g. of a mixture of approximately equal parts by weight of 'Piccotex 100' and 'Isopar G'. Milling is carried out in the dark, and the resultant suspension is stored in the dark until just prior to use.

3. In carrying out the present test, it is necessary to use as the imaging suspension described in step (2) above a suspension in which at least 50 percent, and ideally all, of the electrically photosensitive particles dispersed therein have a positive polarity. If there are more negative polarity particles than positively charged particles present in the test imaging suspension, the results of the present test become difficult to interpret. For this reason, the particular imaging composition and its methods of preparation described in step (2) above have been devised because this particular composition, when made as described, has been found to consistently provide a test suspension in which almost all the charged electrically photosensitive particles exhibit a positive polarity. Because of the importance of the charge polarity of the electrically photosensitive particles used in the present test, a polarity check should be made of the liquid imaging suspension before it is employed in the present test. One convenient means of determining the polarity of the liquid imaging suspensions employs an interdigitated electrode configuration as shown in Figs. 7a and 7b.

Referring to Fig. 7a and Fig. 7b, electrodes 66 and 67 are made from a NESA glass plate 71 by etching away the tin oxide surface between the electrodes so that no electrical contact is made between adjacent electrodes. A voltage source 65 is used to apply a positive potential to electrode 66 and a negative potential to electrode 67. A thin insulating layer 68 of polyethylene terephthalate film, e.g. MYLAR (Trade Mark) sold by E. I. du Pont de Nemours, shown in Fig. 7b is placed over the interdigitated electrode configuration of Fig. 7a. The insulating layer 68 serves as both a "blocking layer" to minimize charge exchange between the photosensitive pigment particles and the electrodes and a layer to receive a permanent record of the polarity test. Then, with the electrode arrangement as shown in Fig. 7b held at an angle of 45°, approximately 1 ml of the imaging suspension to be evaluated is poured on the uppermost surface of the insulating layer 68 and allowed to flow uniformly over that part of the uppermost surface of the insulating layer 68 which is directly above the underlying interdigitated electrode confilguration 66 and 67. As the suspended particles encounter the electric fields associated with the biased electrodes, any positively charged particles 69 will be electrostatically attracted to the negative electrodes 67 and any negatively charged particles 70 will be electrostatically attracted to the positive electrodes 66. By comparing the amounts of particles which accumulate at the negative and positive electrodes, the relative proportion of positively and negatively charged particles in a given imaging suspension can be determined. For example, if only positive particles are present, all of the particles will accumulate on electrode 67 and no particle accumulation will be noted on electrode 66. An assessment of the proportions of positively and negatively charged particles present in any given imaging suspension may be made by comparing the optical density of the image pattern formed on insulating layer 68 by the positively charged particles 69 (which pattern corresponds to the shape of negative polarity electrode 67) to the optical density of the image pattern formed by the negatively charged particles 70 (which pattern corresponds to the shape of positive polarity electrode 66). To a good approximation, the ratio of the optical densities of the patterns formed by particles 69 and 70 is equal to the ratio of the number of positively charged particles 69 to the number of negatively charged particles 70 present in the particular suspension being evaluated.

4. A conductive metal roller for example, an aluminium roller having a diameter of about 40 mm. and a width of at least 80 mm. has applied to its external surface an electrically insulating coating to serve as a "blocking layer". This may be accomplished by taping a dielectric coated paper over the conducting roller. Suitable dielectric coated papers are readily obtainable, for example, a conductive paper support exhibiting a specific resistivity of about 10^9 ohm-cm. at 50% R.H. and room temperature (i.e. about 21°C.), which paper support has coated thereon a layer of 'Butvar' B—76 (Trade Mark), a poly(vinyl butyral) resin of a thickness of about 10 microns.

5. The test is conducted in the dark, i.e. in the absence of "activating radiation" or under appropriate safelight conditions, by applying about 0.3 ml. of the liquid imaging suspension prepared in step (2) as a thin uniform film over a freshly prepared 80 mm. by 80 mm. layer of the material to be tested for "dark charge exchange properties" coated on the NESA plate as described in step (1). The conductive metal roller bearing a "blocking layer" as described in step (4) is then biased to +1.0 to +1.5 kilovolts relative to the NESA plate bearing the coating of the material to be tested. The biased roller is then rolled across the NESA plate surface bearing the layer of the material to be tested and the film of liquid imaging suspension. The roller may be moved across the NESA plate mechanically or by hand at a speed of about 10 mm./sec.

6. Following step (5) above, the photosensitive particles which have migrated to and remain located on the 80 mm. by 80 mm. layer of the material being tested for "dark charge exchange properties" (which is coated on the NESA plate as described in step (1)) are electrostatically transferred to the surface of a receiving sheet which is identical to the material used as a "blocking layer" in step (4), i.e. a paper coated with a 10 micron thick layer of 'Butvar' B—76. This can be done conveniently with a 1.0 to 2.0 kilovolt transfer potential. The resultant receiving sheet bearing the particles transferred from the surface of the material being tested coated on the NESA plate is referred to hereinafter as the "NESA plate transfer record". This electrostatic transfer should be carefully executed to ensure there is a transfer of substantially all the particles located on the layer of the material being tested for "dark charge exchange properties". The purpose of the transfer carried out in this step of the dark test is to provide an equivalent basis for comparing the optical density of the image created by the photosensitive particles which have migrated to and remain on the 80 mm. by 80 mm. layer of the material being tested (which is coated on the NESA plate as described in step (1)) to the optical density of the image created by the photosensitive particles which have migrated to and remain on the "blocking layer" of the conductive roller (as described in step (4)). The significance of this optical density comparison is described below. In making the optical density comparison noted in this step of the dark test, areas of the NESA plate transfer record and areas of the "blocking layer" of the conductive roller should be selected which fairly represent the overall optical densities of these two surfaces. One convenient way of accomplishing this is to compare the optical density at a given area(s) of the image formed on the "blocking layer" of the conductive roller to the optical density at area(s) of the NESA plate transfer record which correspond to the area(s) selected on the "blocking layer" of the conductive roller.

After carrying out steps (1)—(6) of the above-described test, whether the material to be tested is a "dark charge exchange material" can be decided as follows: if the material to be tested possesses "dark charge exchange properties", then the electrically photosensitive particles of the liquid imaging suspension will form an 80 mm. by 80 mm. square solid area image on the "blocking layer" of the conductive roller (described in step (4) of the test) which corresponds to the 80 mm. by 80 mm. square layer of the material to be tested coated on the NESA plate (described in step (1) of the test); and this image formed in the dark on the "blocking layer" will have a higher optical density than any similar image which may also have been formed on the NESA plate transfer record. By contrast, if there is formed on the NESA plate transfer record a solid area image which has a higher optical density than the image formed on the "blocking layer" of the conductive roller, then conventional PEP operation is occurring, rather than PIER. In the latter case, the material tested is not a "dark charge exchange material" relative to the particular electrically photosensitive particles used in the liquid imaging suspension. For example, materials, such as tin oxide, provide conventional PEP operation when run through the above test using 'Cyan Blue GTNF' as the photosensitive particles. Similarly, thin layers of electrically insulating materials such as poly(ethylene)terephthalate and 'Lexan' polycarbonate provide conventional PEP operation when run through the above test using 'Cyan Blue GTNF' as the photosensitive particles. Thus, it can be concluded that tin oxide and thin layers of poly(ethylene)terephthalate and 'Lexan' polycarconate possess no significant "dark charge exchange properties" relative to 'Cyan Blue GTNF' particles.

As will be apparent, the above-described dark test is based on the PIER and PEP processes described hereinbefore with reference to Figs. 1a—1d and Figs 2a—2d. That is, a material which exhibits "dark charge exchange properties", as shown in Fig. 1c, will exchange charge with unexposed positive polarity electrically photosensitive particles so that these particles, merely by making electrical contact with the material being tested, will undergo a net change in charge polarity in the dark. Thus, a material which exhibits very strong "dark charge exchange properties", when subjected to the above-described dark test, will effectively cause a net change in charge polarity of all or almost all the positively-charged electrically photosensitive particles with which it comes into electrical contact. As a result, these particles will be repelled from the surface of the material being tested and will be attracted to the adjacent, positive polarity, blocking electrode surface. (See Fig. 1d.) Therefore, a dense, clearly visible, solid area image formed by the unexposed photosensitive particles will be produced on the "blocking layer" of the roller electrode; and, ideally, little or no visible image will be formed on the NESA plate transfer record. If the material being tested for "dark charge exchange properties" is of intermediate strength, as a result of the above-noted dark test, visible images on both the "blocking layer" of the roller electrode and the NESA plate transfer record will be obtained. However, the image formed on the "blocking layer" of the roller electrode will have the greater optical density. If the material being tested possesses little or no "dark charge exchange property", then as a consequence of the above-noted dark test, a conventional PEP result, namely a visible image

on the NESA plate transfer record will be obtained, which image has a greater optical density than any similar image which may also be formed on the "blocking layer" of the roller electrode.

To assist in forming a smooth, uniform layer of the "dark charge exchange material", it has been found convenient in many cases to apply the "dark charge exchange material" to the surface of the electrode to be coated in admixture with a film-forming, binder material that is, in a solid solution therewith. The binder, typically a natural or synthetic polymeric material, assists the "dark charge exchange material" to adhere to the electrode surface and also assists in obtaining a resultant layer which is smooth, uniform, and continuous. Useful binder materials typically have been found to be electrically insulating materials having a resistivity of greater than 10^9 ohm-cm, preferably greater than 10^{12} ohm-cm, at 25°C. When a binder is used, the particular binder material selected should, of course, be substantially insoluble in any liquid contained in the liquid imaging suspension, if such a liquid is used.

Among the various binder materials which may be useful are polycarbonates, such as a bisphenol A polycarbonate, e.g., 'Lexan 145'; poly(vinyl acetals), e.g., 'Butvar B—76'; polyesters, e.g. 'Vital PE 101' (Trade Mark) poly-[ethylene - coalkylenebis(alkyleneoxyaryl)-phenylene-dicarboxylate].

When a binder is used in the "dark charge exchange layer", the amount of binder used may vary over a considerable range. The optimum amount of binder depends, in part, on the efficiency of the "dark charge exchange material" relative to a particular kind of electrically photosensitive particle, i.e., the ability of the material to exchange charge with the unexposed photosensitive particles, and the compatibility of a given binder with a given "dark charge exchange material", e.g., certain binders because of their particular composite physical, chemical, and electrical properties may enhance or detract from the "dark charge exchange properties" of a given "dark charge exchange materials". Thus, for very efficient "dark charge exchange materials", larger amounts of binder, if a binder is used, may be used in comparison to the amount of binder which may be used with less efficient "dark charge exchange materials". Of course, the amount of binder should not be so large in comparison with the amount of the "dark charge exchange material", that the resultant "dark charge exchange properties" of the combined layer become too diluted. (See Examples 16 and 17 following.)

For "dark charge exchange materials" having an efficiency comparable to, for example, 2,4,7-trinitro-9-fluorenone, the amount of binder may be typically within the range of 22 percent to 50 percent by weight, preferably 25 to 40 percent by weight, based on the dry weight of the "dark charge exchange layer". The amount of "dark charge exchange material" used when a binder is employed is preferably 20 to 75 percent by weight, based on the dry weight of the "dark charge exchange layer".

The "dark charge exchange layers" may be applied by various methods, as discussed above in the procedure for testing for "dark charge exchange properties". To obtain a uniform coating of "dark charge exchange material" and binder wherein the "dark charge exchange material" is distributed homogeneously throughout the layer, it has been found particularly useful to employ the solvent coating technique. "Dark charge exchange layers" having varying thicknesses may be employed. Inorganic crystalline "dark charge exchange layers" applied by vacuum evaporation, such as indium, typically would have a thickness of 5 to 20 nanometres. "Dark charge exchange layers" comprising a binder have been found to be effective at dry thicknesses of from 5 microns to 50 microns. Thinner or thicker "dark charge exchange layers" may also be used. As suggested above, however, the layers of "dark charge exchange material" must contain a sufficient surface density of "dark charge exchange material" to permit uniform coverage of the exposure zone surface with an effective amount of the "dark charge exchange material". For example, it is possible to apply such a thin layer of a "dark charge exchange material", for example 2,4,7-trinitro-9-fluorenone, that there may be an insufficient surface density of "dark charge exchange material" deposited to cause PIER operation, and the photosensitive particles may tend to revert to a PEP mode of operation. (That is, the exposed particles, rather than the unexposed particles, may begin to exchange charge and reverse their polarity upon contact with such extremely thin layers of "dark charge exchange material"). See Example 16 below.

Although certain of the "dark charge exchange layers" described herein are known to possess at least some degree of photoconductivity in at least certain areas of the electromagnetic spectrum, it has been determined that the "dark charge exchange properties" of these layers are not equivalent to any photoconductive properties these layers may possess, and it is believed that the "dark charge exchange properties" of these layers are substantially independent of any photoconductivity these layers may exhibit. On this point, reference may be made to Example 9 below which demonstrates an operative PIER process wherein a "dark charge exchange layer" composed of (a) 2,4,7-trinitro-9-fluorenone and (b) a poly-(vinyl butyral) binder is subjected to a white tungsten light exposure which has been filtered to remove virtually all of the small amount of the ultraviolet radiation generated by such a

light source. (Compositions composed of a binder and 2,4,7-trinitro-9-fluorenone are generally regarded as non-photoconductive in the presence of visible light but do exhibit some degree of photoconductivity in the presence of ultraviolet radiation.)

The electrically photosensitive particles used in PIER may be selected from a variety of photoconductive materials. Extensive discussion and description of such materials appear in the literature, for example, in U.S. Patent No. 3,383,993. For this reason, extensive discussion regarding these materials is considered unnecessary in the present specification.

It may be noted that the physical composition of these electrically photosensitive particles may vary widely. For example, single component particles which are both photosensitive to activating radiation of the desired wavelength and have the desired colour may be used as described in U.S. Patent 2,758,939. Examples are such inorganic pigments as oxides, sulphides, selenides, tellurides, or iodides of cadmium, zinc, mercury, antimony, bismuth, thallium, indium, molybdenum, aluminium and lead. Other photoconductive inorganic materials include arsenic trisulphide, cadmium arsenide, lead chromate, selenium, sulphur. Various organic photoconductive pigments such as phthalocyanine pigments, azo pigments, quinacridone pigments, and anthraquinone pigments, may also be used. The above-noted substances are well known photoconductive materials.

In addition, known multi-component electrically photosensitive particles may be used. In such a case, the particles may comprise a separate photoconductive component and a separate colorant component such as a dye or pigment and, optionally, a binder such as a polymeric material, a filler material, for example, glass or plastic beads, and chemical and spectral sensitizers such as various sensitizing dyestuffs. In addition, one or more filter layers may be present in these multi-component particles.

The electrically photosensitive particles used in the present invention may be all of one colour to form a monochrome image, or alternatively, an admixture of different coloured particles may be used to form multi-colour images. For example, is illustrated in Fig. 3a—3c a mixture of cyan, magenta, and yellow particles which are electrically photosensitive to red, green, and blue light, respectively, may be used to form, through subtractive colour formation, multi-colour images corresponding to the colour of the original exposure. In Fig. 3a—3c, a multicolour mixture of cyan, magenta, and yellow particles 20 which are electrically photosensitive to red, green, and blue light, respectively, are dispersed in an electrically insulating liquid 24 between electrodes 21 and 23. The electrode 23 is transparent and has coated on the surface thereof a transparent "dark charge exchange layer" 22. The electrode 21 preferably has coated on the surface thereof a "blocking layer" 26, although useful multicolour images can also be obtained in PIER by employing electrode 21 free from blocking layer 26. The particles 20 initially carry a positive polarity electrostatic charge. As illustrated in Fig. 3a, an electric field is applied using a potential source 25 between the electrodes 21 and 23, and simultaneously therewith the particles 20 are exposed to red light. As a result the positively charged particles 20 migrate to the "dark charge exchange layer" 22 where the cyan coloured particles which are sensitive to red light are immobilized. The magenta and yellow coloured particles which are not sensitive to red light exchange charge with the layer 22 thereby reversing polarity to become negatively charged and are repelled from the layer 22 to the positive polarity electrode 21. Thus, as shown in Fig. 3a, a cyan coloured negative appearing image of the original red light exposure is formed on the surface of the layer 22 and a positive appearing red coloured image (formed by the subtractive colour combination of the magenta and yellow particles) of the original red light exposure is formed on the "blocking layer" 26. In a similar manner, as shown in Fig. 3b and 3c, green and blue light exposures of the particles 20 will result in the formation of green and blue positive appearing images, respectively, on the layer 26 and magenta and yellow negative appearing images, respectively, on the "dark charge exchange layer" 22. In various multicolour embodiments of PIER, random mixtures of two, three, or more differently coloured electrically photosensitive particles may be employed. Each differently coloured particle is responsive to a specific given wavelength of "activating radiation" so that multicoloured images are produced by a single exposure of the electrically photosensitive particle mixture to light composed of a mixture of the various specific wavelengths of radiation to which each of the differently coloured particles are sensitive.

The intensity of the exposure to "activating radiation" used in PIER may vary depending on the particular electrically photosensitive particles selected, the relative transparency of the electrode and the "dark charge exchange layer" or the "blocking layer" through which exposure may be effected. The intensity of the exposure should be sufficient to prevent the exposed particles from undergoing a net change in charge polarity upon electrical contact with the "dark charge exchange layer". For example, when a liquid imaging suspension employing finely-divided copper phthalocyanine pigment particles dispersed therein is exposed to visible light through a "dark charge exchange layer" containing 2,4,7-trinitro-9-fluorenone coated on a NESA glass electrode,

a tungsten light source providing an exposure intensity greater than 50 footcandles on the liquid imaging suspension has been found to provide readily discernible visible images.

The size of the electrically photosensitive particles used in PIER may vary considerably, depending upon the image resolution desired, whether the particles are used in a liquid suspension or simply disposed as a dry powder in the gap between the two electrodes. Typically, the size of the particles varies from 0.1 micron to 100 microns, although larger or smaller particles may be employed under certain conditions. Generally, where liquid particle suspensions are used, the average particle size is less than 3 microns, generally from 0.1 to 1 microns. Where a dry powder is used, the particles typically are larger, generally having an average particle size of from 2 to 20 microns. Where high resolution, continuous tone images are desired, it is generally preferable to use a liquid imaging particle suspension.

In a preferred embodiment of the present invention, the electrically photosensitive particles used in the invention are suspended in an electrically insulating carrier liquid between the two spaced electrodes. The process of the present invention is referred to herein as "electrophoretic" which, of course, connotes movement or migration of charge-bearing particles in a fluid, generally a liquid. It should be understood, however, that as stated hereinbefore it is believed that the PIER process may also be used in other fluid media such as air or other gas and in a vacuum wherein electrically photosensitive particles having a positive polarity electrostatic charge are simply randomly deposited as a dry powder in the gap between the two spaced electrodes.

The use of an electrically insulating carrier liquid is preferred as, normally, a much better image resolution has been obtained by dispersing the electrically photosensitive particles as extremely finely-divided particles in a liquid carrier medium. In addition, it is possible to operate with higher electrical field strengths between the spaced electrodes when using a liquid carrier, rather than gaseous carriers such as air. This is because gases will break down and ionize at relatively low operating voltages compared with many readily available electrically insulating liquid materials.

Typically, when a liquid carrier is used, a material having a resistivity greater than 10^9 ohm-cm., preferably greater than 10^{11} ohm-cm., and, preferably, a dielectric constant less than 3.0 is employed. Among the various useful liquid carrier vehicles are alkyl-aryl materials, for example, the alkylated benzenes, e.g., xylenes, and other alkylated aromatic hydrocarbons described in U.S. Patent 2,899,335. Other useful liquid carrier vehicles are various hydrocarbons and halogenated hydrocarbons, for example, cyclohexane, cyclopentane, n-pentane, n-hexane, carbon tetrachloride, fluorinated lower alkanes, for example, trichloromonofluoromethane, trichlorotrifluoroethane, typically having a boiling range of from 2°C. to 55°C. Particularly useful hydrocarbon liquid carrier vehicles are the paraffinic hydrocarbons, for example, isoparaffinic hydrocarbon liquids having a boiling point in the range of 145°C. to 185°C., for example, as sold as "Isopar" solvents. Various other petroleum distillates and mixtures thereof may also be used as liquid carrier vehicles. Additional useful insulating liquids include 'Sohio' (Trade Mark) Odorless Solvent. Molten liquid insulating thermoplastic materials could also be used.

When a liquid imaging suspension is used, the concentration of the electrically photosensitive particles in the liquid should be considered. In contrast to known PEP liquid imaging suspensions generally containing from 5 to 6 percent by weight of electrically photosensitive particles, it is generally preferred to use from 0.01 to 3.5 percent by weight of electrically photosensitive particles in PIER. In some cases, it has been observed in PIER that as the particle concentration approaches 5 to 6 percent by weight, the image quality provided by PIER tends to degrade, particularly the quality of the image formed on the "blocking layer" electrode.

To date, the best multicolour imaging results have generally been obtained using multicolour imaging suspensions containing from 0.1 to 1.5 percent by weight of electrically photosensitive particles.

As indicated previously, when a liquid imaging suspension is used, it is frequently desirable to incorporate a charge control agent in the suspension. Such materials are well known in the field of liquid electrographic developer compositions where they are employed for purposes substantially similar to that described herein. Thus, extensive discussion of these materials herein is deemed unnecessary. These materials typically are polymeric materials incorporated by admixing the polymer in the liquid carrier vehicle of the suspension. The charge control agents appear to function as dispersion and electrostatic charge stabilizers for the suspension. For example, it has been found that upon addition of 'Piccotex 100' (Trade Mark), a styrene-vinyl toluene copolymer to an imaging suspension containing photosensitive materials which normally provide both positive polarity and negative polarity particles in the suspension, a reduction in negative polarity particles is achieved so that one obtains a greater uniformity in the charge polarity exhibited by the suspended particles. In addition to and possibly related to the aforementioned enhancement of uniform charge polarity, it has been found that the charge control agents often provide more stable suspensions, i.e., suspensions which exhibit substantially less settling out of the dispersed

photosensitive particles.

Typical polymeric materials which may be used as charge control agents in the above-described liquid imaging suspensions are electrically insulating (i.e. have an electrical resistivity at 25°C. of greater than 10^9 ohm-cm.) natural and synthetic polymeric materials and waxes, which are wholly or at least partially soluble in the liquid carrier vehicle of the imaging suspension. The selection of a particular charge agent will depend, in large part, on the particular electrically photosensitive particles and liquid carrier vehicle which are used.

The strength of the electric field applied between the spaced electrodes used in PIER may vary considerably depending upon a number of factors such as the impedance of the specific "dark charge exchange layer" and "blocking layer" (if one is used), the desired image density, the dielectric strength of the fluid medium (for example, as is well-known many electrically insulating liquids can withstand higher field strengths than gaseous media such as air), the degree of image resolution desired, and the particular charge control agent and electrically photosensitive particles employed. Generally, as in PEP processes, it has been found in PIER that optimum image density and resolution are obtained by increasing the field strength to as high a level as possible without causing breakdown of the fluid medium in the interelectrode gap. For example, when electrically insulating liquids, such as an isoparaffinic hydrocarbon, e.g., 'Isopar G' (Trade Mark), are used, field strengths greater than 10,000 volts/mm. have been found to give discernible images, although higher field strengths ranging from 20,000 volts/mm.—160,000 volts/mm. are preferred, especially to improve image resolution and to achieve improved colour separation when multicolour images are formed. In general, for a given set of imaging conditions, there is no critical field strength below which an image suddenly disappears and above which an image suddenly reappears. Rather, it is observed that as the field strength is decreased, image quality gradually declines. Comparing PIER to PEP, it has been observed that readily discernible images may be formed (using a liquid imaging suspension) in PEP with field strengths as low as 4000—4800 volts/mm.

Fig. 4 represents diagrammatically the total voltage drop, V_T, occurring in PIER using a liquid imaging suspension 61 disposed between a pair of spaced electrodes 50 and 51. As indicated, the interelectrode voltage drop V_I, occurring across the gap occupied by liquid imaging suspension is actually only one of three components contributing to the total voltage drop between electrodes 50 and 51. There is also a voltage drop, V_B, occurring across the "blocking layer" 59 (if one is used) and a voltage drop, V_D, occurring across the "dark charge exchange layer" 54. The total voltage drop, V_T, is equal to the sum of V_D, V_I, and V_B. In practice, V_T is the actual voltage measured. V_I may be computed by experimentally determining the voltage drop occurring across the "blocking layer" and "dark charge exchange layer" and then subtracting these values from the measured V_T. Alternatively, in some instances one can approximate V_I by using a liquid imaging suspension having a thickness known to be much greater than the thickness of either the "blocking layer" 59 or the "dark charge exchange layer" 54, and then assuming that the sum of V_B and V_D is relatively small compared to V_I so that to a first approximation $V_T \sim V_I$. It will be appreciated, however, that where (as often is the case in actual practice) the electrode surfaces are closely spaced to one another such that the interelectrode gap becomes comparable with the thickness of the "dark charge exchange layer" and/or the "blocking layer", the voltage drops which occur across these layers become significant and cannot be ignored.

The electrode spacing used in PIER may vary depending on whether a liquid imaging suspension or a gaseous fluid or vacuum is used and on whether an electrically insulating binder is used in the "dark charge exchange layer". For example, in the case where liquid imaging suspensions are employed, it is preferred to use electrode spacings of the order of 50 microns or less, with only a very thin film of the liquid imaging suspension sandwiched between the electrodes. In the case where a vacuum or an air gap is used, larger interelectrode spacings may have to be employed due, in part, to the larger photosensitive particle size then employed.

The electrodes used in PIER may be composed of a variety of different conducting materials and may have a variety of different shapes. The electrodes may be composed of substantially inflexible materials, for example, various metallic plates or metal-coated supports, e.g., NESA glass, or flexible materials, for example, film supports coated with thin conducting films, e.g., evaporated metal films. The electrically conducting material forming the electrodes may be selected from such diverse materials as conducting inorganic materials such as an optically transparent conductive ceramic and various conducting metals, e.g., nickel, aluminium, tin oxide, etc.; conducting organo-metallic materials; and conducting organic materials such as various conducting polymers. Typically, the conducting materials useful as the electrodes used in PIER have a specific resistivity less than 10^4 ohm-cm. at 25°C.

The electrodes used in PIER may, for example, be in the form of a substantially flat plate bearing a conductive surface, a web or belt support bearing a conducting surface, or

a roller or drum bearing a conductive surface. In this regard, the spaced electrodes used in PIER may both be of the same general shape and material composition or may be of differing shapes and material composition. For example, two conducting drum electrodes may be used, each bearing an appropriate "blocking layer" or "dark charge exchange layer", with the electrically photosensitive particles disposed in the nip between the two drum electrodes. Alternatively, one of the electrodes may be a drum or flexible web electrode and the other electrode may be a substantially flat plate. In addition, one or both electrodes may move relative to one another (as illustrated in Figs. 5 and 6); or both electrodes may be fixed. It will be apparent, that the specific electrode shape, composition, and whether the electrode moves or is fixed, is not critical. Of course, any one of these factors may become highly significant depending upon the particular application in which the general PIER process is employed, for example, in a camera, a document copier, an optical display device. Various non-interfering adhesive subbing layers may be used, if desired, to promote adhesion between a particular electrode and a particular "blocking layer" and/or "dark charge exchange layer".

Preferably, at least one of the electrodes used in PIER is at least partially transparent to the particular "activating radiation" employed to facilitate exposure of the photosensitive particles. If the electrode bearing the "dark charge exchange layer" is the electrode through which exposure is effected, then the "dark charge exchange layer" should also be at least partially transparent. In certain situations, for example, if the PIER process is to be used in an optical display device, it may be useful to employ two transparent electrodes. Exposure could then be made through one transparent electrode and read-out could be effected through the other transparent electrode. The use of transparent electrodes is not essential as may be seen by reference to Fig. 6 which illustrates an apparatus for practising PIER which does not require the use of a transparent electrode. (In Figs. 5 and 6 like numbers refer to like apparatus and materials.) In Fig. 6, a liquid imaging suspension 14 is exposed by projection exposure means 81 in the nip 80 formed between conductive roller electrode 10 and electrode 12. Electrode 12 bears on the surface thereof a "dark charge exchange layer" 13 and an electrode 10 bears on the surface thereof a "blocking layer" 11. A potential difference between the electrodes 10 and 12 is created as illustrated by the circuit 9 in Fig. 6 such that the electrode 12 is the negative polarity electrode and the electrode 10 is the positive polarity electrode.

As discussed above, one of the electrodes used in PIER advantageously bears a "blocking layer" on its surface. This "blocking layer" may be permanently affixed to the electrode to which it is applied or merely temporarily affixed thereto as explained hereinafter with reference to Fig. 5. The "blocking layer" is generally composed of various electrically insulating materials including various papers, dielectric coated papers, natural or synthetic polymer films, and waxes. Typical materials which have been found useful are film-forming materials which have an electrical resistivity greater than 10^9 ohm-cm., preferably greater than 10^{12} ohm-cm., at 25°C., for example, poly(ethylene terephthalate), and poly(vinyl butyral). Useful "blocking layers" typically have a dry thickness within the range of 5 to 200 microns, although thicker and somewhat thinner layers may also be used. It should be recognized, that if the "blocking layer" is too thin, the "blocking layer" may become ineffective. Of course, it will be appreciated that the useful thickness of a particular "blocking layer" will depend, in large part, on the specific material selected.

One electrode configuration which has been found useful in PIER is illustrated in Fig. 5 and is used in each of Examples 1—26 below. The electrode configuration of Fig. 5 comprises a conductive metal roller 10 bearing a "blocking layer" 11, for example, a dielectric coated paper, a transparent conductive plate 12, such as NESA glass, bearing a "dark charge exchange layer" 13. A liquid imaging suspension 14 containing a multiplicity of positively charged electrically photosensitive particles 8 is applied to the surface of the "dark charge exchange layer" 13. "Activating radiation" from a source 16 is transmitted through the plate 12. An original 17 to be projected on to the plate 12, such as a photographic transparency is typically positioned together with any necessary or desired colour separation filters 18 and other filters 19, such as ultra-violet filters, between the source 16 and the plate 12. In such a configuration, as the roller 10 is rolled over the layer 13 bearing the imaging suspension 14 a potential difference is applied between the plate 12 and the roller 10 (which are connected to an electrical source 9) by closing a switch 15, and the imaging suspension 14 is exposed to a pattern of "activating radiation".

The roller 10 is moved relative to the plate 12 at a rate which permits the photosensitive particles 8 which are not exposed to radiation to reverse their charge polarity upon electrical contact with the "dark charge exchange layer" 13 while the photosensitive particles 8 which are exposed to radiation are immobilized at the layer 13 upon making electrical contact therewith.

As a result an image composed of unexposed photosensitive particles is formed on the "blocking layer" 11 and a complementary image of exposed particles is formed on the

"dark charge exchange layer" 13. Either image or both may be used. In the electrode configuration of Fig. 5, varying roller speeds may be used, roller speeds of 100 mm./sec. or less, preferably 5 to 100 mm./sec., have been found satisfactory. It has been observed that when the electrode configuration of Fig. 5 is used, roller speeds greater than 150 mm./sec. can result in degradation of PIER image quality. It has been found possible to avoid a certain amount of the image degradation which can occur at such higher roller rates by using higher intensity exposures and higher electrical field strengths.

As indicated, using the electrode configuration of Fig. 5, two complementary images typically are formed. The image formed on the "blocking layer" 11 is a positive appearing image of the original 17 and the image formed on the "dark charge exchange layer" 13 is a negative-appearing image. If it is desired, as often may be the case, to reuse the apparatus of Fig. 5 to form additional images, either one or both of the images on the "blocking layer" 11 and the "dark charge exchange layer" 13 may be transferred to other receiver elements. Various well-known electrographic image transfer techniques, for example, electrostatic transfer, or adhesive transfer using an adhesive tape material to pick off the image, may be employed.

Alternatively, the images formed on the "blocking layer" 11 and the "dark charge exchange layer" 13 may be permanently fixed to these layers. This may be accomplished by various conventional means, for example, by overcoating the image with a thin protective polymer film. A separate polymer overcoat may be applied subsequent to the image formation, or if a suitable polymeric binder is contained in the liquid imaging suspension, it may be used as a fixing agent.

Although it will be appreciated that the actual imaging apparatus constructed as illustrated in Fig. 5 may vary in many respects, the following information is provided, for reference, regarding the specific apparatus used in the following Examples 1—26. The conductive metal roller 10 was of aluminfum and 40 mm. diameter. All exposure readings recorded for Examples 1—26 were measured in footcandles at the surface of the imaging suspension 14. These exposure readings, however, were the exposure readings measured for the "unfiltered" light source used in each example; that is, these readings were not corrected for the filter factors of the filters 18 and 19 (used in some of the following examples) or any filtration effect caused, for example, by the light passing through the original image pattern 17. The readings do take into account the filtration effect caused by the plate 12, the layer 13, and the suspension 14. The spacing between the "dark charge exchange layer" 13 and the "blocking layer" 11 in Examples 1—12B and 13—26 was solely the thickness of a thin film of the liquid imaging suspension 14. In Example 12C, 50 micron thick spacers, not shown in Fig. 5, are inserted between the "blocking layer" 11 on the roller electrode 10 and the "dark charge exchange layer" 13 during imaging.

Example 1:

Two Colour Images with an Indium "Dark Charge Exchange Layer".

Indium metal was vacuum evaporated at about 0.4 optical density onto the surface of a conductive glass plate composed of NESA glass to form a transparent "dark charge exchange layer" 13 in an imaging apparatus of the type illustrated in Fig. 5. A dielectric paper covered conductive roller electrode 10 was used to receive unexposed migrated photoconductive pigment particles. The dielectric paper 11 was a paper support coated with an insulating layer of 'Butvar B—76'; a poly(vinyl butyral) resin having a dry thickness of about 10 microns.

Two separate photoconductive pigment dispersions (A) and (B) were prepared for use in this Example by ball milling the formulations given below for approximately two weeks in 60 ml. brown glass bottles filled to one-half volume with 3.2 mm. diameter stainless steel balls.

Pigment Dispersion A:

0.1 gram of 'Cyan Blue GTNF'

35 grams of a mixture of 'Piccotex 100' a styrenevinyl toluene copolymer and 'Isopar G' an isoparaffinic aliphatic hydrocarbon liquid in equal parts by weight.

Pigment Dispersion B:

As pigment dispersion A except that magenta particles composed of 'Watchung Red B' (Trade Mark) a barium salt of 1 - (4' - methyl - 5 - chloroazobenzene-2' - sulphonic acid) - 2 - hydroxy - 3-naphthoic acid, C.I. No. 15865, replaced the 'Cyan Blue GTNF'.

Prior to imaging, equal volumes of dispersions A and B were combined and a small amount of this blended cyan and magenta pigment dispersion was spread onto the indium surface as the liquid imaging suspension 14. An electrical potential of +1.0 Kv was applied to the paper covered roller electrode while it was rolled at a rate of 30—50 mm./sec. across the indium "dark charge exchange layer" bearing the suspension 14. Simultaneously with the movement of the roller electrode, an exposure was made, using a tungsten source first passed through KODAK 'Wratten' Filter No. 47B (blue), KODAK 'Wratten' Filter No. 58 (green), and KODAK 'Wratten' Filter No. 29 (red) colour separation filters, each filter located in a different exposure area, then through the original 17 a black-and-white photographic negative and finally through the indium/NESA glass transparent electrode carrying the imaging suspension. KODAK and 'Wratten' are Registered Trade Marks.

Observations

On the indium "dark charge exchange layer" a low density cyan image was observed in the red light exposed areas and a magenta image was observed in the green light exposed areas. A two colour pigment image was formed on the dielectric paper receiver 11 in areas corresponding to the areas of the pigment dispersions not exposed to light, thus illustrating that the exposed particles did not transfer or migrate from the indium surface to the dielectric paper covered roller electrode 10.

Example 2:

Two Colour Images with a Modified "Dark Charge Exchange Layer".

In this example the imaging apparatus and materials were identical to Example 1 except that the "dark charge exchange layer" of this example was formed by coating from dichloromethane an overcoat layer of the following composition on the surface of the NESA glass plate.

Dispersion C:

0.5 g. indium particles
0.2 g. 2,4,7-trinitro-9-fluorenone
0.2 g. 'Lexan 145' Bisphenol-A polycarbonate
20 ml. dichloromethane

The overcoat layer was dried to remove substantially all of the dichloromethane coating vehicle. The resultant layer was about 25 microns thick. The pigment dispersions for imaging were identical to Dispersions A and B described in Example 1 with the exception that they were milled for approximately 10 days and then stored for 1 week. The separate dispersions were mixed as in Example 1 just prior to use.

The blended pigment dispersion was applied to the overcoated NESA glass plate to form the liquid imaging suspension. A conductive roller electrode 10 bearing a dielectric coated paper as in Example 1 was rolled over the coated NESA plate bearing the liquid imaging suspension using an electrode bias of +1.5 Kv with simultaneous white light exposure from a tungsten lamp through an original 17 composed of a black-and-white photographic negative transparency. (No colour filters were used in the exposure of this example.)

Observations:

The image formed on the "dark charge exchange layer" coated on the NESA plate indicated that particles in exposed areas did not migrate to the roller. The image on the "dark charge exchange layer" coated on the NESA plate exhibited low background and red and green separation. This image was subsequently transferred to a suitable dielectric paper receiver sheet by applying a −1.0 Kv potential to a conductive roller serving as a temporary conductive backing for the paper receiver.

The image initially formed on the dielectric paper covering roller 10 was the same sense as the original, that is, a positive image, indicating that the unexposed particles migrated to the roller. This image had some background density and good image quality.

Example 3:

Three Colour Images with a Modified "Dark Charge Exchange Layer".

Cyan and magenta pigment dispersions as prepared in Example 2 were used in this example. In addition, a yellow photoconductive pigment dispersion (D) was prepared from the following formulation:

Dispersion D:

0.2 gram of a flavanthrone pigment, C.I. No. 70600, 'Indofast Yellow' (Trade Mark)
35 grams of a mixture of equal parts by weight of 'Piccotex 100' resin and 'Isopar G'

Dispersion D was ball milled for four weeks, rested for one week and combined in equal volumes just prior to use with the cyan and magenta dispersions to form a blended pigment dispersion as the liquid imaging suspension.

The "dark charge exchange layer" and imaging apparatus were identical to those in Example 2.

The PIER process was carried out by biasing the dielectric paper covered aluminium roller at an electrical bias of +1.5 Kv using the same procedure described in Example 2. The aluminium roller velocity was 30 to 50 mm./sec.

Observations:

The image formed on the "dark charge exchange layer" had well-separated magenta, yellow and cyan pigments in those areas exposed by green, blue and red light, respectively.

The image formed on the dielectric paper covered aluminium roller electrode showed that the pigment particles migrated to the roller in the unexposed areas of the "dark charge exchange layer".

Example 4:

Cyan Image with a 2,4,7-trinitro-9-fluorenone "Dark Charge Exchange Layer".

A photoconductive cyan pigment dispersion (E) of the following composition was prepared:

Dispersion E:

0.2 gram 'Cyan Blue GTNF'
35 grams of a mixture of equal parts by weight of 'Piccotex 100' and 'Isopar G'

The above pigment dispersion was ball milled for two weeks in a small brown glass bottle containing 3.2 mm. diameter stainless

steel balls filled to the level of the dispersion.

In this example, the "dark charge exchange layer" 13 coated on the NESA glass plate electrode 12 of Fig. 5 was a saturated solid solution of 2,4,7-trinitro-9-fluorenone in a 'Lexan 145' polycarbonate binder. The layer was coated from a 50% solution of the binder in dichloromethane solvent and then dried to form a transparent layer approximately 25 microns thick of polycarbonate and 2,4,7-trinitro-9-fluorenone. The layer consisted of equal parts by weight polycarbonate and 2,4,7-trinitro-9-fluorenone.

Pigment dispersion E was used as liquil imaging suspension 14 and was spread across layer 13 by a dielectric coated paper identical to that used in Example 1 mounted on roller electrode 10. The roller electrode 10 was held at an electrical bias of +1.5 Kv relative to plate 12 and moved across plate 12 at a velocity of 30—50 mm./sec. The pigment dispersion E was simultaneously subjected to a tungsten light exposure through the plate 12. The light exposure originated from a tungsten light source and first passed through a red KODAK 'Wratten' 29 filter and then an original 17 composed of a black-and-white photographic negative transparency before passing through the plate 12.

Observations:

The image formed on the "dark charge exchange layer" indicated that the red-light exposed particles remained on the "dark charge exchange layer". The image formed on the "blocking layer" 11 mounted on the roller electrode indicated that the pigment particles migrated in the unexposed areas to form a red image on the layer 11 having the same image sense as the black-and-white negative original.

Example 5:

Magenta Image with a 2,4.7-trinitro-9-fluorenone "Dark Charge Exchange Layer".

A magenta pigment dispersion (F) was prepared according to the following formulation:

Dispersion F:

0.2 gram 'Watchung Red B'

35 grams of a mixture of equal parts by weight of 'Piccotex 100' and 'Isopar G'

The pigment dispersion F was used as the liquid imaging suspension 14. The "dark charge exchange layer" 13 and the method of imaging were similar to that of Example 4 except that a green KODAK 'Wratten' 58 filter was used in place of the red KODAK 'Wratten' 29 filter used in Example 4.

Observations:

The image formed on the "dark charge exchange layer" indicated that the green light exposed particles remained on the "dark charge exchange layer". The image formed on the "blocking layer" 11 of the roller electrode 10 indicated that pigment particles migrated in unexposed areas of the "dark charge exchange layer" to form a magenta image on the "blocking layer" 11 having the same image sense as the original.

Example 6:

Three Colour Imaging with 'Sohio' Odorless Solvent 3440 and a 2,4,7-trinitro-9-fluorenone/poly(vinyl butyral) "Dark Charge Exchange Layer".

Separate magenta, yellow and cyan photoconductive pigment dispersions were formed. Each dispersion contained 2.0 grams of pigment, either 'Watchung Red B', or 'Indofast Yellow' or 'Monolite Fast Blue GS' (Trade Mark) (C.I. No. 74100, the alpha form of metal free phthalocyanine) and was prepared by ball milling (using stainless steel balls) each of these pigments in separate bottles for 7 days in 12 grams of 'Sohio' Odorless Solvent 3440. These three pigment dispersions were blended together in equal volumes and then diluted with additional 'Sohio' Odorless Solvent 3440 (20 parts volume of solvent to 1 part volume of dispersion) just prior to use to form a single multi-colour liquid imaging suspension 14 having an overall black colour.

A "dark charge exchange layer" 13 was prepared by coating and drying to 20—25 micron thickness the following formulation on a NESA glass plate 12:

0.5 gram 2,4,7-trinitro-9-fluorenone

0.5 gram 'Butvar B—76' poly(vinyl butyral) containing approximately 9% of polyvinyl alcohol

30 ml. p-dioxane solvent

To produce an image, the above-described multi-colour suspension was spread on the "dark charge exchange layer" 13 by the movement of a dielectric paper covered conductive roller 10 (having a construction identical to that described in Example 1) across the plate 12 at a velocity of 30—50 mm./sec. and with an electrical bias of +1.5 Kv. A white light exposure through a continuous-tone colour positive transparency and then through the plate 12 was effected simultaneously with the movement of the conductive roller.

Observations:

The "blocking layer" 11 of the roller 10 exhibited a good quality three-colour positive appearing image of the original colour positive, indicating pigment migration or transfer in the unexposed areas of the "dark charge exchange layer".

By way of comparison, using the NESA glass substrate alone as an electrode without the "dark charge exchange layer" there resulted an image on the "blocking layer" 11 of the roller 10 which showed pigment migration or transfer in the exposed areas of the NESA glass electrode. Excessive magenta particle transfer was observed in the red exposed areas.

Example 7:
A Cyan Monocolour Image without a Charge Control Agent.

A liquid imaging suspension 14 was prepared by manually mixing the following components:

0.1 gm 'Cyan Blue GTNF'
10 ml 'Isopar G'

This suspension contained a mixture of both positive and negative polarity particles.

A "dark charge exchange layer" 13 was prepared by coating the following formulation on a NESA glass plate 12:

0.5 gm. 2,4,7-trinitro-9-fluorenone
0.25 gm. 'Lexan 145' polycarbonate
10 ml. p-dioxane
20 ml. dichloromethane

The "dark charge exchange layer" 13 was air dried to form a layer 8—10 microns thick.

A dielectric paper covered conductive roller identical to that used in Example 1 was held at an electrical bias of +1.5 Kv while moving the roller across the above-described liquid suspension covering the "dark charge exchange layer" at a rate of 10—20 mm/sec. A simultaneous red light exposure of approximately 2000 foot-candles was made through a black-and-white negative and then through the plate 12.

Observations:

The "blocking layer" 11 of the roller electrode 10 showed that cyan pigment had migrated from the "dark charge exchange layer" 13 in the background or unexposed areas. However, the pigment particles had remained on the exposed areas of the "dark charge exchange layer".

In a control test using a NESA glass electrode without a "dark charge exchange layer", the image formed on the NESA glass surface illustrated the migration of the pigment particles in the exposed areas and the retention of the pigment particles in the unexposed areas of the electrode.

Example 8:
Roller Speed Comparison.

Separate dispersions of 0.1 gm. of each of 'Cyan Blue GTNF', 'Watchung Red B' and 'Indofast Yellow' in 35 gm. liquid mixture composed of equal parts by weight of 'Piccotex 100' and 'Isopar G' were prepared by ball milling each of these pigments in separate bottles. The 'Cyan Blue GTNF' and 'Watchung Red B' dispersions were milled for 36 hours. The 'Indofast Yellow' dispersion was milled for 7 days.

The milled pigment dispersions were rested for 7 days and then combined 5 minutes before use to form a single multicolour liquid imaging suspension 14 by blending together 35 drops of the cyan dispersion, 30 drops of the magenta dispersion and 20 drops of the yellow dispersion.

A "dark charge exchange layer" 13 was prepared by coating a NESA glass plate 12 with a dispersion of 2,4,7-trinitro-9-fluorenone and 'Butvar B—76' (1:1 weight ratio) in p-dioxane solvent. A dried coating thickness of 13 microns was obtained.

A dielectric paper covered conductive roller 10, as described in Example 1, biased at +1.5 Kv was used to produce an image by moving the roller across the "dark charge exchange layer" bearing the multi-colour imaging suspension at 50 to 100 mm/sec. Simultaneously with the movement of the roller, a white light exposure (1800 footcandles) was made. The exposure originated from a white light source and proceeded first through colour separation filters, i.e. a red KODAK 'Wratten' Filter No. 29 or a blue KODAK 'Wratten' Filter No. 47B or a green KODAK 'Wratten' Filter No. 58 which were located in three different exposure areas, then through an original composed of a black-and-white photographic negative transparency, and then through the plate 12.

Observations:

The three-coloured image formed on the "dark charge exchange layer" 13 at a roller speed of 50 mm/sec. had a greater image density and better colour balance than the image formed at 100 mm/sec. In both cases, the pigment particles in the exposed areas remained on the "dark charge exchange layer" 13 and the pigment particles in the unexposed areas migrated to the "blocking layer" 11 mounted on the roller electrode 10.

Example 9:
Ultraviolet Filtered Exposures with a 2,4,7-trinitro-9-fluorenone/'Butvar B—76' "Dark Charge Exchange Layer".

Cyan, magenta and yellow pigment dispersions were prepared as in Example 8 and blended together in equal volumes just prior to use to form a liquid imaging suspension 14.

A layer of 2,4,7-trinitro-9-fluorenone/'Butvar B—76', as in Example 8, was used as the "dark charge exchange layer" 13.

A dielectric paper covered conductive roller, as described in Example 1, biased at +1.0 Kv was moved across the "dark charge exchange layer" 13 bearing the liquid imaging suspension at a rate of 30 to 50 mm/sec. simultaneously with a tungsten light exposure. The exposure first proceeded through a filter arrangement and then through a black-and-white photographic negative and then through the surface 13. The filter arrangement consisted of a series of ultraviolet absorbing filters, KODAK 'Wratten' Filters Nos. 2E, 2B, 4 and 3, underlying a different KODAK 'Wratten' Filter in each of three different exposure areas. In the first exposure area, a

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red KODAK 'Wratten' Filter No. 29 was used. In the second exposure area, a blue KODAK 'Wratten' Filter No. 47B was used. In the third exposure area, a green KODAK 'Wratten' Filter No. 58 was used. Although a tungsten source produces very little ultraviolet radiation component, the ultraviolet absorbing filters, KODAK 'Wratten' Filters Nos. 2E, 2B, 4 and 3 were used to eliminate virtually all of the ultraviolet radiation from the tungsten source. This was done to eliminate any possible photoconductive effect in the "dark charge exchange layer" 13 due to the 2,4,7-trinitro-9-fluorenone which is known to be slightly photoconductive in the presence of ultraviolet radiation.

Observations:

The images formed on the "dark charge exchanges layer" indicated that there was no migration of the pigment particles in the exposed areas of the "dark charge exchange layer". The removal of the ultraviolet radiation from the tungsten source did not appear to affect the migration of the pigment particles.

Example 10:

A poly(ethylene terephthalate) Dielectric Film Covering the Conductive Roller Electrode

Cyan, magenta and yellow pigment dispersions were prepared as in Example 8 and blended together in equal volumes just prior to use to form an imaging suspension 14.

A 13 micron thick layer of a 2,4,7 - trinitro-9 - fluorenone/'Butvar B-76' "dark charge exchange layer" coated on a NESA plate 12, as in Example 8, was used.

A 100 micron thick 'Mylar' film covering a conductive roller electrode 10 was used as the "blocking layer" 11 in place of the dielectric paper used in the previous examples. The roller electrode 10 was biased to a potential of + 1.5 Kv relative to the surface 13 and rolled across the surface 13 bearing the suspension 14 at a roller velocity of 50 mm/sec. Simultaneously as in Example 8, a white light exposure was made through the plate 12, the exposure first passing through red, green and blue filters in each of three different exposure areas and then through a black-and-white photographic negative before passing through the plate 12.

Observations:

The image formed on the 'Mylar' "blocking layer" 11, mounted on the roller electrode 10, indicated that the pigment particles migrated from unexposed areas of the "dark charge exchange layer" 13 to the 'Mylar' film covered roller electrode 10.

Example 11:

A "Dark Charge Exchange Layer" on an Optical Transparent Conductive Ceramic Electrode

The pigment dispersions used to form the multi-colour imaging suspension 14 used in this example are identical to those in Example 6 with the exception that they were rested for about 10 days prior to use.

A "dark charge exchange layer" 13 was prepared by coating equal parts by weight of 2,4,7 - trinitro - 9 - fluorenone and 'Lexan 145' polycarbonate from a dichloromethane solvent onto an optically transparent conductive ceramic conductive support 12. The conductive support 12 was composed of an optically transparent conductive ceramic material (e.g. SiO.Cr) coated on a poly(ethylene terephthalate) film support. Coating 13 was dried to obtain a "dark charge exchange layer" thickness of about 15 microns.

To produce an image, a dielectric paper covered conductive roller electrode, as described in Example 1, was maintained at an electrical bias of + 1.5 Kv relative to surface 13, and roller 10 was moved across the "dark charge exchange layer" 13 bearing suspension 14 at a speed of 30—50 mm/sec. with a simultaneous light exposure through red, green and blue filters as in Example 8.

Observations:

The image formed on the roller electrode indicated that cyan, magenta, and yellow pigment particles migrated from the unexposed areas of the "dark charge exchange layer" 13 while exposed pigment particles remained immobilized on the "dark charge exchange layer".

Example 12:

Three Colour Images on Nickelized Poly(ethylene terephthalate) Film

Part A

In Part A of this Example, a three-colour liquid imaging suspension 14 containing cyan, magenta and yellow electrically photosensitive particles was made as described in Example 8. A "dark charge exchange layer" was then made by coating on the conductive surface of an electrode a solution containing one part by weight of 2,4,7 - trinitro - 9 - fluorenone and 2 parts by weight of 'Lexan 145' from an organic vehicle of methylene chloride. The electrode consisted of a poly(ethylene terephthalate) film support bearing a thin, electrically conductive substantially transparent evaporated nickel overcoat having an optical density of 0.4.

The above-described liquid imaging suspension and electrode bearing the "dark charge exchange surface" were then used to form multi-colour images in an imaging process and apparatus as described in Example 8 except that the roller electrode was biased at +1.2 Kv relative to the "dark charge exchange layer" and the roller speed was 10 to 20 mm/sec.

Observations:

Good red, green and blue positive appearing images of the original were formed on the electrically insulating paper covered roller electrode. Good neutral coloured background areas also were formed on the paper covered electrode.

Part B

Results similar to those of Part A of this Example were obtained by exposing to white light of approximately 300 footcandles a "dark charge exchange layer" 13 with the following compositions:

2.5 gm 2,4,7-trinitro-9-fluorenone
4.5 gm 'Lexan 145' polycarbonate
100 gm dichloromethane

This composition was coated on unsubbed, 0.4 neutral density, nickelized, poly(ethylene terephthalate) film support and air dried to form a layer about 6 microns thick.

A three-colour liquid imaging suspension was made for use with the "dark charge exchange layer" of Part B by blending the following pigment dispersions:

Cyan pigment dispersion
0.5 gm 'Cyan Blue GTNF'
150 gm mixture of equal parts by weight 'Piccotex 100' and 'Isopar G'
Milling time — 28 days

Magenta pigment dispersion
0.5 gm 'Watchung Red B'
150 gm mixture of equal parts by weight of 'Piccotex 100' and 'Isopar G'
Milling time — 31 days

Yellow pigment dispersion
0.6 gm 'Indofast Yellow'
150 mg mixture of equal parts by weight of 'Piccotex 100' and 'Isopar G'
Milling time — 49 days

The individual cyan, magenta, and yellow pigment dispersions described above were each ball milled separately for the times noted, in a 250 ml brown glass bottle filled with 635 gm of 3.2 mm diameter stainless steel balls and then combined in equal volumes just prior to use to form a blended three-colour pigment dispersion to be used as the liquid imaging suspension 14. This three-colour liquid imaging suspension was then used to form a multi-colour image in an imaging process and apparatus as described in Example 8 except that the roller electrode 10 was biased at + 1.6 Kv relative to the "dark charge exchange layer" 13 and the roller speed was 10 mm/sec.

Part C

Results similar to those of Part B of this Example were obtained when 50 micron thick spacer strips of poly(ethylene terephthalate) were inserted between the "dark charge exchange layer" 13 and the roller electrode 10 to form a gap therebetween. The three-colour imaging suspension used in Part C of this Example was made by blending a cyan pigment dispersion prepared as illustrated below with the magenta and yellow pigment dispersions prepared as illustrated in Part B of this Example.

Cyan pigment dispersions
0.5 'Cyan Blue GTNF'
150 gm mixture of equal parts by weight of 'Piccotex 100' and 'Isopar G'
Milling time — 31 days

This three-colour liquid imaging suspension was used to form a multi-colour image in an imaging process and apparatus as described in Example 8 except that a white light exposure of 300 footcandles was made through a positive transparency 17 in the absence of colour separation filters. The roller electrode was biased at + 1.5 Kv relative to the "dark charge exchange layer" 13 and the roller speed was 10 mm/sec.

Example 13:
A comparison of PIER-PEP Single Colour Processes

A cyan pigment dispersion was prepared by mixing the following components in a glass bottle just prior to imaging:

.05 gm 'Cyan Blue GTNF'
20 ml 'Isopar G'

One half of the exposure zone (57 mm by 57 mm) of a NESA glass plate 12 was coated with a 20 micron thick layer of a dark charge exchange layer" 13 composed of 2,4,7-trinitro-9-fluorenone and a 'Butvar B-76' binder as described in the formulation given in Example 6. The other half of the NESA glass plate 12 was left uncoated.

The above-described cyan pigment dispersion was then applied as a liquid imaging suspension 14 to both the coated and uncoated surfaces of the NESA plate described above. A biased conductive roller electrode bearing a dielectric coated paper, as described in Example 1, was rolled at a speed of 40 mm/sec. over the area of the NESA plate coated with the cyan dispersion. Using an electrode bias of + 1.5 Kv, a simultaneous white light exposure of 1800 footcandles from a tungsten lamp was made through a black-and-white photographic negative modulated with a red KODAK 'Wratten' Filter No. 29. The exposure was made through the NESA plate.

Observations:

The images formed on the dielectric paper covered conductive roller 10 indicated that the exposed cyan particles migrated from the uncoated areas of the NESA plate but remained

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immobilized in the areas of the NESA plate coated with the "dark charge exchange layer". The unexposed cyan particles did not migrate from the uncoated areas of the NESA plate but did migrate from the areas of the NESA plate bearing the "dark charge exchange layer".

Example 14:
Comparison of PIER and PEP—Multi-Colour Process

Three separate liquid imaging dispersions were prepared as follows:

Cyan Dispersion

0.2 gm of 'Cyan Blue GTNF' in 35 gm of a mixture composed of equal parts by weight of 'Isopar G' and 'Piccotex 100' was milled for three weeks in a 60 ml. brown glass jar filled to one-half volume with 3.2 mm diameter stainless steel balls.

Magenta Dispersion

This dispersion was made using 'Watchung Red B' pigment, 'Piccotex 100' and 'Isopar G' in the same manner as the above-described cyan dispersion.

Yellow Dispersion

This dispersion was made using 'Indofast Yellow', 'Piccotex 100' and 'Isopar G' in the same manner as the above-described cyan dispersion except that milling was carried out for a longer period, approximately 2 months.

Equal volumes of each the cyan, magenta and yellow dispersions described above were then mixed together, just prior to imaging, to form a single multi-coloured pigment particle-containing liquid imaging suspension. This blended multi-coloured suspension was then applied over the conductive surfaces of two NESA plates. One of the conductive NESA plate surfaces had previously been covered with a "dark charge exchange layer" 13 composed of 1 part by weight 2,4,7-trinitro-9-fluorenone and 2 parts by weight of 'Lexan 145'. The other conductive NESA plate surface was covered solely with the liquid imaging suspension and had no "dark charge exchange layer". Imaging was carried out on both NESA plates as follows: a 1800 footcandle white light exposure was made through a photographic colour transparency and through the NESA plate to the blended multi-colour imaging suspension. Simultaneously with exposure, a biased dielectric paper covered conductive roller 10, as described in Example 1, was moved at a rate of about 5 to 10 mm/sec. across the blended imaging suspension through the exposure zone thereof. The roller was biased to + 1.3 Kv. relative to the NESA plate.

Observations:

A multi-colour positive-appearing image corresponding to the original colour transparency was formed on the dielectric paper covering the conductive roller which was used in combination with the NESA plate bearing the "dark charge exchange layer". This was a PIER image since the pigment particles in the exposed areas had been immobilized on the "dark charge exchange layer" of the NESA plate while the particles in the unexposed areas had migrated to the dielectric paper to form, by subtractive colour formation, a positive appearing image of the original colour transparency.

A multi-colour negative-appearing image of the original colour transparency was formed on the dielectric paper covering the conductive roller which was used in combination with the NESA plate which had no "dark charge exchange layer". This was a PEP image since the pigment particles in the exposed areas had migrated to the dielectric paper to form, by subtractive colour formation, a negative appearing image.

Example 15:
Comparison of PIER and PEP at Increased Exposure

Part A

A cyan pigment dispersion prepared as described in Part B of Example 12 was used as a liquid imaging suspension on a "dark charge exchange layer" prepared as described in Part B of Example 12 on unsubbed, 0.4 neutral density, nickelized, poly(ethylene terephthalate) film support. In Part A of this example the "dark charge exchange layer" 13 was employed in an apparatus as shown in Fig. 5 except that filters 18 and 19 were removed and a black-and-white negative test pattern 17 with clear letter areas was interposed between a 0.3 neutral density step tablet with 10 steps of 6 mm width (not shown in Fig. 5) and the light source 16. A 4000 footcandle tungsten white light exposure was made through the step tablet and the test pattern 17 while maintaining the dielectric paper covered roller electrode 10 at a potential of + 1.6 Kv relative to the "dark charge exchange layer" 13 and a roller speed of 10 mm/sec.

Observations:

Part A (PIER)

A good image of the same image sense as the test pattern was formed on the "blocking layer" 11 of the roller electrode 10 at exposure levels ranging from about 4000 footcandles to less than about 300 footcandles, which indicated PIER operation. At every exposure level, further including no exposure, the pigment particles in the unexposed areas migrated from the "dark charge exchange layer" to the "blocking layer" on the roller electrode.

Part B

The same cyan liquid imaging suspension of Part A was used on a PEP type electrode surface, i.e. a 0.4 neutral density, nickelized poly(ethylene terephthalate) film support. This surface did not exhibit "dark charge exchange properties". This PEP type electrode bearing the cyan liquid imaging suspension was then employed in an apparatus as shown in Fig. 5 in a manner identical to that described in Part A of this example. (That is the "dark charge exchange layer" 13 of Fig. 5 was deleted). The dielectric paper covered roller electrode 10 was biased at + 1.4 Kv relative to the nickel conducting layer 12.

Observations:

Part B (PEP)

In "overexposed", i.e. high light intensity areas there was some evidence that certain portions of the image formed on the 'blocking layer" 11 or roller 10 exhibited the same image sense as the original image. However, as the light exposure was diminished to more acceptable levels by the step tablet it was apparent that for exposure levels below the 0.9 neutral density step (plus the 0.4 neutral density nickel layer) the image sense on the "blocking lever" 11 was the reverse of the original, indicating conventional PEP operation. Under the high light intensity ("overexposed") conditions the images formed on the "blocking layer" 11 of roller 10 were generally of poor quality and exhibited the following characteristics: the images contained relatively clear back ground (non-letter) areas in which unexposed particles did not migrate from the nickelized film support and discernible, generally denser, letter areas. However, certain portions of these letter areas appeared partially clear indicating that exposed particles apparently migrated from the nickelized film support to the "blocking layer" of the roller electrode as in normal PEP operation and then subsequently migrated backwards from these letter areas on the "blocking layer" of the roller electrode to the nickelized film support.

In summary, in the PEP mode of operation (Part B of this example) there was observed a tendency towards a partial switching of image sense which occurred when exposing at a high light intensity. However, this change in image sense did not indicate PIER operation because, as illustrated in Part A of this example, in actual PIER operation, images of the same image sense as the original are formed at the roller electrode at normal and low exposure levels and in total darkness as well as under high intensity exposure conditions.

Example 16.

In this example the results of a series of imaging tests illustrate certain characteristics of the "dark charge exchange layer" used in PIER, for example, the importance of using a sufficient amount of a "dark charge exchange material", such as 2,4,7-trinitro-9-fluorenone, to obtain PIER operation, rather than conventional PEP operation.

In each of the following imaging tests A—E, the following test conditions were employed:

A dielectric paper "blocking layer" 11 covered a conductive roller electrode 10, the roller electrode and the dielectric paper used were identical to those described in Example 1. The liquid imaging suspension 14 used was composed of 0.1 gm. of finely-divided particles of 'Cyan blue GTNF' pigment estimated to have an average diameter on the order of about 0.5—1 micron, dispersed (by mixing) in 20 gm. of 'Sohio' Odorless Solvent 3440. Exposure pattern 17 consisted of a black and white negative photographic transparency of printed matter, the printed matter appearing as clear areas of the transparency. The light source 16 was a tungsten source. The exposure intensity on the imaging plane of the liquid imaging suspension was about 1000 foot-candles. Activating radiation from source 16 first passed through a single filter, i.e. a KODAK 'Wratten' Filter No. 29, before passing through exposure pattern 17. Electrode 12 was a NESA glass plate. The conductive roller electrode 10 was biased during imaging to about + 1200 volts relative to electrode 12. The speed of the conductive roller electrode 10 during imaging was 5—20 mm/sec.

In each test, the "dark charge exchange layer" 13 was varied as indicated below to illustrate the effect of certain physical parameters on the "dark charge exchange layer".

Test A

In this test, no "dark charge exchange layer" was employed. A thin film of liquid imaging suspension 14 was applied directly to the conductive tin oxide surface of electrode 12. As was expected, conventional PEP imaging was produced by this test; that is, a negative appearing image of the exposure pattern 17 was recorded on the "blocking layer" 11 and a positive appearing image of the exposure pattern 17 was recorded on electrode 12.

Test B.

In this test, a mixture composed of 0.03 parts by weight of 2,4,7-trinitro-0-fluorenone admixed in 500 parts by weight of 'Sohio' Odorless Solvent 3440 was coated and dried on electrode 12. Most of the 'Sohio' solvent evaporates during drying. This layer, showed no "dark charge exchange properties" when tested; that is, a negative-appearing image of the exposure pattern 17 was formed on the "blocking layer" 11 and a positive-appearing image of the pattern 17 was formed on the above-described layer containing a very small amount of 2,4,7-trinitro-9-fluorenone. As a result of this test it was concluded that an in-

sufficient amount of 2,4,7-trinitro-9-fluorenone was applied to electrode 12 to provide PIER operation.

Test C.

In this test a very thin layer having a dry thickness of less than about 3 microns was coated on the electrode 12. This layer consisted of approximately equal parts by weight of 2,4,7-trinitro-9-fluorenone and 'Lexan 145' coated from methylene chloride. The results of this imaging test showed a mixture of both PEP and PIER operation occurring; that is, certain areas of the image obtained on the "blocking layer" 11 were a negative-appearing image of exposure pattern 17 (thus indicating conventional PEP operation in these areas) whereas other areas of the image obtained on the "blocking layer" 11 were a positive-appearing image of exposure pattern 17 (thus indicating PIER operation in these areas). It was concluded as a result of Test C that the 3 micron layer used was so thin that it contained an insufficient amount of the "dark charge exchange material" 2,4,7-trinitro-9-fluorenone to provide complete PIER operation.

Tests D—1 and D—2.

In these two tests, two layers much thicker than the 3 micron layer of Test C were applied to electrode 12. The layers used in Test D—1 and D—2 were composed of 0.03 parts by weight of 2,4,7-trinitro-9-fluorenone and 4 parts by weight of 'Lexan 145'. The layers were solvent coated from methylene chloride. The layer of Test D—1 had a dry thickness of about 30 microns and the layer of Test D—2 and had a dry thickness of about 75 microns. In both tests D—1 and D—2, conventional PEP imaging was obtained as indicated by the negative-appearing image of exposure pattern 17 formed on the "blocking layer" 11. Both images were of relatively poor quality, the image obtained in Test D—2 being barely discernible.

Test E.

In this test a layer composed of 2,4,7-trinitro-9-fluorenone and 'Lexan 145' was coated from methylene chloride onto electrode 12 to form a layer having a dry thickness of 13 microns and having a dry composition consisting of 1 per cent by weight of 2,4,7-trinitro-9-fluorenone and 99 per cent by weight of 'Lexan 145'. The image obtained using this layer coated on electrode 12 was a conventional PEP image; no PIER operation was evident. That is, a negative-appearing image of the exposure pattern 17 was formed on the "blocking layer" 11 and a positive-appearing image of the pattern 17 was formed on the 2,4,7-trinitro-9-fluorenone layer coated on the electrode 12. From this test, it was concluded that an insufficient amount of 2,4,7-trinitro-9-fluorenone was used in the layer coated on the electrode 12 so that merely conventional PEP imaging was obtained.

Example 17:

Concentration of 2,4,7-trinitro-9-fluorenone in a Representative "Dark Charge Exchange Layer".

Five different layers were prepared for testing as "dark charge exchange layer" 13 with 2,4,7-trinitro-9-fluorenone (TNF) at 35.7%, 26.8%, 17.6%, 8.8% and 0% of the total solids in each layer according to the formulations listed below. The purpose of this example is to illustrate the importance of using the proper portion of a "dark charge exchange material" in a "dark charge exchange layer".

Formulation 1:

2.5 gm	TNF
4.5 gm	'Lexan 145' polycarbonate
100 gm	dichloromethane

Formulation 2:

1.88 gm	TNF
5.12 gm	'Lexan 145'
100 gm	dichloromethane

Formulation 3:

1.25 gm	TNF
5.75 gm	'Lexan 145'
100 gm	dichloromethane

Formulation 4:

0.625 gm	TNF
6.375 gm	'Lexan 145'
100 gm	dichloromethane

Formulation 5:

7.0 gm	'Lexan 145'
100 gm	dichloromethane

The formulations were hand coated with a .006 mil coating knife at a wet thickness of 150 microns on unsubbed 0.4 neutral density, nickelized, poly(ethylene terephthalate) film support at a coating block temperature of 21°C. The coatings were air dried at room temperature.

A cyan pigment dispersion was prepared as described in Part B of Example 12 and was used as a liquid imaging suspension in an imaging process and apparatus as described in Example 7 except that the roller electrode bias was + 1.6 Kv, the roller speed was 10 mm/sec., the white light exposure was about 1000 footcandles intensity and a 0.3 neutral density step tablet with 10 steps of 6 mm width was used to modify the exposure. Due to electrical breakdown, the test of the layer produced from Formulation 5 contained no TNF was modified in that the roller electrode bias was lowered to + 1.3 kv. and the white light exposure was lowered to about 900 footcandles. Before using the cyan dispersion, the pigment particles were

allowed to settle for about 6 weeks after which 50 gm of the supernatant liquid was decanted. The remaining dispersion was hand mixed just prior to use in the imaging process.

Observations:

At 35.7% by weight of TNF in layer 13 (Formulation 1 above) the "blocking layer" 11 of the roller electrode 10 showed a good image of the same image sense as the original. This TNF-containing-layer had an image of opposite sense from the original and this image, when electrostatically transferred to a receiver sheet, had a very low background density indicating that this TNF-containing-layer was acting as a "dark charge exchange layer" by exchanging charge with the cyan pigment in unexposed areas. This test indicated PIER operation.

At 26.8% by weight of TNF (Formulation 2 above) the "blocking layer" 11 of the roller electrode showed a good image of the same image sence as the original. The image transferred to a receiver sheet from this TNF-containing-layer had an opposite image sense from the original and showed a low background density though it was somewhat higher than the previous test. This test indicated PIER operation.

At 17.6% by weight of TNF (Formulation 3 above) the "blocking layer" of the roller electrode showed a poor image of the opposite image sense to the original. There was observable density in the letter areas and low background density indicating a PEP mode of operation. The TNF-containing-layer had a poor image also of the opposite image sense as the original. The electrostatic transfer record of this TNF-containing-layer image showed high density background areas surrounding higher density letter areas.

At 8.8% by weight of TNF (Formulation 4 above) the "blocking layer" of the roller electrode showed an image of opposite image sense from the original, indicative of PEP operation. The image electrostatically transferred to a receiver sheet from this TNF-containing layer also had an opposite image sense from the original and, as in the previous test, showed high background density. The TNF-containing-layer was not acting as a "dark charge exchange layer". The inability of the above-noted 17.6% TNF-containing-layer and this 8.8% TNF-containing layer to adequately exchange charge with the cyan pigment particles in the unexposed (ie. background) areas indicated that these layers at these TNF concentration levels were not acting as "dark charge exchange layers".

At 0% of TNF (Formulation 5 above) the "blocking layer" of the roller electrode showed an image of opposite image sense from the original indicative of PEP operation. The results showed a partial tendency for the same image sense as the original occurring on the "blocking layer" of the roller electrode in "overexposed", ie. high exposure, areas. The image electrostatically transferred to a receiver sheet from the 0% TNF-containing-layer had a poor image of the same image sense as the original, again indicative of PEP operation. At high exposure areas the results indicated a partial tendency for the opposite image sense from the original to occur on this transfer record. These results illustrated that the layer containing 'Lexan 145' only was not acting as a "dark charge exchange layer".

Example 18:

Pigment Speed Test—Three-Colour.

This test was intended to determine if any speed differences existed between the cyan, magenta and yellow pigment particles of a typical multicolour liquid imaging suspension used in PIER.

A multicolour liquid imaging suspension was prepared by mixing cyan, magenta and yellow pigment dispersions prepared as described in Part B of Example 12.

A "dark charge exchange layer" was also prepared as described in Part B of Example 12.

The liquid imaging suspension and the electrode bearing a "dark charge exchange layer" 13 were then used to form separate colour images in an imaging process and apparatus as described in Example 8 except that the roller electrode was biased at + 1.2 Kv, the roller speed was 10 mm/sec. and the exposure was approximately 800 footcandle intensity. The exposure originated from a tungsten white light source and proceeded first through colour separation filters, i.e. a red KODAK 'Wratten' Filter No. 29 or a green KODAK 'Wratten' Filter No. 58 or a blue KODAK 'Wratten' Filter No. 47B which were located in alternating bands of 3.2 mm. width across the entire exposure area, then through an image composed of a step tablet with 6 mm wide, 0.3 neutral density steps, then through the NESA glass plate, and finally through the "dark charge exchange layer" to the liquid imaging suspension.

Observations:

The image formed on the "blocking layer" of the roller electrode had the same image sense as the original. The red, green, blue and neutral areas were good quality. Dense neutral tones opposite the highest density steps were expected because the low exposure favours the migration of all of the pigment particles from the "dark charge exchange layer" to the roller electrode. As noted previously, one of the advantages of PIER is that it provides excellent reproduction of neutral tones.

The image electrostatically transferred to a receiver surface from the "dark charge exchange layer" showed an image sense opposite from the original. This transfer record of the

image formed on the "dark charge exchange layer" indicated that the cyan and magenta pigment particles had about the same number of visible steps or the same speed for the conditions of this test. The yellow pigment particles appeared to be about three steps slower in speed than either the cyan or magenta pigment particles. A faint step in the red and green low exposure areas was visible on the transfer record at an exposure lever of about 2.5 footcandles. This indicated that for the conditions of this test there was a threshold sensitivity of at least 2.5 footcandles exposure.

Example 19:
Electrical Bias Changes.

Two identical "dark charge exchange layers" were prepared as described in Part B of Example 12. One surface was used for imaging tests at roller electrode biases of +250 V, +350 V, and +650 V. The other surface was tested at +600 V, +900 V, +1400 V, +2000 V, and +2500 V.

A cyan pigment dispersion was prepared as described in Part B of Example 12 and was used as a liquid imaging suspension in an imaging process and apparatus as described in Example 7 except that the roller electrode bias was varied from +250 V to +2500 V, the roller speed was 10 mm/sec. and the white light exposure was about 350 footcandles.

Observations:

At each roller electrode bias the image formed on the "blocking layer" of the roller electrode had the same image sense as the original indicating PIER operation. As the roller electrode bias was increased from +250 V to +2500 V there was an observable increase in the density of the image formed on the "blocking layer" of the roller electrode.

Example 20:
NIP Exposure of PIER.

A "dark charge exchange layer" was prepared as described in Part B of Example 12.

A cyan pigment dispersion was prepared as described in Part B of Example 12 and was used as a liquid imaging suspension in an imaging process and apparatus as described in Example 7 except that the roller electrode bias was +1.6 Kv, the roller speed was 10 mm/sec. and the exposure was about 500 footcandles directed at the nip formed between the roller electrode and the liquid imaging suspension. To obtain the nip exposure an 800 H KODAK 'Carousel' Projector was used as the exposure source and was directed at about a 45° angle from the horizontal towards the nip of the roller electrode as illustrated diagrammatically in Fig. 7. Simultaneously with the nip exposure, the biased roller electrode was moved across the "dark charge exchange layer". 'Carousel' is a Registered Trade Mark.

Observations:

In the test of the "dark charge exchange layer" the image formed at the roller electrode was the same image sense as the original indicating PIER operation.

The nip exposing technique illustrated in this example shows that, if desired, both of the spaced electrodes can be opaque in PIER.

Example 21 Pigment Concentration Series

TABLE 3

Dispersion No.	Pigment	Weight of Pigment in Dispersion	Milling Time
1	'Cyan Blue GTNF' (CB)	0.1 gm.	28 days
2	'Indofast Yellow' (IY)	0.1	28
3	'Watchung Red B' (WR)	0.1	28
4	CB	0,2	28
5	IY	0.2	28
6	WR	0.2	28
7	CB	0.3	28

(36)

TABLE 3 (Continued)

Dispersion No.	Pigment	Weight of Pigment in Dispersion	Milling Time
8	IY	0.3 gm.	28 days
9	WR	0.3	28
10	CB	0.4	28
11	IY	0.4	28
12	WR	0.4	28
13	CB	0.5	28
14	IY	0.5	28
15	WR	0.5	28
16	CB	0.6	28
17	IY	0.6	28
18	WR	0.6	28
19	CB	0.7	28
20	IY	0.7	28
21	WR	0.7	28
22	CB	0.8	28
23	IY	0.8	28
24	WR	0.8	28
25	CB	0.9	33
26	IY	0.9	33
27	WR	0.9	33
28	CB	1.0	33
29	IY	1.0	33
30	WR	1.0	33
31	CB	1.1	33
32	IY	1.1	33
33	WR	1.1	33

Cyan, magenta and yellow pigment dispersions were prepared according to the weights and milling times given in Table 3 above. Each dispersion was milled in a small brown bottle containing a 35 gm liquid mixture or equal parts by weight of 'Piccotex 100' and Isopar G' and 240 gm of 3.2 mm diameter stainless steel balls.

Blended dispersions, i.e. cyan, magenta and yellow dspersions blended together, were prepared at various pigment concentrations as illustrated in Table 4 below.

TABLE 4

Blended Dispersion No.	Table 3 Pigment Dispersion Nos.	Total Pigment Concentration in Blended Dispersion (Weight %)
1	1, 2, 3	0.3%
2	4, 5, 6	0.6
3	7, 8, 9	0.9
4	10, 11, 12	1.2
5	13, 14, 15	1.5
6	16, 17, 18	1.7
7	19, 20, 21	2.0
8	22, 23, 24	2.2
9	25, 26, 27	2.5
10	28, 29, 30	2.8
11	31, 32, 33	~3.1

The blended dispersions were used as liquid imaging suspension on a "dark charge exchange layer" prepared as described in Part B of Example 12.

The liquid imaging suspensions were used to form multi-coloured images in an imaging process and apparatus as described in Example 8 except that the roller electrode was biased at +1.6 Kv relative to the "dark charge exchange layer", the roller speed was 10 mm/sec and the white light exposure was at about 320 footcandles intensity. The blended dispersion No. 11 was also tested at a roller electrode bias of +2.0 Kv.

Observations:

At all pigment concentrations tested, i.e. 0.3%—3.1%, the images formed on the "blocking layer" of the roller electrode had the same image sense as the original, indicating PIER operation. The results showed that image density increased with increasing pigment concentration. Good quality images were observed at about 0.3% to about 2.1% pigment levels.

The "dark charge exchange layer" had a good quality image of opposite sense from the original and this image showed a very low background density. At pigment concentrations higher than 2.1%, the image on the "blocking layer" of the roller electrode and the image of opposite image sense on the "dark charge exchange layer" showed higher background densities. Improved image quality and lower background density using these higher pigment concentration suspensions was achieved by increasing the electrical bias on the roller electrode as evidenced by the testing of blended dispersion No. 11 at +2.0 Kv.

Example 22:

2,4,5,7-tetranitro-9-fluorenone as a "dark charge exchange material".

A "dark charge exchange layer" was prepared from the formulation:

2.5 gm 2,4,5,7-tetranitro-9-fluorenone
4.5 gm 'Lexan 145' polycarbonate
100 gm dichloromethane

Some undissolved solids were allowed to settle out. The dissolved portion of the formulation was coated on unsubbed, 0.4 neutral density, nickelized, poly(ethylene terephthalate) film support at a wet thickness of about 150 microns. The coating was allowed to dry in air at room temperature.

Cyan, magenta and yellow pigment dispersions were prepared as described in Part B of Example 12 except that the magenta pigment dispersion was ball milled for 28 days and the yellow pigment dispersion ball milled for 81 days.

A blended dispersion was prepared by mixing equal volumes of each of the cyan, magenta and yellow pigment dispersions. This three-colour, liquid imaging suspension was used to form a multi-colour image in an imag-

ing process and apparatus as described in Example 8 except that the roller electrode was biased at +1.6 Kv relative to the "dark charge exchange layer", the roller speed was 10 mm/sec. and the white light, tungsten exposure was at 900 footcandles intensity through 1.0 and 2.0 neutral density filters (in separate imaging tests), through a positive colour transparency and through the 0.4 neutral density, nickel, conducting layer on the film support.

Observations:

A good image of the same image sense as the original appeared on the "blocking layer" of the roller electrode indicating PIER operation. This test illustrated that 2,4,5,7-tetranitro-9-fluorenone was acting as a "dark charge exchange material" by allowing pigment particles to migrate from the unexposed areas of the "dark charge exchange layer" to the "blocking layer" of the roller electrode.

Example 23:

9 - (Dicyanomethylene) - 2,4,7 - trinitrofluorenone as a "Dark Charge Exchange Layer".

A "dark charge exchange layer" was prepared from the formulation:

1.0 gm 9 - (Dicyanomethylene) - 2,4,7-trinitrofluorene
2.25 gm 'Lexan 145' polycarbonate
100 gm tetrahydrofuran

This formulation was coated as described in Example 22 except that the coating temperature was held at 27°C.

Cyan, magenta and yellow pigment dispersions were prepared and mixed to form a blended dispersion as described in Example 22. This three-colour, liquid imaging suspension was used in the imaging process and apparatus described in Example 22.

Observations:

Results were similar to those obtained in Example 22. This test illustrated that 9-(Dicyanomethylene)-2,4,7-trinitrofluorene acted as a "dark charge exchange material".

Example 24:

Methyl-2,7-dinitro-9-fluorenone carboxylate as a "Dark Charge Exchange Material".

A "dark charge exchange layer" was prepared from the formulation:

1.0 gm Methyl - 2,7 - dinitro - 9 - fluorenone carboxylate
1.8 gm 'Lexan 145' polycarbonate
50 gm Tetrahydrofuran

This formulation was coated in the manner described in Example 22.

The three-colour liquid imaging suspension, imaging process and apparatus were the same as described in Example 22.

Observations:

Results were similar to those obtained in Example 22. This test illustrated that methyl-2,7-dinitro-9-fluorenone carboxylate acted as a "dark charge exchange material".

Example 25:

2 - Dicyanomethylene - 1,3 - indandione as a "Dark Charge Exchange Material".

A "dark charge exchange layer" was prepared from the formulation:

0.4 gm 2 - dicyanomethylene - 1,3 - indandione
0.6 gm 'Lexan 145' polycarbonate
14.4 gm Tetrahydrofuran

This formulation was coated in the same manner as the formulation described in Example 22.

A cyan pigment dispersion prepared as illustrated in Part B of Example 12 was used as a liquid imaging suspension in the imaging process and apparatus described in Example 22.

Observations:

Results were similar to those obtained in Example 22. This test illustrated that 2-dicyanomethylene-1,3-indandione acted as a "dark charge exchange material".

Example 26:

Polyester Binder used in a "Dark Charge Exchange Layer".

Two different "dark charge exchange layers" were prepared from the following formulations:

Formulation 1:

3.0 gm 2,4,7-trinitro-9-fluorenone
4.0 gm polyester
100 gm dichloromethane

Formulation 2:

2.5 gm 2,4,7-trinitro-9-fluorenone
4.5 gm polyester
100 gm dichloromethane

These formulations were coated on unsubbed, 0.4 neutral density nickelized poly(ethylene terephthalate) film support at a wet thickness of about 150 microns and a coating temperature of 16°C. The coatings were allowed to air dry overnight at room temperature.

Cyan, magenta and yellow pigment dispersions were prepared as described in Part B of Example 12 except that the magenta pigment dispersion was ball milled for 28 days.

A blended dispersion was prepared by mixing equal volumes of each of the cyan,

magenta and yellow pigment dispersions. This three-colour liquid imaging suspension was held for 24 hours in darkness and used in an imaging process and apparatus as described in Example 8 except that the roller electrode was biased at +1.6 Kv, the roller speed was 10 mm/sec, and the white light exposure was at 800 footcandles intensity through a multi-colour transparency.

Observations:

A good multi-colour image of the same image sense as the original appeared on the roller electrode, indicating PIER operation.

WHAT WE CLAIM IS:—

1. A recording process wherein electrically photosensitive particles, at least a proportion thereof having a positive polarity electrostatic charge, are disposed between two spaced electrodes and are caused to migrate by application of an electric field and are substantially simultaneously imagewise exposed to activating radiation, as hereinbefore defined, to form a corresponding image comprising the particles, one of the electrodes having on the surface thereof adjacent the particles, a layer comprising a dark charge exchange material as hereinbefore defined.

2. A recording process wherein electrically photosensitive particles, at least some of which bear a positive polarity electrostatic charge, are disposed between two spaced electrodes, subjected to an electric field, and imagewise exposed to activating radiation, one of the electrodes having as an overcoat for the surface thereof adjacent to the particles, a uniform layer comprising an amount of a dark charge exchange material, sufficient to provide a net change in charge polarity of at least a portion of the positive polarity particles upon electrical contact therewith in the presence of the field and in the absence of activating radiation, the process comprising, substantially simultaneously, establishing a potential difference between the electrodes to create the field such that at least a portion of the positive polarity particles move into electrical contact with the layer of dark charge exchange material, and imagewise exposing the particles to activating radiation such that at least a portion of the exposed, positive polarity particles are immobilized at the surface of the layer of dark charge exchange material and at least a portion of the unexposed, positive polarity particles, upon electrical contact with the layer of dark charge exchange material, undergo a net change in charge polarity and are repelled therefrom, whereby an image is formed.

3. A recording process as claimed in claim 1 or 2, wherein the photosensitive particles are dispersed in an electrically insulating carrier liquid.

4. A recording process as claimed in claim 1, 2 or 3, wherein the electrically photosensitive particles comprise a mixture of at least two differently coloured photosensitive particles, each of which are primarily responsive to activating radiation of a different wavelength.

5. A recording process as claimed in claim 3, or 3 and 4, wherein the electrically insulating carrier liquid contains a polymeric charge control agent.

6. The recording process as claimed in any preceding claim, wherein the dark charge exchange material is crystalline and has an effective work function which is less than that of the photosensitive particles.

7. A recording process as claimed in claim 6, wherein the dark charge exchange material is a metal having an effective work function of less than 4 electron volts.

8. A recording process as claimed in any one of claims 1 to 5, wherein the dark charge exchange material is an electron acceptor compound.

9. A recording process as claimed in any preceding claim, wherein the activating radiation is visible light.

10. A recording process as claimed in claim 3 or any claim appendant thereto, wherein the carrier liquid has dispersed therein from 0.1 to 1.5 per cent by weight of the electrically photosensitive particles.

11. A recording process as claimed in any one of claims 1 to 5, or 8, or claim 9 as appendant to any one of claims 1 to 5, or 8, the dark charge exchange layer comprising a solid solution of a binder and a dark charge exchange material.

12. A recording process as claimed in claim 8, 9, 10 or 11, wherein the dark charge exchange material layer has a thickness of from 5 to 50 microns.

13. A recording process as claimed in claim 4 or any claim appendant thereto, wherein the particles comprise a mixture of cyan, magenta, and yellow particles which are primarily responsive to red, green and blue light, respectively.

14. A recording process as claimed in Claim 12 wherein the layer of dark charge exchange material comprises a solid solution of a binder and at least 20 per cent by weight of the electron acceptor compound.

15. A recording process as claimed in claim 3 or any claim appendant thereto, wherein the other electrode is a conductive roller and wherein during application of the field and exposure to the activating radiation, the other electrode rolls in line contact with the dispersion at a rate of from 5 to 100 mm/sec. across the layer of dark charge exchange material.

16. A recording process as claimed in claim 3, or any one of claims 4 to 15 as appendant to claim 3, wherein at least one electrode is a continuous web.

17. A recording process as claimed in claim 3, or any one of claims 4 to 15 as appendant

magenta and yellow pigment dispersions. This three-colour liquid imaging suspension was held for 24 hours in darkness and used in an imaging process and apparatus as described in Example 8 except that the roller electrode was biased at +1.6 Kv, the roller speed was 10 mm/sec, and the white light exposure was at 800 footcandles intensity through a multi-colour transparency.

Observations:

A good multi-colour image of the same image sense as the original appeared on the roller electrode, indicating PIER operation.

WHAT WE CLAIM IS:—

1. A recording process wherein electrically photosensitive particles, at least a proportion thereof having a positive polarity electrostatic charge, are disposed between two spaced electrodes and are caused to migrate by application of an electric field and are substantially simultaneously imagewise exposed to activating radiation, as hereinbefore defined, to form a corresponding image comprising the particles, one of the electrodes having on the surface thereof adjacent the particles, a layer comprising a dark charge exchange material as hereinbefore defined.

2. A recording process wherein electrically photosensitive particles, at least some of which bear a positive polarity electrostatic charge, are disposed between two spaced electrodes, subjected to an electric field, and imagewise exposed to activating radiation, one of the electrodes having as an overcoat for the surface thereof adjacent to the particles, a uniform layer comprising an amount of a dark charge exchange material, sufficient to provide a net change in charge polarity of at least a portion of the positive polarity particles upon electrical contact therewith in the presence of the field and in the absence of activating radiation, the process comprising, substantially simultaneously, establishing a potential difference between the electrodes to create the field such that at least a portion of the positive polarity particles move into electrical contact with the layer of dark charge exchange material, and imagewise exposing the particles to activating radiation such that at least a portion of the exposed, positive polarity particles are immobilized at the surface of the layer of dark charge exchange material and at least a portion of the unexposed, positive polarity particles, upon electrical contact with the layer of dark charge exchange material, undergo a net change in charge polarity and are repelled therefrom, whereby an image is formed.

3. A recording process as claimed in claim 1 or 2, wherein the photosensitive particles are dispersed in an electrically insulating carrier liquid.

4. A recording process as claimed in claim 1, 2 or 3, wherein the electrically photosensitive particles comprise a mixture of at least two differently coloured photosensitive particles, each of which are primarily responsive to activating radiation of a different wavelength.

5. A recording process as claimed in claim 3, or 3 and 4, wherein the electrically insulating carrier liquid contains a polymeric charge control agent.

6. The recording process as claimed in any preceding claim, wherein the dark charge exchange material is crystalline and has an effective work function which is less than that of the photosensitive particles.

7. A recording process as claimed in claim 6, wherein the dark charge exchange material is a metal having an effective work function of less than 4 electron volts.

8. A recording process as claimed in any one of claims 1 to 5, wherein the dark charge exchange material is an electron acceptor compound.

9. A recording process as claimed in any preceding claim, wherein the activating radiation is visible light.

10. A recording process as claimed in claim 3 or any claim appendant thereto, wherein the carrier liquid has dispersed therein from 0.1 to 1.5 per cent by weight of the electrically photosensitive particles.

11. A recording process as claimed in any one of claims 1 to 5, or 8, or claim 9 as appendant to any one of claims 1 to 5, or 8, the dark charge exchange layer comprising a solid solution of a binder and a dark charge exchange material.

12. A recording process as claimed in claim 8, 9, 10 or 11, wherein the dark charge exchange material layer has a thickness of from 5 to 50 microns.

13. A recording process as claimed in claim 4 or any claim appendant thereto, wherein the particles comprise a mixture of cyan, magenta, and yellow particles which are primarily responsive to red, green and blue light, respectively.

14. A recording process as claimed in Claim 12 wherein the layer of dark charge exchange material comprises a solid solution of a binder and at least 20 per cent by weight of the electron acceptor compound.

15. A recording process as claimed in claim 3 or any claim appendant thereto, wherein the other electrode is a conductive roller and wherein during application of the field and exposure to the activating radiation, the other electrode rolls in line contact with the dispersion at a rate of from 5 to 100 mm/sec. across the layer of dark charge exchange material.

16. A recording process as claimed in claim 3, or any one of claims 4 to 15 as appendant to claim 3, wherein at least one electrode is a continuous web.

17. A recording process as claimed in claim 3, or any one of claims 4 to 15 as appendant

to claim 3 or claim 16 as appendant to any one of claims 4 to 14 as appendant to claim 3, wherein at least one electrode is a flat plate.

18. A recording process as claimed in claim 8, or any claim appendant thereto, wherein the dark charge exchange material is an electron acceptor compound which has at least one substituted aromatic ring.

19. A recording process as claimed in claim 18, wherein the dark charge exchange material satisfies the test therefor described herein.

20. A recording process as claimed in claim 18 or 19, wherein the electron acceptor compound has a substituted heterocyclic ring or rings, possessing conjugated aromatic unsaturation in the heterocyclic ring.

21. A recording process as claimed in claim 20, wherein the electron acceptor compound has an electron acceptor strength more positive than - 0.35.

22. A recording process as claimed in claim 18, 19, 20 or 21 having as a substituent in an aromatic ring thereof, at least one electron withdrawing group.

23. A recording process as claimed in claim 22 wherein the electron withdrawing group or groups have positive Hammett sigma values greater than 0.35.

24. A recording process as claimed in claim 23 wherein the electron withdrawing group or groups have positive Hammett sigma values greater than 0.70.

25. A recording process as claimed in claim 8, or any claim appendant thereto, wherein the electron acceptor compound has at least two fused aromatic rings.

26. A recording process as claimed in claim 25 as appendant to claim 22, wherein at least two substituents bonded to an aromatic ring of the dark charge exchange material are selected from nitro groups, cyano groups, dicyanoalkylene groups, cationic amino groups, sulphone groups and dicyanomethylene groups.

27. A recording process as claimed in claim 3 or any claim appendant thereto, wherein 0.1 to 1.5 per cent by weight of the photosensitive particles are dispersed in the carrier liquid.

28. A recording process as claimed in any one of claims 8 to 19, wherein the dark exchange material is 2,4,7 - trinitro - 9-fluorenone; 2,4,5,7 - tetranitro - 9 - fluorenone; 9 - (dicyanomethylene) - 2,4,7 - trinitro - fluorene; methyl - 2,7 - dinitro - 9-fluorenone carboxylate or 2 - dicyanomethylene - 1,3 - indandione.

29. A recording process as claimed in any one of claim 11 or claims 12 to 28 as appendant to claim 11, wherein the binder is a poly(vinyl butyral), a polycarbonate, or a polyester.

30. A recording process as claimed in claim 11 or any claim appendant thereto, wherein the percentage of binder is 22 to 50 per cent by weight.

31. A recording process as claimed in claim 30, wherein the precentage of binder is 25 to 40 per cent by weight.

32. A recording process as claimed in any one of claims 11, or claims 12 to 31 as appendant to claim 11, wherein the percentage of dark charge exchange material is 20 to 75 per cent by weight.

33. A recording process as claimed in claim 6 or any claim appendant thereto, wherein the dark charge exchange material is indium.

34. A recording process as claimed in claim 33 wherein the thickness of indium is between 5 and 20 nanometre.

35. A recording process as claimed in claim 3 or any claim appendant thereto, wherein the carrier liquid has a resistivity greater than 10^9 ohm cm.

36. A recording process as claimed in claim 35, wherein the carrier liquid has a resistivity greater than 10^{10} ohm-cm.

37. A recording process as claimed in claim 35 or 36, wherein the carrier liquid has a dielectric constant of less than 3.0.

38. A recording process as claimed in claim 37, wherein the carrier liquid is an isoparaffinic hydrocarbon liquid.

39. A recording process as claimed in claim 35, 36, 37 or 38, wherein the strength of the electric field, as herein defined, between the dark exchange layer and the other electrode is greater than 10 kilovolts per millimetre.

40. A recording process as claimed in claim 39, wherein the strength of the electric field, as herein defined, is from 20 kilovolts to 160 kilovolts per millimetre.

41. A recording process as claimed in any preceding claim wherein one of the electrodes is at least partially transparent to the activating radiation.

42. An imaging apparatus, comprising two spaced electrodes arranged to receive electrically photosensitive particles disposed therebetween, means for applying an electric field between the electrodes whereby the electrically photosensitive particles may be caused to migrate, and means for exposing the photosensitive particles to activating radiation, as hereinbefore defined, one of the electrodes bearing on the surface thereof, a layer comprising a dark charge exchange material, as hereinbefore defined.

43. An imaging apparatus as claimed in claim 42, wherein the dark charge exchange material is a metal having an effective work function of less than 4 electron volts.

44. An imaging apparatus as claimed in claim 42, wherein the dark charge exchange material is an electron acceptor compound.

45. An imaging apparatus as claimed in claim 42, 43 or 44, wherein the activating radiation is visible light.

46. An imaging apparatus as claimed in claim 44 or 45, the dark charge exchange layer comprising a solid solution of a binder

and a dark charge exchange material.

47. An imaging apparatus as claimed in claim 46 wherein the dark charge exchange material layer has a thickness of from 5 to 50 microns.

48. An imaging apparatus as claimed in claim 47 wherein the layer of dark charge exchange material comprises a solid solution of a binder and at least 20 per cent by weight of the electron acceptor compound.

49. An imaging apparatus as claimed in claim 42 or any claim appendant thereto, wherein the other electrode is a conductive roller and wherein during application of the field and exposure to the activating radiation, the other electrode is arranged to roll in line contact at a rate of from 5 to 100 mm/sec. across the layer of dark charge exchange material.

50. An imaging apparatus as claimed in claim 42, or any claim appendant thereto, wherein at least one electrode is a continuous web.

51. An imaging apparatus as claimed in any one of claims 42 to 48, claim 5 as appendant to any one of claims 42 to 48, wherein at least one electrode is a flat plate.

52. An imaging apparatus as claimed in claim 44, or any claim appendant thereto, wherein the dark charge exchange material is an electron acceptor compound which has at least one substituted aromatic ring.

53. An imaging apparatus as claimed in claim 52, wherein the dark charge exchange material satisfies the test therefor described herein.

54. An imaging apparatus as claimed in claim 52 or 53, wherein the electron acceptor compound has a substituted heterocyclic ring or rings, possessing conjugated aromatic unsaturation in the heterocyclic ring.

55. An imaging apparatus as claimed in claim 54, wherein the electron acceptor compound has an electron acceptor strength more positive than – 0.35.

56. An imaging apparatus as claimed in claim 52, 53, 54 or 55 having as a substituent in an aromatic ring thereof, at least one electron withdrawing group.

57. An imaging apparatus as claimed in claim 56 wherein the electron withdrawing group or groups have positive Hammett sigma values greater than 0.35.

58. An imaging apparatus as claimed in claim 57 wherein the electron withdrawing group or groups have positive Hammett sigma values greater than 0.70.

59. An imaging apparatus as claimed in claim 44, or any claim appendant thereto, wherein the electron acceptor compound has at least two fused aromatic rings.

60. An imaging apparatus as claimed in claim 59 as appendant to claim 56, wherein at least two substituents bonded to an aromatic ring of the dark charge exchange material are selected from nitro groups, cyano groups, dicyanoalkylene groups, cationic amino groups, sulphone groups and dicyanomethylene groups.

61. An imaging apparatus as claimed in any one of claims 44 to 53, wherein the dark charge exchange material is 2,4,7 - trinitro - 9 - fluorenone; 2,4,5,7 - tetranitro-9 - fluorenone; 9 - (dicyanomethylene)-2,4,7 - trinitro - fluorene; methyl - 2,7 - dinitro - 9 - fluorenone carboxylate or 2-dicyanomethylene - 1,3 - indandione.

62. An imaging apparatus as claimed in any one of claim 46 or claims 47 to 61 as appendant to claim 46, wherein the binder is a poly(vinyl butyral), a polycarbonate, or a polyester.

63. An imaging apparatus as claimed in claim 46 or any claim appendant thereto, wherein the percentage of binder is 22 to 50 per cent by weight.

64. An imaging apparatus as claimed in claim 63, wherein the percentage of binder is 25 to 40 per cent by weight.

65. An imaging apparatus as claimed in any one of claims 46, or claims 47 to 64 as appendant to claim 4, wherein the percentage of dark charge exchange material is 20 to 75 per cent by weight.

66. An imaging apparatus as claimed in claim 43, wherein the dark charge exchange material is indium.

67. An imaging apparatus as claimed in claim 66, wherein the thickness of indium is between 5 and 20 nanometre.

68. An imaging apparatus as claimed in any one of claims 42 to 67, wherein the means for applying an electric field, between the dark exchange layer and the other electrode provides an electric field of strength as herein defined, greater than 10 kilovolts per millimetre.

69. An imaging apparatus as claimed in claim 68, wherein the means for applying an electric field, provides an electric field of strength as herein defined, of from 20 kilovolts to 160 kilovolts per millimetre.

70. An imaging apparatus as claimed in any one of claims 42 to 69, wherein one of the electrodes is at least partially transparent to the activating radiation.

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