

IMAGING SYSTEM

The present invention relates to an imaging system. As we shall explain below embodiments of our system can be adapted for office based systems suitable for making photocopies.

5 Imaging systems based on photosensitive encapsulates have been previously proposed. There are a number of suggestions in the Patent Literature of which we have become aware of the following:

10 Berman, U.S Patent No. 3,219,446 discloses a transfer imaging process in which azo-blue "B" black dye is encapsulated with a cross-linkable polymer or a polymerizable monomer as a fluid-droplet containing film or a fluid droplet containing microcapsules. As described, the Berman imaging system is a transfer
15 system which relies upon selectively transferring the encapsulated dye to a copy sheet in correspondence with the image. Imaging is accomplished by image-wise exposing a layer of the encapsulate to electromagnetic radiation to cross-link the polymer, causing the liquid
20 in the exposed capsules to assume a rigid condition and not transfer to a copy sheet. Dye transfer is limited to the unexposed areas of the encapsulate-containing layer.

25 Phillips, U.S Patent No. 3,700,439 discloses a photocopy process wherein Michler's ketone is encapsulated in a conventional manner and provided as a layer on a support. Michler's ketone itself is not a colour former, but patterned irradiation of the ketone containing capsules produces a latent image of
30 colourless, acid-colourable, dye precursor from the

ketone such that upon contact with an acid developer such as acid clay a visible image is obtained.

Phillips discloses both a system wherein the exposed imaging sheet is calendered face-to-face with an acid-coated receiving sheet to form images and a system wherein the acid developer is on the same surface as the capsule coating so that after rupturing the capsules on the imaging sheet there is development without transfer.

Berman et al, U.S Patent No. 3,072,481 discloses another type of encapsulated light sensitive element which utilizes a light-sensitive material which is readily converted to a coloured form when carried in a liquid vehicle but which is insensitive to light when solid. By encapsulating such a material with a volatile solvent, image-wise exposing a layer of the encapsulate and rupturing the capsules to evaporate the solvent, an image is obtained and fixed.

Forris, U.S Patent No. 3,001,873 discloses a more complex system wherein the walls of capsules containing a solid dye are photosensitized such that patterned exposure renders the capsules unswellable. By wetting the sheet to swell the unexposed capsules and heating, the dye is immobilized in the unexposed areas. Thereafter, by rupturing the capsules in contact with a receiving sheet there is an image-wise transfer of the dye from the exposed areas only.

While image-forming techniques such as these have been proposed previously, for various reasons they have not matured into commercial photocopy systems. Furthermore, the potential of these systems to afford a low cost imaging system has not been realised.

In contrast, the present invention provides, in a first aspect thereof, imaging media comprising a set of two sheets, namely: an imaging sheet comprising a first substrate having a coating on one surface thereof comprising a chromogenic material, and a photosensitive composition, adapted to undergo a viscosity change when exposed to selected actinic radiation, encapsulated as an internal phase in rupturable capsules; and a developer sheet comprising a second substrate and a developer material capable of reacting with said chromogenic material to form a visible image on one surface of said second substrate; the chromogenic material, the photosensitive composition and the developer material being such that and being present in such quantities that an image may be formed without ~~the need for~~ externally applied wet development agents by image-wise exposing said coating to said actinic radiation, whereby to cause a viscosity change in said photosensitive composition, and subjecting said capsules to a uniform rupturing force with said coating in facial contact with said developer sheet such that said capsules rupture and release said internal phase for image-wise transfer of said chromogenic material to said developer sheet in image areas where said chromogenic material and said developer material react to form said visible image.

There is provided, in a second and alternative aspect of this invention a transfer imaging process comprising: image-wise exposing to actinic radiation an imaging sheet comprising a first substrate having on one surface thereof a coating composition including a chromogenic material and a photosensitive composition adapted to undergo a viscosity change upon exposure to such radiation, at least said photosensitive composition being encapsulated in rupturable capsules, to produce exposed and unexposed areas; subjecting said capsules to a uniform rupturing force; and transferring said chromogenic material from the exposed or unexposed areas of said imaging sheet to a developer sheet comprising a second substrate having

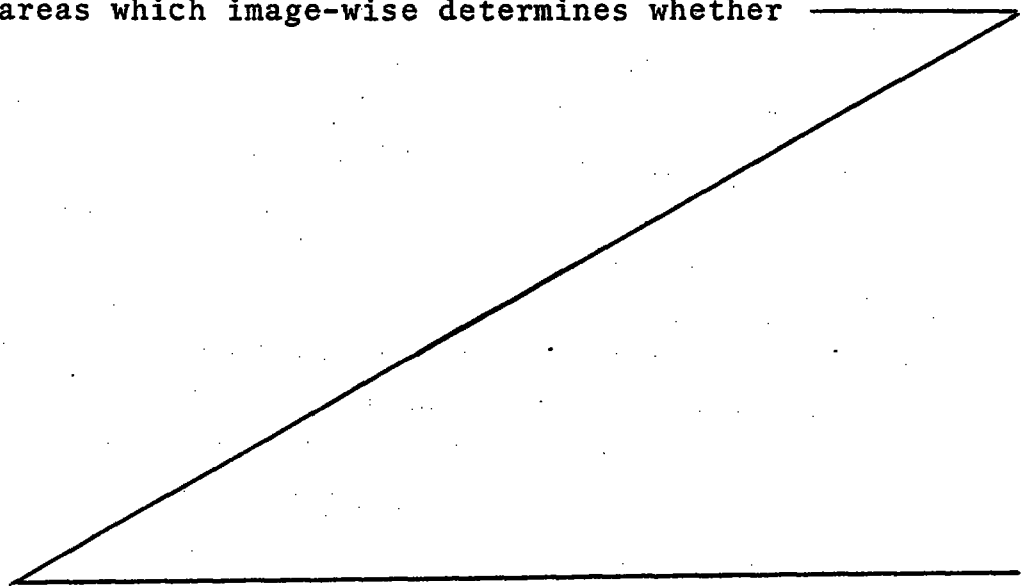
a developer material on one surface thereof such that there is a patterned reaction between said developer material and said chromogenic material which produces an image.

5 The term "encapsulated" as used herein, refers both to so-called resin dispersion or open phase systems in which the internal phase containing the photosensitive composition and optionally the chromogenic material is dispersed as droplets throughout a dispersion medium and
10 to systems in which the capsule is formed with a discrete capsular wall, the latter encapsulation typically being in the form of microcapsules. "Rupturable capsules" are, accordingly, considered to exist in either of these "encapsulated" systems. Furthermore, while the capsules
15 may be "pressure rupturable" means other than pressure may be used to rupture them with a uniform rupturing force, as will be explained.

 In our transfer imaging systems, images are formed by exposing an imaging sheet coated with composition
20 containing the chromogenic material and the encapsulated photosensitive composition to actinic radiation and rupturing the capsules in the presence of a developer carried by a developer sheet. No externally applied wet development agent is needed. The system is designed such
25 that when these steps are carried out, the image-forming reaction between the chromogenic material and the developer discriminately occurs in the exposed or unexposed areas and produces a detectable image. This is accomplished by image-wise photochemically controlling
30 whether the chromogenic material can transfer from the imaging sheet to the developer sheet. By "image-wise" it is meant that upon exposure and transfer the chromogenic material and the developer react to form a positive or negative image of the original.

We believe the imaging sheets themselves to be novel and inventive. Accordingly, in a third alternative aspect of this invention, we provide an imaging sheet useful in forming images by exposure-controlled, image-wise reaction of a chromogenic material and a developer, said sheet comprising: a support having, on one surface thereof, a layer of microcapsules having discrete capsule walls which encapsulate an internal phase including a photosensitive composition which undergoes a change in viscosity, upon exposure to actinic radiation, sufficient to control the release of said internal phase from said microcapsules; and a chromogenic material associated with said microcapsules such that, upon image-wise exposing said layer of microcapsules to said actinic radiation and subjecting said layer of microcapsules to a uniform rupturing force, said chromogenic material image-wise becomes available for forming an image.

In a preferred arrangement, the chromogenic material is encapsulated with the photosensitive composition. The photosensitive composition is such that upon exposure to actinic radiation, there is a change in the viscosity of the internal phase in the exposed areas which image-wise determines whether



the chromogenic material is accessible to the developer. The photosensitive composition may be a radiation curable composition which, upon exposure to light, increases in viscosity and immobilizes the chromogenic material, thereby preventing it from transferring to the developer sheet and reacting with the developer material entirely or in proportion to the tonal depth of the image in the exposed areas. [The term "curable" as used herein is not limited to materials which are cross-linked, but is open to materials which are simply polymerized.] In another case the chromogenic material is encapsulated with a substance which is depolymerized or otherwise decreased in molecular weight upon exposure, resulting in a decrease in viscosity which renders the chromogenic material accessible (transferable) to the developer in the exposed areas.

It will be evident that in the former case the system is a positive working system, whereas in the latter case it is a negative-working system. Using a radiation curable material, when the internal phase contains the chromogenic material, it is rendered inaccessible to the developer in the exposed areas, thereby preventing the formation of an image in those areas. More particularly, the chromogenic material is immobilized in the cured matrix of the photosensitive composition such that it cannot transfer to the developer sheet and react to form an image. In the unexposed areas, which in reflection imaging correspond to the printed areas of printed documents, the internal phase remains liquid and the chromogenic material can react with the developer to form a positive image. In a

negative-working system, the photosensitive composition in a chromogenic material containing encapsulate is viscous and upon exposure it liquefies so that the chromogenic material is transferable to the developer sheet. Thus, in this system, exposure renders the chromogenic material accessible to the developer, the chromogenic material being inherently immobilized in the unexposed material.

The chromogenic material is not necessarily encapsulated with the photosensitive composition although this is a preferred means for carrying out the present invention. The chromogenic material may be co-deposited on the supporting substrate with the encapsulated photosensitive composition or contained in the capsular wall such that upon capsule rupture the chromogenic material is dissolved and carried to the developer material in a discriminate manner. Hence, the photosensitive composition may be encapsulated with a solvent for the chromogenic material or the unpolymerized monomer may dissolve the chromogenic material such that as a result of the exposure, the access between the developer and the chromogenic material is controlled as described herein.

It should be apparent that the system does not necessarily require a given capsule to completely release or completely retain its chromogenic encapsulate as long as there is a difference in the amount of chromogenic material transferring or migrating to the developer in the exposed versus the unexposed areas. Indeed, practical examples of our systems can produce images having tonal quality superior to that obtained in most conventional photocopy systems. One reason for the good tonal

quality of the images obtained is that the amount of chromogenic material released from a given area of a microcapsule coated sheet depends on the degree of exposure of the internal phase of the capsules in that area.

It is not clear whether the amount of chromogenic material transferred is determined by differential capsule rupture (image versus non-image areas) in our systems. Under one theory all of the capsules (in both image and non-image areas) are uniformly ruptured and they transfer chromogenic material in proportion to the viscosity of the internal phase in that area or at that point of the image. Under another theory the tonal range of the images are formed by a matrix of ruptured and unruptured capsules. In actuality, a combination of both theories may occur. Regardless of the theory, upon rupture of the capsules there is patterned release and immobilization of the encapsulate which it has been found corresponds to the degree of exposure such that tonal gradation is obtained.

Embodiments of imaging system can be adapted to be sensitive to various forms of radiation, and as such, the term "actinic radiation" as used herein includes the full spectra of electromagnetic radiation including ultraviolet, infrared, the entire visible spectrum, as well as X-ray and ion beam radiation. The preferred forms of actinic radiation are ultraviolet radiation and visible light having a wavelength of 190 to 800 nm (with the most preferred range being 380 to 480 nm (blue light)).

We regard ultraviolet sensitive systems as advantageous because they can be handled in room light for sufficiently long periods of time to permit the

photosensitive material to be removed from the light-shielding packaging in which it is stored and installed in an exposure apparatus without incorporating auxiliary shielding elements into the imaging sheet.

5 The disadvantages of ultraviolet sensitivity is that many documents are printed on papers which include optical brighteners or TiO_2 which absorb ultraviolet radiation and, therefore, it is difficult to use ultraviolet radiation to make copies of such documents
10 by reflection imaging.

Blue light sensitivity is advantageous because it avoids the optical brightener problem and we have found that it is a simple matter to build temporary screening means into the system for room light handle-
15 ability.

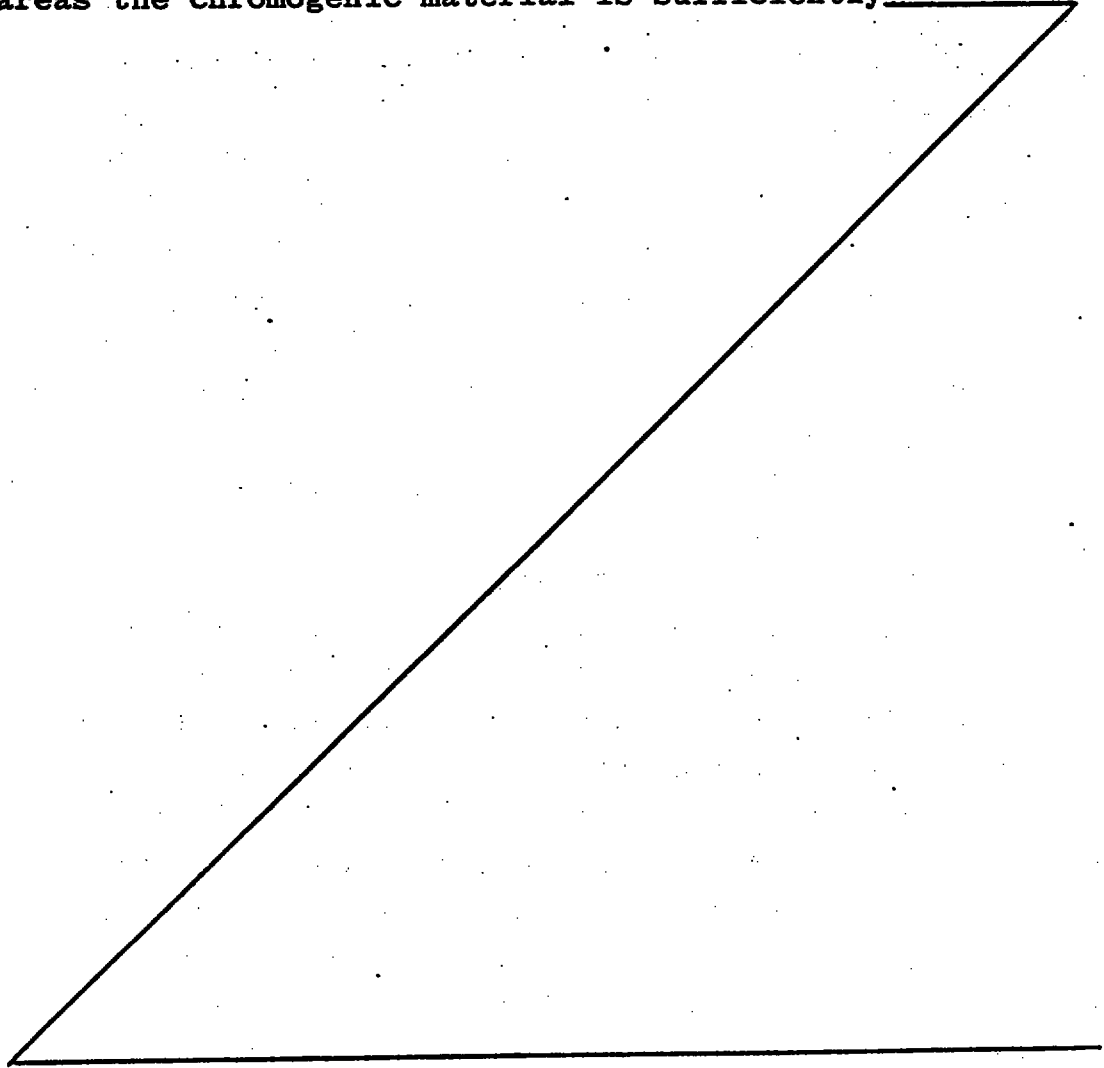
Where the imaging system is sensitive to blue or visible light, the imaging sheet may be constructed with means to temporarily shield the system from visible light to permit room-light handleability. For
20 example, when the imaging system is sensitive to blue light having a wavelength of 380 to 480 nm, imaging sheets may be constructed with a filter layer which incorporates a fugitive yellow dye. The shielding effect of the dye need not be complete, it is sufficient
25 if the imaging sheet can be handled in room light for only the short period of time required to install it in the exposure apparatus. Once installed in the exposure apparatus, the fugitive dye is deactivated, for example, by thermal bleaching, so that the system can
30 be exposed by blue light irradiation in the exposure apparatus. Room light handleability can also be achieved by controlling the sensitivity level of the composition such that exposure to room light of short duration does not interfere with image formation which

is accomplished using more intense radiation.

The transfer imaging system of the present invention may be regarded as one embodiment of the imaging system the subject of our co-pending British Patent Application No: 8232392 (Serial No. 2112536) filed the same day as this application. The present specification is ~~incorporated~~ ^{referred to} in the specification of our said co-pending application, ~~by reference~~. Our said co-pending specification also describes a self-contained copy sheet in which the encapsulated chromogenic material and the developer material are co-deposited on one surface of a single substrate as one layer or as two contiguous layers. As described in more detail hereinbelow the present invention may be embodied in a 2-ply transfer element in which the developer material is coated on a separate substrate as a developer or copy sheet. The systems both of our aforesaid co-pending application and of the present application operate by photographic control of the access between the chromogenic material and a developer forming part of the system, as previously described, no externally applied wet development agent being required. In the self-contained imaging system, following capsule rupture, the chromogenic material and the developer are able to react to form a visible image in the exposed or unexposed areas (depending on the nature of the viscosity change produced by exposure). Gradual development of the visible image is observed following exposure and capsule rupture as the chromogenic material and developer migrate, mix and react on the face of the sheet.

The transfer system addressed herein, on the other hand, operates by selective transfer of the chromogenic material from a transfer or imaging sheet to a developer or copy sheet containing the developer _____

material. Depending on the nature of the photo-sensitive system encapsulated with the chromogenic material, the chromogenic material migrates from the exposed or unexposed areas of the imaging sheet to the developer sheet where it reacts with the developer and forms a visible image. For example, where a radiation curable material such as trimethylol propane triacrylate together with a photoinitiator, constitute the photo-sensitive composition, upon exposure the triacrylate is polymerized into a viscous mass. Thus, in the exposed areas the chromogenic material is sufficiently



immobilized that it cannot transfer to the developer sheet and form colour by reaction with the developer material. In the unexposed areas, which correspond to the image, the internal phase remains liquid such that the chromogenic material can be transferred to the developer sheet where it reacts with the developer and forms a positive image.

In the most typical embodiment, capsule rupture is effected by the application of pressure to the imaging sheet in contact with a developer sheet. Alternative means of capsule rupture can also be used. For example, systems, are envisioned in which the capsules are ruptured ultrasonically, thermally, or by solvent. As previously noted, the invention is applicable to open phase systems as well as systems involving a discrete capsular wall and the method of rupture may depend on the system employed, thermal rupture being a more likely means in conjunction with an open phase system.

Various materials can be used as the chromogenic material and the developer material in the present invention. In this regard, many of the materials conventionally employed in so-called carbonless paper are also suitable for use in the present invention. In the most typical case, the chromogenic material is an electron donating compound and the developer is an electron accepting compound. Preferably, in their unreacted state, these materials are colourless or they are non-absorbing as to the exposure radiation. It is possible to interchange the two materials using an electron accepting compound in conjunction with the photosensitive composition in the internal phase and using an electron donating compound as the developer material. In most cases the chromogenic material is a dye precursor and preferably a black dye precursor, although a variety of other colour precursors are also disclosed below for use in the invention.

(20)

In the preferred case, the internal phase contains a radiation curable material. The radiation curable materials used in one embodiment of the invention are preferably free radical addition polymerizable materials. Preferred materials are ethylenically unsaturated compounds and, more particularly, compounds having two or more ethylenically unsaturated terminal groups.

The imaging system of the present invention is quite versatile. Embodiments of our system can be produced for making copies from printed documents, or duplicating blue prints and other line drawings, among other utilities. Our system can be used to produce monochromatic copies in black or any other colour. Some of the principal advantages of embodiments of our system are the superior tonal quality of the images that are obtained and the fact that imaging can be accomplished using a fairly simple exposure apparatus.

The invention is hereinafter more particularly described by way of example only with reference to the accompanying drawings, in which:-

Fig. 1 is a schematic illustration in cross-section of an imaging sheet and a transfer sheet constructed in accordance with the invention;

Fig. 2 is a schematic illustration of exposure of the imaging sheet; and

Fig. 3 is a schematic illustration of transfer development.

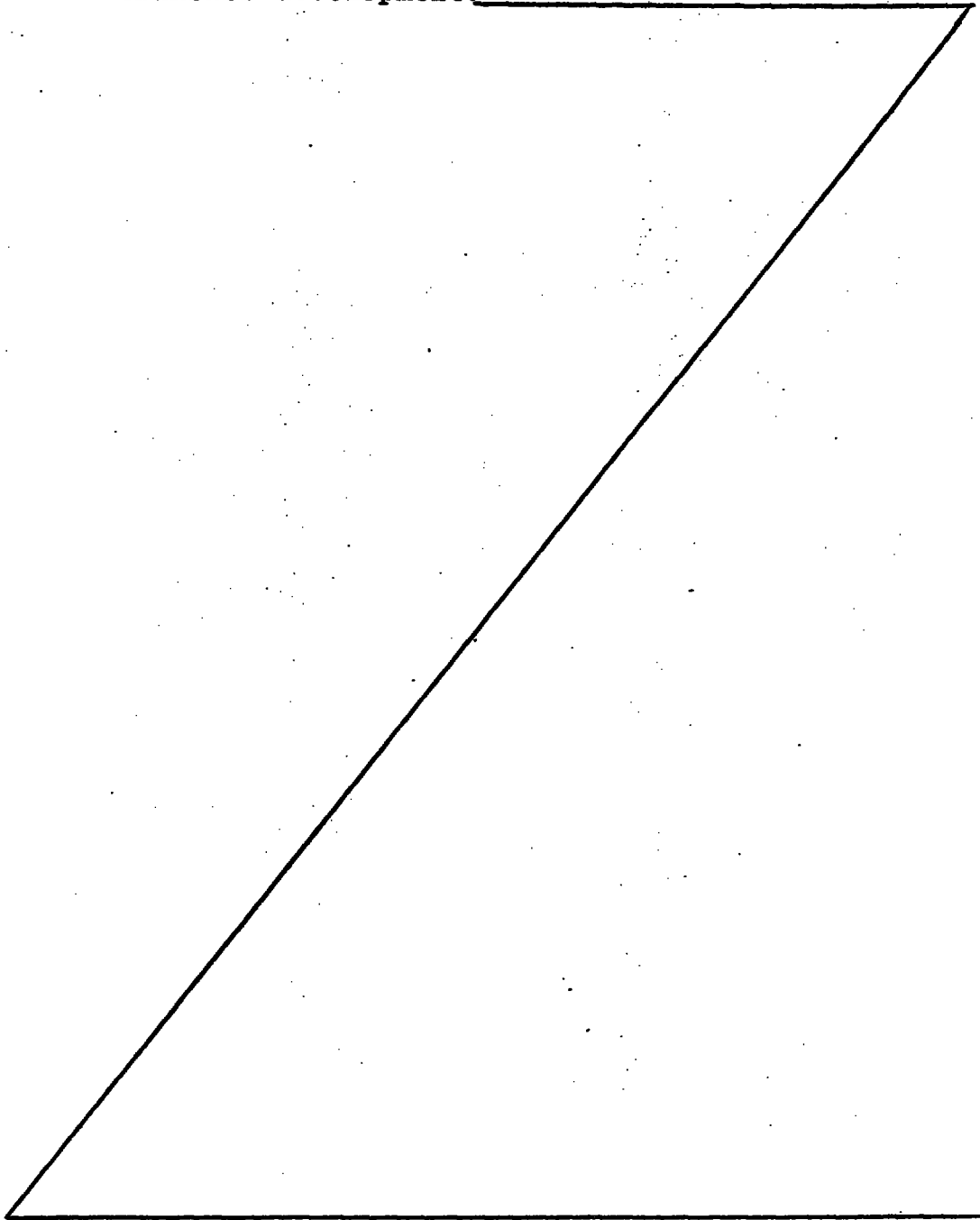


Fig. 1 illustrates one embodiment of the imaging system of the present invention. Therein an imaging sheet 10 is shown comprising a substrate 12 coated with a layer of microcapsules 14. The microcapsules are filled with an internal phase 16 containing a chromogenic material and a photosensitive composition. In actuality, the microcapsules 14 are not visible to the unaided eye. Associated with the imaging sheet 10 is a developer sheet 19 comprising a substrate 20 and a layer 21 of a developer material. Again, in actuality, the developer material is not seen by the unaided eye as a separate layer.

Exposure of the imaging sheet 10 by transmission imaging is shown in Fig. 2 wherein a source of radiant energy 22 is positioned above the surface of the imaging sheet 10 with a mask 24 therebetween. In this illustration the substrate 12 is opaque and the photosensitive material is a positive working resin curable material. Irradiation of the exposed areas 28 causes the radiation curable material in the internal phase 16 to polymerize, thereby gelling, solidifying or otherwise immobilizing the chromogenic material. To simplify the illustration internal phase 16' in the exposed areas 28 is shown as a solid whereas the internal phase 16 remains liquid in the unexposed areas 26. Those skilled in the art will appreciate that while transmission imaging has been used to illustrate the invention for its simplicity, reflected light imaging is the preferred means of copying printed documents.

Image formation or development is shown in Fig. 3 wherein the now exposed imaging sheet 10 becomes a transfer sheet and is placed with its microcapsule layer 14 in face to face contact with

the developer material 21 of developer sheet 19 and a pressure P is uniformly applied across the sheets. For simplification, the pressure is shown as rupturing the microcapsules in the unexposed areas 26 and not rupturing the capsules in the exposed areas 28. This is in accordance with one theory of operation which holds that in the exposed areas the internal phase is hardened to such an extent that the microcapsules can no longer be ruptured. There is another theory, however, which holds that all the capsules are ruptured but the chromogenic material is immobilized by the increased viscosity which results in the internal phase 16' in the exposed areas 28 upon exposure. In actuality all or a portion of the capsules may also be ruptured in exposed areas 28. Typically, the capsules are ruptured by passing the imaging sheet 10 and the developer sheet 20 together through a pressure nip. This causes the internal phase 16 from the unexposed areas 26 to transfer to the developer sheet 19, as shown schematically by arrows in Fig. 3. Upon transfer of the internal phase 16 to the developer sheet 19, the chromogenic material reacts with the developer layer 21 and forms an image 30 on the developer sheet. It should be apparent that while the radiation curable material provides a positive working imaging sheet in that the exposed areas are non-transferable and the unexposed areas are transferable, the transferred image 30 is reversed (right-left) compared to the latent image in the imaging sheet 10 but is a positive duplicate of the mask 24. This presents no problem if the radiation passes through an imaged transparency or mask 24 as shown in Fig. 2. But ordinary copying involves use of opaque documents which can not be used in this manner. Thus, a reflection or optical projection

system is used for copying ordinary documents and is well known in other photocopying technologies.

5 The operational centre of the imaging system of the present invention is the encapsulate or internal phase of the coating composition. In accordance with the invention, the internal phase comprises a photosensitive composition. Typically, the photosensitive composition comprises a photoinitiator and a substance which undergoes a change in viscosity upon exposure to light in the presence of the photoinitiator. That substance may be a monomer, dimer, or oligomer which is polymerized to a higher molecular weight compound or it may be a polymer which is cross-linked. Alternatively it may be a compound which is depolymerized or otherwise decomposed upon exposure, thereby undergoing a change in viscosity.

10 In the most typical case, the photosensitive composition includes a radiation curable material. The radiation curable materials useful in the practice of the present invention are preferably materials curable by free radical initiated chain propagated addition polymerization or ionic polymerization. Substantially any photopolymerizable composition which can be encapsulated and which does not interfere with the image-forming capability of the chromogenic material can be used. These materials may be inherently sensitive to the actinic radiation, in which case they may be hardened without a photoinitiator but usually they are materials which are curable in the presence of a photoinitiator. Furthermore, while in the most typical case, the radiation-curable materials are monomers which undergo an increase in viscosity as a result of polymerization, they may also be oligomers, prepolymers, or polymers which undergo an increase in viscosity as a result of cross-linking upon exposure. In addition to free radical polymerizable

materials they may also be materials which are polymerized or cross-linked ionically, e.g., by generation of a Lewis acid.

5 Representative radiation curable materials are ethylenically unsaturated organic compounds. These compounds contain at least one terminal ethylenic group per molecule. Typically they are liquid and can also double as a carrier oil for the chromogenic material in the internal phase.

10 A preferred group of radiation curable materials is ethylenically unsaturated compounds having two or more terminal ethylenic groups per molecule. Representative examples of these compounds include ethylenically unsaturated acid
15 esters of polyhydric alcohols such as trimethylol propane triacrylate.

Another preferred radiation curable substance is an acrylate prepolymer derived from the partial reaction of pentaerythritol with acrylic
20 acid or acrylic acid esters. Radiation curable compositions based on such prepolymers having an acrylate functionality of between approximately two and three are available commercially in two-package system radiation curable compositions from the
25 Richardson Company, Melrose Park, Illinois, such as RL-1482 and RL-1483 which are recommended to be mixed together to form a radiation curable clear varnish in a ratio of 4.4 parts of RL-1482 to 1 part RL-1483.

30 Isocyanate modified acrylate, methacrylic and itaconic acid esters of polyhydric alcohols as disclosed in U.S. Patent Nos. 3,783,151; 3,759,809 and 3,825,479 all to Carlick et al which are specifically incorporated by references, are also useful.
35 Radiation curable compositions based on these isocyanate modified esters and including reactive

diluents such as tetraethylene glycol diacrylate as well as photoinitiators such as chlorinated resins, chlorinated paraffins and amine photoinitiation synergists are commercially available as overprint
5 varnishes from Sun Chemical Corporation, Carlstat, New Jersey, under the trade name of Suncure resins.

Another class of curable materials useful in the present invention are found in radiation curable inks as the photosensitive component such as
10 a mixture of a pentaerythritol acrylate and halogenated aromatic, alicyclic or aliphatic photoinitiator as disclosed in U. S. Patent No. 3,661,614 to Bessemir et al, which is also incorporated by reference. Still another type of radiation curable
15 material is halogenated resins which can be cross-linked by ultraviolet radiation.

Some typical examples of radiation de-polymerizable materials useful in other embodiments of the invention are 3-oximino -2- butanone
20 methacrylate which undergoes main chain scission upon U.V. exposure and poly 4'-alkyl acylo-phenones. See Reichmanis, E.; Am. Chem. Soc. Div. Org. Coat. Plast. Chem. Prepr. 1980, 43, 243-251 and Lukac, I.; Chmela S., Int. Conf. on Modif. Polym. 5th. Bratislava, Czech. July 3-6, 1979, I.U.P.A.C. Oxford, England 1979, 1, 176-182.
25

The radiation curable or depolymerizable material usually makes up the majority of the internal phase. A radiation curable material must
30 be present in an amount sufficient to immobilize the chromogenic material upon exposure. With a depolymerizable material, on the other hand, the internal phase must be constituted such that the chromogenic material is immobilized prior to exposure but is
35 released after exposure and capsule rupture. Typically these materials constitute 40 to 99 wt %

of the internal phase (based on the weight of the oil solution containing the chromogen, the photosensitive composition and the carrier oil when present). In some embodiments, it has been found desirable to dilute the photosensitive composition with a carrier oil to improve half-tone gradation. In these cases, a carrier oil is present in the amounts disclosed below and the aforesaid materials make up to 40 wt % of the internal phase.

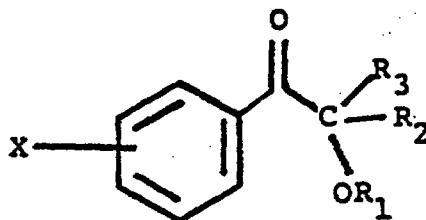
Those skilled in the art will appreciate that various photoinitiators can be selected for use in the present invention depending on the sensitivity that is desired in accordance with the present invention. These compounds absorb the exposure radiation and generate a free radical alone or in conjunction with a sensitizer. Conventionally, there are homolytic photoinitiators which cleave to form two radicals and initiators which radiation converts to an active species which generates a radical by abstracting a hydrogen from a hydrogen donor. There are also initiators which complex with a sensitizer to produce a free radical generating species and initiators which otherwise generate radicals in the presence of a sensitizer. Both types can be used in the present invention. If the system relies upon ionic polymerization to tie up the chromogen, the initiator may be the anion or cation generating type depending on the nature of the polymerization. Where, for example, ultraviolet sensitivity is desired, as in the case of direct transmission imaging using ultraviolet light, suitable photoinitiators include α -alkoxy phenyl ketones, O-acylated α -oximinoketones, polycyclic quinones, benzophenones and substituted benzophenones, xanthenes, thioxanthenes, halogenated compounds such as chlorosulfonyl and chloromethyl

polynuclear aromatic compounds, chlorosulfonyl and chloromethyl heterocyclic compounds, chlorosulfonyl and chloromethyl benzophenones and fluorenones, haloalkanes,

- 5 α -halo α -phenylacetophenones; photoreducible dye-reducing agent redox couples, halogenated paraffins (e.g., brominated or chlorinated paraffin) and benzoin alkyl ethers.

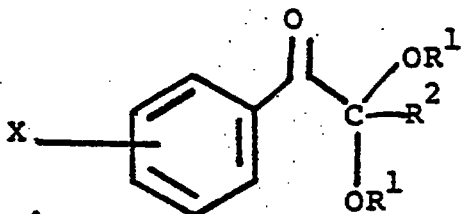
10 The following compounds may be useful as photoinitiators in the present invention:

α -alkoxyphenyl ketones of the formula I

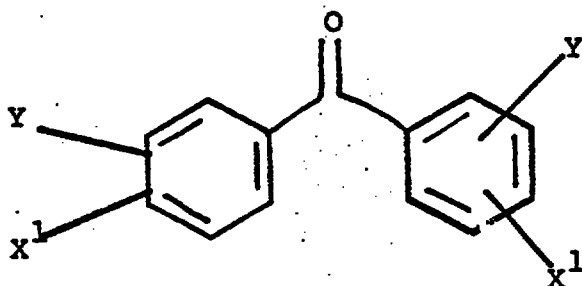


- where R¹ is a C(1-4) alkyl group (e. g., methyl, ethyl, n-propyl, i-propyl, t-butyl, etc.), R² is a phenyl group or a substituted phenyl group wherein said substituent is as defined for X below, R³ is hydrogen or a C(1-4) alkyl group, and X is hydrogen, an alkoxy group having 1 to 4 carbon atoms (e. g., methoxy, ethoxy, propyloxy, etc.), a dialkylamino group wherein said alkyl group contains 1 to 4 carbon atoms, a nitro group, a nitroso group, a cyano group, a mercapto group, chlorine, bromine or iodine, an alkyl group having 1 to 4 carbon atoms, an alkenyl group having 1 to 4 carbon atoms, an acyl group, a phenyl group, or a carboalkoxy group having 2 to 5 carbon atoms;

an α,α dialkoxyphenyl ketone of the formula II



where R¹, R² and X are defined as in formula I;
 1-phenyl-1,2-propanedione-2-O-benzoyloxime,
 9,10-phenanthraquinone,
 9,10-anthraquinone,
 a benzophenone of the formula III



where X¹ is hydrogen, an amino group, or a dialkylamino group, the alkyl group having 1 to 4 carbon atoms, and Y is hydrogen, an alkyl group having 1 to 4 carbon atoms, an alkoxy group having 1 to 4 carbon atoms, an alkenyl group having 1 to 4 carbon atoms, a phenyl group, a substituted phenyl group, a dialkylamino group, a nitro group, a nitroso group, a cyano group, a mercapto group, chlorine, bromine, iodine, or an acyl group;

xanthone, a chloroxanthone, a chloromethyl xanthone, a chlorosulfonyl xanthone,

thioxanthone, a chlorothioxanthone, a chloromethyl thioxanthone, a chlorosulfonyl thioxanthone,

- chloromethylnaphthalene,
- 5 chlorosulfonyl naphthalene,
- chloromethyl anthracene,
- chlorosulfonyl anthracene,
- chloromethyl benzoxazole,
- chloromethyl benzothiazole,
- 10 chloromethyl benzimidazole,
- chlorosulfonyl benzoxazole,,
- chlorosulfonyl benzothiazole,
- chlorosulfonyl benzimidazole,
- a chloromethyl quinoline,
- 15 a chlorosulfonyl quinoline,
- a chloromethyl benzophenone,
- a chlorosulfonyl benzophenone,
- a chloromethyl fluorenone,
- a chlorosulfonyl fluorenone,
- 20 carbon tetrabromide,
- benzoin methyl ether,
- benzoin ethyl ether,
- desyl chloride,
- desyl amine,
- 25 methylene blue/ascorbic acid,
- chlorinated aliphatic hydrocarbons and combinations thereof.

The sensitivity among these compounds can be shifted by adding substituents such that the compounds generate radicals when exposed to the desired radiation wavelength. For visible (blue) light sensitivity, the aforementioned photoinitiators may be combined with a sensitizer such as Michler's ketone or an analogous dialkylamino benzophenone thereof, a substituted coumarin, a linear polyene (e.g., trans B-carotene) or sensitizing dye, e.g., a yellow dye.

For ultraviolet sensitivity a preferred photoinitiator-sensitizer is a combination of Michler's ketone and benzoin methyl ether (preferred ratio 2:5).

5 The photoinitiator is present in the internal phase in an amount sufficient to initiate polymerization or cross-linking within a short exposure time. Using benzoin methyl ether as an example, this photoinitiator is typically present in
10 an amount of up to 10% based on an amount of radiation curable material in the internal phase. Naturally, the amount varies depending on the nature of the other components of the photosensitive composition. Those skilled in the art can readily
15 determine amounts suitable for the desired exposure properties. An instantaneous system would be desirable, i. e., one which will provide an image with less than 0.5 to 1 second exposure, however, exposure times ranging from 0.5 to up to 1 minute
20 are sometimes required. The actual exposure time will also depend on a number of variables such as coat weight, coat thickness, the radiation curable substance (rate of photopolymerization), the type and source of radiation, the radiation intensity and
25 its distance from the sheet.

It is also possible to reduce the exposure time by incorporating a scattering agent in the capsule layer. A scattering agent increases the mean free path and thereby intensifies exposure.
30 One such scattering agent that can be used in the present invention is magnesium dioxide.

The chromogenic materials used in the present invention are preferably oil soluble color formers which will produce a color upon reaction
35 with a developer material in the presence of a carrier oil. Substantially any of the chromogenic

materials conventionally used in carbonless paper can be used in the present invention. In general, these materials are colorless electron donating type compounds. Representative examples of such color
5 formers include substantially colorless compounds having in their partial skeleton a lactone, a lactam, a sultone, a spiropyran, an ester or an amido structure. Specifically, there are triaryl-methane compounds, bisphenylmethane compounds,
10 xanthene compounds, thiazine compounds, spiropyran compounds and the like. Typical examples of them include Crystal Violet lactone, benzoyl leuco methylene blue, Malachite Green Lactone, p-nitrobenzoyl leuco methylene blue,
15 3-dialkylamino-7-dialkylamino-fluoran, 3-methyl-2,2'-spirobi(benzo-f-chrome), 3,3-bis(p-dimethylaminophenyl)phthalide, 3-(p-dimethylaminophenyl)-3-(1,2dimethylindole-3-yl)phthalide, 3-(p-dimethylaminophenyl)-3-
20 (2-methylindole-3-yl)phthalide, 3-(p-dimethylamino-phenyl)-3-(2-phenylindole-3-yl)phthalide, 3,3-bis(1,2-dimethylindole-3-yl)-5-dimethylaminophthalide, 3,3-bis-(1,2-dimethylindole-3-yl)6-dimethylaminophthalide,
25 3,3-bis-(9-ethylcarbazole-3-yl)-5-dimethylamino-phthalide, 3,3-bis(2-phenylindole-3-yl)-5-dimethylaminophthalide, 3-p-dimethylaminophenyl-3-(1-methylpyrrole-2-yl)-6-dimethylaminophthalide, 4,4'-bis-dimethylaminobenzhydrin benzyl ether,
30 N-halophenyl leuco Auramine, N-2,4,5-trichlorophenyl leuco Auramine, Rhodamine-B-anilinolactam, Rhodamine-(p-nitroanilino)lactam, Rhodamine-B-(p-chloroanilino)lactam, 3-dimethylamino-6-methoxyfluoran,
35 3-diethylamino-7-methoxyfluoran, 3-diethylamino-7-chloro-6-methylfluroan,

3-diethylamino-6-methyl-7-anilino-fluoran,
3-diethylamino-7-(acetylmethylamino) fluoran,
3-diethylamino-7-(dibenzylamino) fluoran,
3-diethylamino-7-(methylbenzylamino) fluoran,
3-diethylamino-7-(chloroethylmethylamino) fluoran,
5 3-diethylamino-7-(diethylamino) fluoran,
3-methyl-spiro-dinaphthopyran,
3-ethyl-spiro-dinaphthopyran,
3,3'-dichloro-spiro-dinaphthopyran,
3-benzyl-spiro-dinaphthopyran,
10 3-methyl-naphtho-(3-methoxybenzo)-spirpyran,
3-propyl-spirodibenzoidipyrans, etc.

Mixtures of these color precursors can be used if desired. Also useful in the present invention are the fluoran color formers disclosed in U.S. Patent 3,920,510, which is incorporated by reference.

The present invention, however, is not limited to the use of the aforementioned color precursors as chromogenic materials. In addition, organic chemicals which are capable of reacting with heavy metal salts to give colored metal complexes, chelates or salts can be adapted for use in this invention.

Substantially any color forming material which can be encapsulated and which will react with a developer material to form an image can be used in the present invention. Furthermore, it is not necessary to maintain the conventional distinction between color formers and color developers in the invention system. That is, in some embodiments, the chromogenic material may be what is commonly referred to as a color developer provided it does not absorb in the exposure radiation range so as to interfere with imaging.

In addition to the chromogenic material and the photosensitive material, the internal phase of

the present invention may also include a carrier oil. Preferred carrier oils are weakly polar solvents having boiling points above 170°C and preferably in the range of 180°C to 300°C. The carrier oils used in the present invention are typically those conventionally used in carbonless paper manufacture. These oils are generally characterised by their ability to dissolve Crystal Violet Lactone in a concentration of 0.5 wt % or more. However, a carrier oil is not always necessary. Whether a carrier oil should be used will depend on the solubility of the chromogenic material in the photosensitive composition before exposure, the nature of the chromogenic material and the viscosity of the characteristics of the internal phase. When present, examples of carrier oils are alkylated biphenyls (e.g., monoisopropylbiphenyl), polychlorinated biphenyls, castor oil, mineral oil, deodorized kerosene, naphthenic mineral oils, dibutyl phthalate, dibutyl fumarate, brominated paraffin and mixtures thereof. Alkylated biphenyls are generally less toxic and preferred.

The presence of a carrier oil affects and can be used to control the tonal quality of the images obtained. While tonal quality (half-tone gradation) is not critical when copying printed documents, it is an important factor in faithfully reproducing pictorial images. Initial studies show that where trimethylol propane triacrylate is used in the radiation curable material, 20% of a carrier oil such as brominated paraffin improves tonal qualities.

The chromogenic material is incorporated in the internal phase in an amount sufficient to produce a visible image of the desired density upon reaction with the developer. In general, these amounts range from approximately 0.5 to about 20.0 percent based on the weight of the internal phase solution (e.g., monomer or monomer and oil) containing the chromogen. A preferred

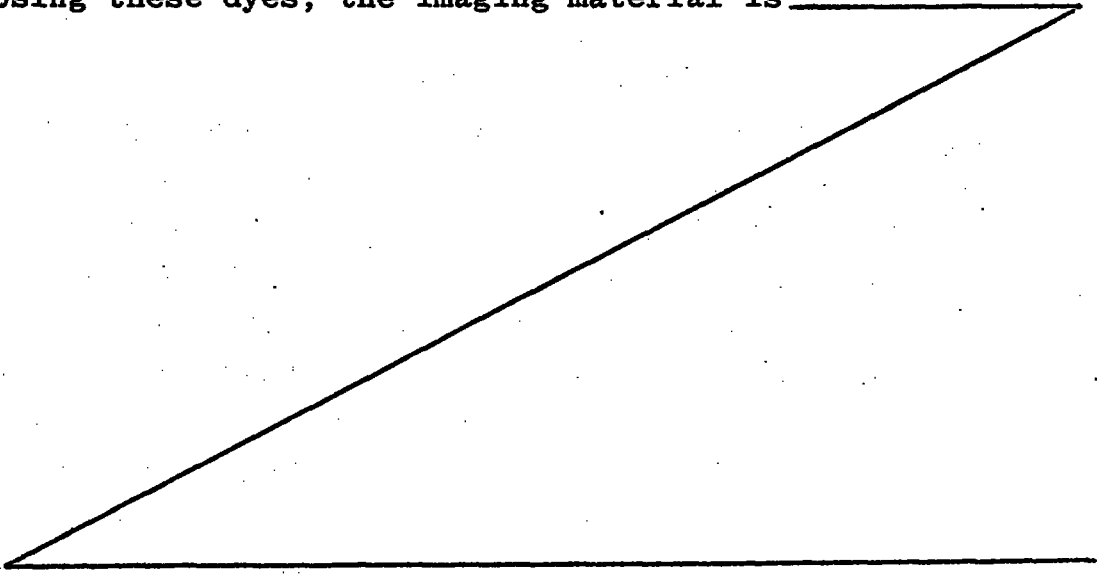
range is from about 2 percent to about 7 percent. The amount of the chromogenic material required to obtain suitable images depends on the nature of the chromogen, the nature of the internal phase, and the type of imaging system. Typically more chromogenic material may be used in the internal phase of a transfer imaging system in comparison to a self-contained system. This is because the developer material is co-deposited on a common substrate with the chromogenic encapsulate in the self-contained system and there would be a tendency for the chromogenic material to diffuse through the capsule wall and react with the developer material during storage, and because there may be some inherent loss in a transfer system.

Typically a transfer imaging sheet contains 6 percent chromogenic material in the internal phase whereas we have formed self-contained imaging sheets using 1.5 to 3 percent of chromogenic material.

As indicated above, the imaging systems of the present invention may be formulated such that they are sensitive to any of ultraviolet, infrared, X-ray, ion beam, and visible radiation. For room light handleability, ultraviolet sensitive imaging systems are preferred. Ultraviolet sensitive imaging systems are suitable for recording images from a cathode ray tube as well as in reproducing images from a transparent or translucent photomask. Both of these systems rely upon transmitted ultraviolet radiation to expose the imaging system. It has been found, however, that ultraviolet sensitivity is generally not suitable when it is desired to reproduce a printed document by reflection imaging (e.g., contact reflection imaging or optical projection imaging using reflected light). The reason for this is that the vast majority of printed documents are on papers containing optical brightening agents or TiO_2 . These agents act as black dyes in an ultraviolet imaging system and absorb the

ultraviolet radiation. Hence the background and image areas are both ultraviolet absorbers and there is no image discrimination by reflection imaging.

In making copies of printed documents, it has been found desirable to use a blue-light sensitive material. Using a blue-light sensitive material, it is possible to make the system handleable in room light by incorporating in the system a fugitive yellow filter dye which is bleached or otherwise rendered inactive or removed from the imaging system prior to exposure. The yellow dye absorbs blue-light and so would prevent a blue-light sensitive imaging material in accordance with the present invention from being exposed, for example, as it is removed from a light-shielded container and installed in an exposure apparatus. The fugitive dye may be incorporated in the imaging system in a separate layer which overcoats the layer of the encapsulated chromogenic and photosensitive materials or the fugitive dye may be fixed in the wall of a discrete walled microcapsulate. Yellow fugitive dyes are well known in the art. The preferred dyes are those which can be inactivated or removed from the imaging system with the greatest ease. Using these dyes, the imaging material is _____



heated in the exposure apparatus to a temperature at which the dye is bleached prior to exposure. Thereafter, the imaging material can be exposed by the application of light in the visible blue range.

5 In addition to thermally bleachable fugitive dyes, the invention is also open to the use of dyes which are bleached by oxidation. Although, using these dyes, a liquid processing step would normally be required to bleach the dye.

10 An internal phase as described above can be encapsulated in a conventional manner. Oil soluble chromogenic materials have been encapsulated in hydrophilic wall-forming materials such as gelatin wall-forming materials (see U.S. Patent Nos.

15 2,730,456 and 2,800,457 to Green et al) including gum arabic, polyvinyl alcohol, carboxymethyl-cellulose; resorcinol-formaldehyde wall-formers (see U.S. Patent No. 3,755,190 to Hart et al), isocyanate wall-formers (see U.S. Patent No. 3,914,511 to Vassiliades) isocyanate-polyol wall-formers (see U.S. Patent No. 3,796,669 to Kiritani et al) ureaformaldehyde wall-formers and more particularly Urea-resorcinol-formaldehyde wall forms (in which oleophilicity is enhanced by the addition of resorcinol) (see U.S. Patent Nos. 4,001,140; 4,087,376 and 4,089,802 to Foris et al)

25 melamine-formaldehyde resin and hydroxypropyl cellulose (see commonly assigned U.S. Patent No. 4,025,455 to Shackle). To the extent necessary for

30 complete disclosure of those wall-forming materials, the above mentioned patents are specifically incorporated by reference. Microencapsulation has been accomplished by a variety of known techniques including coacervation, interfacial polymerization, polymerization of one or more monomers in an oil, as
35 well as various melting, dispersing and cooling

methods.

The capsule forming material used in a given imaging system is selected based on the photosensitive composition present in the encapsulate. Thus, the formed capsule wall must be transmissive to the exposure radiation. Of the above systems urea-resorcinol-formaldehyde and gelatin capsules are preferred.

The mean size of the capsules used in our systems generally range from approximately 1 to 25 microns. As a general rule, image resolution improves as the capsule size decreases with the caveat that if the capsule size is too small, depending on the nature of the substrate on which the capsules are coated, the capsules may disappear in the pores or the fibre in the substrate, but even capsules as large as 25 microns have been found to provide satisfactory resolution in our systems. In the latter case, the incongruities in the substrate may screen the capsules from exposure and thereby diminish image quality. They may also fail to rupture, for example, upon the application of pressure. In view of the foregoing, we have found that a preferred mean capsule size range is approximately 3 to 15 microns and particularly approximately 3 to 10 microns although, technically, the capsules can range in size up to the point that they are visible to the human eye.

Capsular coating compositions may be prepared in conventional manner for use in the present invention. Since the photosensitive encapsulate is usually hydrophobic, the wall-forming constituents and the film forming binder should be hydrophilic and soluble in an aqueous based liquid as is conventional in forming capsule containing coating compositions. Otherwise in certain known reverse system the aqueous phase may be dispersed in a hydrophobic continuous phase. The microcapsules used in embodiments of our system can be prepared by the methods disclosed in the aforementioned

U.S patents or by similar methods. For example, an oil solution of an internal phase comprising the chromogenic and photosensitive composition may be dispersed in a continuous phase containing the wall-forming constituents, and microencapsulation is accomplished by, for example, 5 coacervation or interfacial polymerization, among others. Open phase systems can be prepared by dispersing the internal phase in a solution of polymeric binder and adjusting the viscosity of the dispersion for coating. 10 Among a wide variety of suitable binders are gelatin, polyvinyl alcohol, polyacrylamide, acrylic latices etc.

Coating compositions so formulated are applied and dried on a continuous web of paper. Any ordinary coating or printing technique can be used in making 15 imaging sheets in accordance with the invention including such means as roller or blade coating.

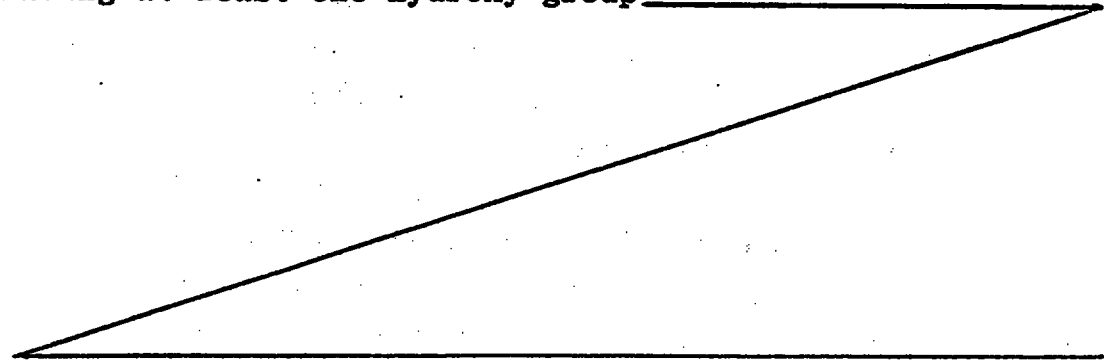
The coating compositions may contain any of the various additives known in the carbonless paper art to improve the handling characteristics of the coated copy 20 sheet such as a stilt material (e.g., starch particles), silica particles to prevent specking when a pressure nip is used for capsule rupture, etc.

In its principal embodiment, our imaging system is used to produce copies of printed documents, and, as 25 such, the substrate upon which the coating composition is coated is paper. The paper may be a commercial impact raw stock, or a special grade paper such as cast-coated paper and chrome rolled paper. The latter examples are desirable when using very fine microcapsules, e.g., 30 capsules ranging in size from approximately 1 to 5 microns, as the surface of these papers is smoother and the microcapsules are not as easily embedded in the stock fibres. Transparent substrates such as polyethylene terephthalate and translucent substrates can also be 35 used and have the advantage that the latent image formed

in the imaging sheets need not be reversed for printing.

5 The developer material used in our systems is a
compound or material capable of reacting with the
particular chromogenic material to produce a colour
10 image. In the most typical case, the developer material
is an electron accepting compound or a so-called colour
developer. In the broadest sense, however, when one
half of the colour-forming reactants is encapsulated
with the photosensitive composition, the term "developer
15 material" as used herein may refer to the other half of
the colour-forming reactant combination not encapsulated
with the photosensitive composition. Hence, as stated
before, compounds conventionally recognized as colour
20 developers can be encapsulated as the chromogenic
material, and compounds conventionally recognized as
colour formers can be used on the second substrate as
'developer'.

 The developer materials which may be used in the
practise of the present invention include those con-
20 ventionally employed in carbonless paper technology and
which are well known. Illustrative specific examples
are clay minerals such as acid clay, active clay,
attapulgit, etc.; organic acids such as tannic acid,
gallic acid, propyl gallate, etc.; acid polymers such as
25 phenol-formaldehyde resins, phenol acetylene condensation
resins, condensates between an organic carboxylic acid
having at least one hydroxy group



and formaldehyde, etc.; metal salts or aromatic carboxylic acids such as zinc salicylate, tin salicylate, zinc 2-hydroxy naphthoate, zinc 3,5 di-tert butyl salicylate, oil soluble metal salts of phenol-formaldehyde novolak resins (e. g., see U. S. patents Nos. 3,672,935; 3,732,120 and 3,737,410) such as zinc modified oil soluble phenol-formaldehyde resin as disclosed in U. S. Patent No. 3,732,120), zinc carbonate etc. and mixtures thereof. Again, to the extent necessary for complete disclosure of these developer materials, the above noted patents are specifically incorporated by reference.

When used in a developer sheet, the color developer may be mixed with a binder such as latex, polyvinyl alcohol, maleic anhydride-styrene copolymer, starch and gum arabic. It is to be understood that all binders well known as film-forming materials can be used in this capacity.

Imaging sheets embodying the invention imaging system can be exposed using a fairly simple exposure apparatus. In its simplest form for reflection imaging, the apparatus requires only a radiation source, means of focusing the exposure radiation from the original onto the imaging sheet means to join the imaging sheet with the developer sheet and means for rupturing the encapsulate. Simplified means such as this can be used with the invention because development is essentially a dry process with the developer and chromogenic material reacting in only the infinitesimal droplets of solvent encapsulated in the internal phase. Furthermore, the chromogenic material and the developer are on the imaging and developer sheets in the amounts (coverage) required for imaging, hence, the invention obviates the elaborate means required in most prior photocopy systems for coating and

metering the developing agent onto the imaging sheet in sufficient amounts.

The present invention is illustrated in more detail by the following non-limiting examples:

5

Example 1

Ultraviolet Photosensitive Microcapsule Preparation (UF Capsules)

To 25 parts of a filtered solution prepared by dissolution of 5.0 parts of gum arabic (Celanese; grade A-13, gum arabic special) in 50.0 parts of distilled water was added with stirring 26.9 parts of a 17.1% (total solids) solution of isobutylene/maleic anhydride copolymer and sodium hydroxide, prepared by addition of 5.44 parts of isobutylene/maleic anhydride copolymer (average molecular weight = 1.0×10^6) and 2 parts of sodium hydroxide in 32.5 parts of distilled water with stirring and heating to 92°C for 2 hours. Subsequently 38.3 parts of distilled water was added and after heating to 60°C the pH of the resulting mixture was adjusted to 4.0 (from an initial pH of 8.8) by the portionwise addition of 10% (V/V) aqueous sulfuric acid. With maintenance of the 60°C temperature and constant stirring, 6.6 parts of urea and 0.8 parts of resorcinol were added and the pH of the mixture was readjusted to 4.0 with 10% (V/V) aqueous sulfuric as previously described. The completed solution, hereafter referred to as the aqueous phase, was maintained at 60°C for immediate use.

Preparation of the internal phase, hereafter known as the organic phase, proceeded as follows: in a mixture of 40.0 parts of trimethylolpropane triacrylate (TMPTA) and 10.0 parts of methyl methacrylate (MMA) was dissolved with stirring and heating to 90°C, 3.0 parts of the color precursor,

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3-diethylamino-6-methyl-7-anilino-fluoran. While allowing the mixture to cool to 60°C, 2.5 parts of benzoin methyl ether and 1.0 parts of 4,4'-bis(dimethylamino) benzophenone were added and the mixture was allowed to stir until complete dissolution of these materials. The completed organic phase was maintained at 60°C for immediate use.

Preparation of the urea-formaldehyde micro-capsules proceeded as follows: to a commercial Waring blender equipped with a speed control consisting of a variable voltage power supply (variable autotransformer; 0 to 140 volt range) and preheated to 60°C by means of a heated, forced air supply was added the entire aqueous phase. With the blender operating at 40 volts, the entire organic phase, also preheated to 60°C, was carefully added in a thin continuous stream. With provisions made for maintenance of the internal temperature at 60°C, the blender was operated at 90 volts for 45 seconds to effect emulsification. Directly after this 45 second period, the power supply setting was reduced to 40 volts, an aliquot was taken and the average particle size was determined by visual examination of the emulsion under a microscope. The average particle size was 4.5 microns.

Following this determination, 18.4 parts of a 37% (W/V) aqueous formaldehyde, preheated to 60°C, were added in one portion. After blending for 2 hours the mixture was transferred to a heatable container equipped with an efficient mechanical stirrer, the temperature was maintained at 60°C and a solution of 0.6 parts of ammonium sulfate in 12.2 parts of water was added with high speed stirring. After 1.0 hours of stirring, the mechanical stirrer was removed, provision was made for magnetic

stirring and the pH was adjusted to 9.0 (from an initial pH of 3.2) by the portion-wise addition of 10% (W/V) aqueous sodium hydroxide. Microcapsule emulsion preparation was completed by the addition of 2.8 parts of sodium bisulfite followed by an additional 10 minutes of stirring.

Preparation of Light Sensitive Sheets from the Above Microcapsule Preparation

A slurry consisting of 10 parts of the above light sensitive microcapsule and 10 parts of distilled water was coated on 80 lb. black and white enamel paper stock using a #10 drawdown rod as the coating device and the coated papers were dried briefly in a circulated hot air oven at 95°C. The resulting dry sheets were immediately useable or could be stored for later use.

Preparation of Developer Sheet

To 218 parts of water were added with slow stirring 5.8 parts of a 50% aqueous suspension of styrene-butadiene latex, 40 parts of 10% aqueous 1.5% ethylated starch, 17 parts of hydrated silica gel, 21 parts of zinc carbonate, 13 parts of 47% aqueous sodium silicate, 1 part sodium hexa-meta-phosphate and 130 parts of Silton F-150 clay. After stirring at ambient temperature for 1 hour, the mixture was stabilized by the addition of 0.1 part of 37% aqueous formaldehyde and coated upon 80 lb. black and white enamel paper stock using a #10 drawdown bar as the coating device. The sheets were completed by brief drying in a recirculated hot air (95°C) oven.

Reproduction of Images Using the Above Light Sensitive Sheets

The apparatus used in the reproduction of images using the light sensitive sheets consisted of: a near UV light source (2, 15 watt F-15-T8-BLB

black light bulbs), a positive photographic transparency, a plate glass cover plate and a calender stack capable of providing at least 30 lb. per lineal inch crushing pressure. Images were reproduced in the following way: a light sensitive sheet was positioned with light sensitive surface uppermost on a horizontal surface, the positive transparency was superimposed upon this sheet, followed by the glass cover plate and the assembly was irradiated for periods of 1, 2, 3 and 4 seconds by the above mentioned UV light source positioned parallel to and approximately 5 inches from the above assembly. Following exposure, the light sensitive sheet was placed against an image receiving and developing sheet prepared as above.

The sheets were positioned such that the active layers of each were in intimate contact and the assembled sheets were calendered. Such treatment and separation of the sheets resulted in the production of a reversed positive black image. Exposures of 1 and 2 seconds gave images of essentially similar quality, with good resolution and half-tone gradation. The 2 second exposure gave somewhat less transferred and developed dye background. Exposures of 3 and 4 seconds gave lower image intensity typical of over exposure.

Example 2

Ultraviolet Photosensitive Microcapsule Preparation (UF Capsules)

An aqueous phase was prepared in exactly the same manner and proportions as described in Example #1.

Preparation of an organic phase proceeded as follows: to 50.0 parts of tetraethylene glycol diacrylate (TEGDA) was added with heating to 90°C and stirring 3.0 parts of the same color precursor

mentioned in Example 1. After complete dissolution of the dye precursor the mixture was allowed to cool to 60°C and 2.5 parts of benzoin methyl ether and 1.0 parts of bis-4,4'-(dimethylamino) benzophenone were added successively and the mixture was stirred at 60°C until complete dissolution occurred. The organic phase was maintained at 60°C for immediate use.

The preparation of the urea-formaldehyde capsules proceeded exactly as described in Example 1, with the following important modification and observation: after careful addition of the organic phase to the aqueous phase in the blender, the blender was operated at 90 volts for 60 seconds instead of 45 seconds and the observed size of the emulsion droplets was, on the average, 5.0 microns instead of 4.5 microns. Capsule preparation was completed exactly as described in Example 1.

Preparation of Light Sensitive Sheets from the Above Microcapsule Preparation

A slurry consisting of 10 parts of the above microcapsule preparation and 10 parts distilled water was coated on 80 lb. black and white enamel paper stock using a #10 drawdown rod as described in Example 1. Preparation of the light sensitive sheets was completed exactly as described previously and the resulting light sensitive sheets were immediately useable or could be stored for later use.

Reproduction of Images Using the Above Light Sensitive Sheets

The apparatus used for image reproduction was exactly the same as described in Example 1. Exposures of from 1 to 4 seconds resulted in no developed image, however; exposures of 1 and 2 minutes gave high quality black image reproduction

after development by calendering against the same image receiving sheet as was used and described in Example 1.

CLAIMS

1. For use in a transfer imaging system, imaging media comprising a set of two sheets, namely: an imaging sheet comprising a first substrate having a coating on one surface thereof comprising a chromogenic material, and a
5 photosensitive composition, adapted to undergo a viscosity change when exposed to selected actinic radiation, encapsulated as an internal phase in rupturable capsules; and a developer sheet comprising a second substrate and a developer material capable of reacting with said chromo-
10 genic material to form a visible image on one surface of said second substrate; the chromogenic material, the photosensitive composition and the developer material being such that and being present in such quantities that an image may be formed without ~~the need for~~ externally
15 applied wet development agents by image-wise exposing said coating to said actinic radiation, whereby to cause a viscosity change in said photosensitive composition, and subjecting said capsules to a uniform rupturing force with said coating in facial contact with said developer sheet
20 such that said capsules rupture and release said internal phase for image-wise transfer of said chromogenic material to said developer sheet in image areas where said chromogenic material and said developer material react to form said visible image.

2. Imaging media according to Claim 1, wherein said imaging system is positive-working, said chromogenic material being effective to react with said developer material in said unexposed areas.

3. Imaging media according to Claim 1 or Claim 2, wherein said capsule is a microcapsule having a discrete capsule wall.

4. Imaging media according to any preceding claim, wherein said chromogenic material is encapsulated with said photosensitive composition.



5. Imaging media according to any preceding claim, wherein said photosensitive composition comprises a radiation curable material.

6. Imaging media according to Claim 5, wherein said photosensitive composition comprises a photoinitiator.

7. Imaging media according to Claim 4, wherein said chromogenic material is a substantially colourless electron donating compound.

8. Imaging media according to Claim 7, wherein said developer material is an electron accepting compound.

9. Imaging media according to Claim 8, wherein said electron accepting compound is a colour developer.

5 10. Imaging media according to Claim 8, wherein said electron accepting compound is selected from clay minerals, organic acids, acid polymers, metal salts of phenol-formaldehyde novolak resins, zinc carbonate and combinations thereof.

11. Imaging media according to any preceding claim, wherein said photosensitive composition is sensitive to ultraviolet, infrared, X-ray, electron beam, or visible radiation.

12. Imaging media according to Claim 11, wherein said photosensitive composition is sensitive to blue light having a wavelength in the range from 380 to 480 nm.

5 13. Imaging media according to Claim 11, and further comprising means for temporarily shielding said coating composition from ambient radiation such that said media can be handled in room light for at least a short period of time without interfering with the image-forming capability of said system.

14. Imaging media according to Claim 13, wherein said shielding means is contained in the wall of said rupturable capsule.



15. Imaging media according to Claim 13, wherein said shielding means includes a yellow fugitive dye which absorbs light at a wavelength in the region of 380 to 480 nm.
16. Imaging media according to Claim 15, wherein said yellow fugitive dye is contained in a layer overcoating said coating composition.
17. Imaging media according to any preceding claim, wherein said chromogenic material is an oil soluble colour former.
18. Imaging media according to Claim 17, wherein said colour former is a colourless electron donating compound.
19. Imaging media according to Claim 18, wherein said colourless electron donating compound is a compound having a lactone, a lactam, a sultone, a spiropyran, an ester or an amido structure.
20. Imaging media according to Claim 3 or any claim appendent thereto, wherein said capsule wall is formed by a hydrophilic material which transmits said actinic radiation.
21. Imaging media according to Claim 20, wherein said capsule wall is formed by a material selected from gelatin, polyamide, polyvinyl alcohol, resorcinol-formaldehyde resin, polyisocyanate resin, urea-formaldehyde resin, urea-resorcinol-formaldehyde resin, melamine-formaldehyde resin, and hydroxypropyl cellulose, and combinations thereof.
- 5 22. Imaging media according to Claim 5, wherein said radiation curable material is a material polymerizable by free radical addition polymerization or ionic polymerization.



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23. Imaging media according to Claim 22, wherein said radiation curable material is an ethylenically unsaturated compound.

24. Imaging media according to Claim 23, wherein said radiation curable material contains two or more ethylenically unsaturated terminal groups.

5 25. A transfer imaging process comprising: image-wise exposing to actinic radiation an imaging sheet comprising a first substrate having on one surface thereof a coating composition including a chromogenic material and a photosensitive composition adapted to undergo a viscosity change upon exposure to such radiation, at least said photosensitive composition being encapsulated in rupturable capsules, to produce exposed and unexposed areas; subjecting said capsules to a uniform rupturing force; and transferring
10 said chromogenic material from the exposed or unexposed areas of said imaging sheet to a developer sheet comprising a second substrate having a developer material on one surface thereof such that there is a patterned reaction between said developer material and said chromogenic
15 material which produces an image.

26. A process according to Claim 25, wherein said rupturable capsule is a microcapsule defined by a discrete capsule wall.

5 27. A process according to Claim 26, wherein said photosensitive composition comprises a radiation curable material, and wherein said capsules are ruptured in and said chromogenic material is transferred from said unexposed areas.

28. A process according to Claim 27, wherein said photosensitive composition comprises a material which is photo-decomposable, and wherein said capsules are ruptured in and said chromogenic material is transferred from said
5 exposed areas.



29. A process according to any of Claims 25 to 28, wherein said image-wise exposing is by transmission imaging.

5 30. A process according to any of Claims 25 to 28, wherein said image-wise exposing is by reflection imaging.

31. A process according to any of Claims 25 to 30, wherein said capsules are ruptured by applying pressure to said imaging sheet and said developer sheet, said sheets being superposed with said developer material facing on said coating composition.

32. A process according to any of Claims 25 to 31, wherein said actinic radiation is ultraviolet radiation, infrared radiation, visible light, X-ray, or ion beam irradiation.

15 33. A process according to Claim 32, wherein said actinic radiation is blue light having a wavelength in the range 380 to 480 nm.

34. An imaging sheet useful in forming images by exposure-controlled, image-wise reaction of a chromogenic material and a developer, said sheet comprising: a support having, on one surface thereof, a layer of microcapsules having discrete capsule walls which encapsulate an internal phase including a photosensitive composition which undergoes a change in viscosity, upon exposure to actinic radiation, sufficient to control the release of said internal phase from said microcapsules; and a chromogenic material associated with said microcapsules such that, upon image-wise exposing said layer of microcapsules to said actinic radiation and subjecting said layer of microcapsules to a uniform rupturing force, said chromogenic material image-wise becomes available for forming an image.

35. An imaging sheet according to Claim 34, wherein said chromogenic material is present in said internal phase with said photosensitive composition.

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* C L H S *

36. An imaging sheet according to Claims 34 or 35, wherein said chromogenic material is a substantially colourless electron donating compound.

37. An imaging sheet according to Claim 36, wherein said substantially colourless electron donating compound is a compound having a lactone, a lactam, a sultone, a spiropyran, an ester, or an amido structure.

38. An imaging sheet according to any of Claims 34 to 37, wherein said photosensitive composition is sensitive to ultraviolet and/or visible radiation.

39. An imaging sheet according to any of Claims 34 to 38, wherein said photosensitive composition includes an ethylenically unsaturated compound.

40. An imaging sheet according to any of Claims 34 to 39, wherein said photosensitive composition includes a photoinitiator.

41. An imaging sheet according to any of Claims 34 to 40, wherein said discrete capsule wall is formed from a urea-formaldehyde resin or a melamine-formaldehyde resin.

42. A transfer imaging process comprising image-wise exposing to actinic radiation an imaging sheet according to any of Claims 34 to 41, whereby to expose to said radiation said layer of microcapsules so that said photosensitive composition undergoes the said change in viscosity; assembling said imaging sheet with a cooperating developer sheet; and subjecting said assembly to a uniform rupturing force.

43. For use in a transfer imaging system, imaging media substantially as hereinbefore described with reference to the accompanying drawings.

44. An imaging sheet useful in forming images by exposure-controlled, image-wise reaction of a chromogenic material and a developer, the said sheet being substantially as hereinbefore described with reference to the accompanying drawings.

