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IMAGE-FORMING COMPOSITIONS INCLUDING AN AZIDE AND TRANSITION METAL COMPLEXES OF TRIORGANOPHOSPHINES

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ABSTRACT OF THE DISCLOSURE

Photographic image-forming compositions that include (1) an organoazide such as an aryl azide and (2) a labile phosphine complex that, on chemical treatment, can liberate a triorganophosphine, e.g. a triarylphosphine, which can form a radiation-sensitive complex with the azide, can be activated by chemical treatment and thereafter imagewise exposed to activating rays to yield a species that can react with a dye-forming coupler to form an image-dye. These compositions are substantially light-insensitive prior to chemical treatment which activates the composition by liberating triorganophosphine, whereupon the phosphine-azide complex is formed in situ, and shelf life is desirably extended. When these compositions are carried on a support, image-forming elements are presented. Once the azide-phosphine complex is present in an activated composition, imagewise exposure to activating rays and subsequent or concomitant treatment with a dye-forming coupler or the like produces a negative image (i.e., one corresponding to exposed regions). If a leuco compound, dye forming coupler, etc., is also included in the composition, then a visible image generally forms on exposure. After production of the image, it can be stabilized by overall heating. In certain cases, heat fixation also produces intensification of a low density or substantially latent image. If desired, positive images can be formed by thermophotographic means. Once the phosphine-azide complex is formed, imagewise exposure to heat densitizes the complex in heated regions and a subsequent overall exposure to activating rays produces either a visible or an intensifiable photographic image. No heat fixation is required, but image intensification by heat may be accomplished if desired. Multi-color images can be prepared when an included coupler is of the type that will react with the azide when suitably exposed. Lithographic printing surfaces can be prepared when a hydrophilic, polymeric azide is used to form the complex or when hydrophilic polymeric couplers are used to form the image dye.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to photography and particularly to new image-forming compositions and elements that can be negative-working and positive-working, as well as to processes that are useful in producing stable images in the substantial absence of moisture and of noxious developing agents.

Description of the prior art

Photographic compositions designed for dry or substantially dry processing are known. Widely used such formulations are two-component diazotype compositions that include a diazonium salt and a coupler that, under alkaline conditions, can react with the diazonium salt to form an azo dye. A broad description of diazo-type elements appears in Kosar, Light-sensitive Systems, John Wiley & Sons, Inc., New York (1965), especially at Chapter 6. On exposure to light-sensitive diazonium salt is destroyed and subsequent treatment with an alkaline developer like ammonia promotes a dye-forming reaction in unexposed areas to produce a positive reproduction of an original line transparency or the like. Diazotype compositions, however, have certain disadvantages in that they tend to suffer background printup on storage. This tendency can be diminished by inclusion of an acidic pre-coupling inhibitor, but the addition of such a material slows development rate since the inhibitor must be neutralized before coupling can occur. Additionally, well known developing agents like ammonia are generally toxic and/or noxious.

Another type of diazotype photographic element uses diazosulfonates which, on exposure to light, form diazonium salts that can couple in the normal fashion. These elements are negative-working since they produce image dye in regions of exposure. However, they suffer the disadvantage that image stabilization usually requires a washout step to remove remaining sensitive components.

Still another well-known type of negative-working photographic element uses organic azides and dye precursors. See, for example, U.S. Pat. 3,062,650. Such elements yield a printout image directly on exposure. However, an inconvenient washout step to remove unreacted components is generally necessary to stabilize background areas against subsequent printout.

The desirability of providing new photographic elements that do not use silver as the light-sensitive agent (it being in short supply) and that produce stable images without substantial moisture, stabilization washes, or noxious or toxic developing agent is widely acknowledged. Additionally, widespread contemporary apprehension relative to organic pollutants and their effect on the environment has stimulated activity designed to inhibit the flow of contaminants into the environment. Such goals are also of deep concern to those skilled in the photographic arts.

Accordingly, it is an object of this invention to provide new image-forming compositions.

Still another object of the present invention is to provide new image-forming compositions that include an organoazide and a triorganophosphine precursor from which triorganophosphine can be liberated by chemical treatment.

Yet an additional object of the instant invention is to provide novel image-forming elements that include the present image-forming compositions.

Another object of this invention is to provide new photographic process for preparing stable images.

An additional object of this invention is to provide novel photographic processes for preparing stable images by means of light and heat in the substantial absence of moisture.

Still another object of this invention is to provide new thermophotographic processes for preparing stable images.

STATEMENT OF THE INVENTION

The objects of this invention are accomplished with radiation-sensitive phosphine-azide complexes, they being complexes of a triorganophosphine with an oragnoazide. The present invention includes novel image-forming compositions containing the azide and transition metal complexes which are triorganophosphine precursors from which the phosphine can be released conveniently by chemical treatment. The transition metal complexes described herein are particularly advantageous since they yield two moles of triorganophosphine per mole of metal complex. After liberation of the phosphine, the radiation-sensitive complex forms spontaneously in situ to activate the composition. Optionally, such image-forming compositions can also include a dye precursor, e.g. a dye-forming coupler. Using the present transition metal complexes also results in extending the absorption of the image dye to longer wavelengths presumably due to interaction between the dye molecule and the transition metal.

The activated image-forming compositions yield photographic images directly on exposure to activating rays. No external processing agents are required. The background regions can then be stabilized against printup by simple heat fixation. In certain cases, this heating step also produces an intensification of the image. As used herein, the term photographic image refers to visible and latent photographic images. Additionally, if a particular image-forming composition does not contain a coupler, exposure is desirably followed by treatment with a coupler solution. If desired, positive images can be prepared by thermophotographic means, using an imagewise thermal exposure followed by an overall exposure to activating radiation (i.e. radiation to which the phosphine-azide complex is sensitive). Heat fixation is not required, but heating can be used to effect image intensitivation if desired. Additionally, where the azide of the complex is a hydrophilic polymeric azide or where the coupler is a hydrophilic polymeric coupler, lithographic surfaces can be prepared.

DESCRIPTION OF PREFERRED EMBODIMENT(S)

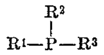
In accordance with the present invention, there are presented new image-forming compositions including an organoazide and a triorganophosphine precursor which on chemical treatment liberates a triorganophosphine that can form a radiation-sensitive complex with the azide in situ. The precursors used in the subject invention include transition metal complexes of the triorganophosphine, which complexes are stable at neutral pH values and can liberate 2 phosphine molecules per molecule of the transition metal complex. Desirable metal complexes include those having the formula

$$(Z)_2MX_2$$

wherein Z represents a triorganophosphine moiety, M represents a transition metal that is one of either cobalt, nickel, palladium or platinum and X represents a monovalent anion. As used herein, the term radiation sensitive described sensitivity to electromagnetic rays including X-rays, ultraviolet rays, visible light and the like. The phosphine-azide complexes described herein are chemical complexes that, on exposure to activating rays, yield a species that can react with a coupler to form an image dye.

A wide variety of triorganophosphines (i.e. phosphines having three organic chemical substituent groups) are useful in forming radiation-sensitive complexes of the present type. In general, any triorganophosphine that will form such a complex with an organoazide is useful. Determination of such utility can be accomplished conveniently by simple screening. For example, any triorganophosphine can be codissolved with an organoazide of the types recited elsewhere herein (e.g. p-morpholinophenylazide and/or 4-azidobenzenesulfonamide) usually in equivalent molar quantities or with a slight excess of phosphine and with a β-naphthol dye-forming coupler, e.g. 2-naphthol, 2,3-naphthalenediol, etc., to form a solution which can be coated onto a support, dried in a layer and thereafter exposed to activating radiation (i.e. rays to which the complex is sensitive) to form a photographic image which is visible or is intensifiable to a visible image. If this image, when visible, is different in color and/or intensity from the photographic image that is formed when a similar preparation, but containing only the azide and coupler (i.e. without the phosphine) is dissolved, coated, dried and exposed in the same manner, then the particular triorganophosphine is useful herein. Although, dye formation can occur on exposure, as mentioned elsewhere herein, subsequent overall heating may be necessary to register or intensify a substantially latent image for convenient viewing.

Of the wide range of triorganophosphines that are useful herein, particularly useful materials include those having the formula



$$R^1-\overset{\displaystyle R^2}{\overset{|}{P}}-R^3$$

wherein:

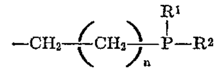
each of R^1, R^2 and R^3 independently represents one of either an alkyl group and preferably lower alkyl, an alkoxy group and preferably lower alkoxy, an aryl group and preferably phenyl, or an amino group having the formula

$$-N-(R^4)_2$$

wherein:

R^4 represents one of either an alkyl group or an aryl group,

and R^3 additionally represents a group having the formula



$$-CH_2-\left(CH_2\right)_n-\overset{\displaystyle R^1}{\overset{|}{P}}-R^2$$

wherein:

n represents a positive integer having a value of from 1 to about 18 and each of R^1 and R^2 is as previously defined.

As used herein the term alkyl group includes substituted or unsubstituted, straight and branched chain alkyl groups having from 1 to about 8 carbon atoms in the aliphatic chain used as a basis for establishing the nomenclature for such group. Representative alkyl groups include, for example methyl groups, ethyl groups, 2-chloroethyl groups, n-propyl groups, isopropyl groups, n-butyl groups, tert-butyl groups, pentyl groups, hexyl groups, heptyl groups, n-octyl groups, tert-octyl groups, etc. The term alkoxy groups as herein defined, includes alkoxy groups the alkyl moiety of which has from 1 to about 8 carbon atoms and corresponds to the alkyl groups recited immediately hereinabove. The term lower alkyl group or lower alkoxy groups refers to such alkyl or alkoxy groups having from 1 to 4 carbon atoms in the aliphatic chain used as a basis for establishing the chemical nomenclature for any such group.

Aryl group, as herein defined, includes unsubstituted and substituted mono and polycyclic aromatized carbocyclic groups having from 6 to 14 atoms in the nucleus, e.g., phenyl, 4-chlorophenyl, 3-methylphenyl, naphthyl, anthryl, etc., with phenyl being preferred.

Especially desirable triorganophosphine compounds include

triphenylphosphine
tris(3-methylphenyl)phosphine
P,P-diphenyl-P-methylphosphine
tris(4-methylphenyl)phosphine
trimethylphosphine
P,P-diphenyl-P-ethoxyphosphine
P,P-dimethyl-P-phenylphosphine
P-pentafluorophenyl-P,P-diphenylphosphine
butyldimethoxyphosphine
tris(n-butyl)phosphine
tris(dimethylamino)phosphine
tris(n-octyl)phosphine
tris(diphenylamino)phosphine
P-methyl-P,P-diphenylphosphine
tris(4-chlorophenyl)phosphine
tris(4-methoxyphenyl)phosphine

triethoxyphosphine
1,2-bis(diphenylphosphino)ethane
1,4-bis(di-n-butylphosphino)butane
1,8-bis(di-4-chlorophenyl)octane

Monovalent anions of the type represented by X include a wide range of acid anions like halide including chloride, bromide and iodide as well as cyanide, thiocyanate, cyanate azide, etc.

According to this invention, at least one triorganophosphine is chemically combined with a transition metal to form a phosphine-metal complex from which triorganophosphine can be liberated by chemical treatment. Such complexes can be prepared conveniently by adding a warm solution of the transition metal salt of an appropriate anion to a boiling saturated solution of the desired triorganophosphine. The complex forms directly and either precipitates on cooling or can be recovered after evaporation of the solvent. Generally, any weakly coordinating solvent like ethanol, 1-butanol, acetic acid or the like is useful for preparations of this type. Ketones can be used, but the reaction products tend to be soluble in ketones so that concentration of the solvent is necessary to isolate the product.

As with the triorganophosphines, that are advantageous in forming the phosphine-azide complexes, a wide range of organoazides are useful. The operability of any particular azide can be established by the convenient procedure outlined hereinabove with respect to the screening of triorganophosphines. In this instance, however, an operator would use a phosphine that is known to operate in the present compositions, elements and processes, e.g. triphenylphosphine.

Desirable organoazides (i.e. organic azides) include a large variety of radiation-sensitive compounds that have been used heretofore in photographic printout compositions of the type that includes the azide and a dye-former that reacts with the azide upon exposure to activating rays to form a dye in exposed regions. Certain such azides include most of the aryl azides, aminoarylazides, and heterocyclyl azides described in U.S. Pat. 3,062,650 and U.S. Pat. 3,282,693. Azides useful as photosensitizers for polymers are also useful herein. Such photosensitizers can be the same as or different from the azides useful in printout materials and they are described in some detail in Kosar, Light-Sensitive Systems, John Wiley & Sons, Inc., New York (1965), especially at pp. 330–336 (including footnotes). Still other descriptions of useful organic azides appear in U.S. Pat. 2,940,853, U.S. Pat. 3,061,435, and U.S. Pat. 3,143,417. With regard to heterocyclyl azides, it is preferred that the azido group is not substituted on the heterocyclic ring at a position ortho to a hetero ring atom. Other advantageous azides include polymeric azides such as those described in U.S. Pat. 3,002,003 and U.S. Pat. 3,096,311.

Particularly useful organoazides include such materials as the following:

4-azidobenzenesulfonamide
ethyl 4-azidobenzoate
ethyl 2-azidobenzoate
glyceryl 4-azidobenzoate
3-azidobenzoic acid
4-azidobenzenearsonic acid
4-azidobenzamide
4-azido-N-methylacetanilide
4-azidobenzophenone
2-(4-azidophenyl)-6-methylbenzothiazole
3-azido-α,α,α-trifluoromethylbenzene
3-azido-4-chloro-α,α,α-trifluoromethylbenzene
4-azidobenzonitrile
3-hydroxypropyl 4-azidobenzoate
phenyl 4-azidobenzoate
2-(3-hydroxynaphthyl)4-azidobenzoate
N-methyl-N-phenyl-4-azidobenzamide
N-(2,6-dimethylphenyl)-4-azidobenzamide
4-azidobenzopiperidide
N-(1-naphthyl)-4-azidobenzamide
N-(pentafluorophenyl)-4-azidobenzamide
phenyl 4-azidophenylsulfonate
2,4,6-trichlorophenyl 4-azidophenylsulfonate
N-(4-azidophenylsulfonyl)phthalimide
N-phenyl-N-methyl-4-azidophenylsulfonamide
N-(4-azidophenylsulfonyl)-piperidine
N-(2,6-dimethylphenyl)-4-azidophenylsulfonamide
N-(4-azidophenylsulfonyl)succinimide
N-(6-azido-2-naphthylsulfonyl)piperidine
N-methyl-N-phenyl-2-azidonaphthalene-6-sulfonamide
phenyl 6-azidonaphthalene-2-sulfonate
N-(6-azido-2-naphthylsulfonyl)succinimide
N-(6-azido-2-naphthylsulfonyl)phthalimide
1-azido-2,4,6-trichlorobenzene
2-azido-3-nitrobenzene
4-azidobenzoic acid
3-azidophthalic anhydride
4-azidocinnamic acid
3-azidobenzenesulfonamide
2-azido-9-fluorenone
1-azido-5-methoxynaphthalene
2-(4-azidophenyl)-5-phenyloxazole
4′-azido-4-chlorochalcone
2-(4-azidophenyl)benzoxazole
1-azidonaphthalene
2-phenyl-5-(4-azidophenyl)oxazole
2-(4-azidobenzylidene-3,4-dihydro-2H-1-naphthone
4-azidochalcone
N-(4-azidobenzylidene)-4-chloroaniline
2-(4-azidophenyl)benzimidazole
1-azido-2,4-dichlorobenzene
2-(3-azidophenyl)-5-phenyloxazole
4,4′-diazido-3,3′-dimethoxybiphenyl
2-azidophenetole
4-azidophenetole
trimethylene bis(4-azidobenzoate)
bis(4-azidophenyl)disulfide
4-azido-3,5-diethoxybenzanilide
N-methyl-4-azidoacetanilide
4-azidophenyl sulfide
4-azido-3-nitroanisole
N-(3-azidophenylsulfonyl)succinimide
4-azido-3,5-dimethoxyphenylmorpholine
3-azidoquinoline
2-azidocarbazole
2-azidobenzoic acid
4-azidophenoxyacetic acid
N-methyl-N-octadecyl-4-azidoaniline
1-azido-4-bromonaphthalene
bis(4-azidophenyl)ether
4-azidoazobenzene
N-(4-azidophenyl)-N-methylmorpholinium
  tetrafluoroborate
4′-azido-4-toluenesulfonanilide
4-azidobenzenesulfonic acid
1-azido-4-methoxynaphthalene
4-azidostyryl 1-naphthyl ketone
3-(4-azidophenyl)coumarin
1,2,3,4,5,6-hexa(4-azidobenzoxy)hexane
4,4′-diazidodibenzalacetone
1-azido-2,4,6-tribromobenzene
4-azidoacetanilide
2-azidodiphenyl ether
2,5-bis(4-azidophenyl)oxazole
2-(4-azidophenethyl)-5-phenyloxazole
2-(4-azidophenethyl)benzoxazole
4,4′-diazido-2,2′-stilbenedi(N,N-dibutylsulfonamide)
2,6-di(4-azidobenzal)-4-methylcyclohexanone
poly(vinyl acetate-co-4-azidobenzoate)
1-azido-3-cyano-4-methoxybenzene
1-azido-3-cyano-4-morpholinobenzene
N-(4-azido-2-cyanophenyl)piperidine
N-butyl-4-azido-2-cyanoaniline

N,N-diethyl-4-azido-2-cyanoaniline
N,N-dibutyl-4-azido-2-cyanoaniline
N-hydroxyethyl-4-azido-2-cyanoaniline
N,N-diethyl-4-azido-2-chloroaniline
4-azidodiphenylamine
4-azido-2-cyanodiphenylamine
4-azido-2-cyano-4′-methoxydiphenylamine
4-azido 2-cyano-4′-dimethylaminodiphenylamine
1-azido-2-methoxy-4-morpholinobenzene
1-azido-3-methoxy-4-morpholinobenzene
N-methyl-4-(4-azidophenyl)-2,6-diphenylpyridinium perchlorate
N-methyl-4-(4 azidostyryl)-2,6-diphenylpyridinium perchlorate, and
2,5-bis(4-azidophenyl) oxadiazole

The image-forming compositions can, if desired, contain a polymeric carrier vehicle. Advantageous carriers include film-forming, substantially hydrophobic polymers that can be coated using solvents of low polarity, but which are sufficiently permeable to bases including gasses and liquids so as not to restrain either convenient phosphine release from a precursor or imagedye development. Especially useful such carrier or binder vehicles include polymers like, for example, cellulosic compounds such as ethyl cellulose, butyl cellulose, as well as cellulose esters like cellulose acetate, cellulose triacetate, cellulose butyrate, cellulose acetate butyrate, etc.; vinyl polymers such poly(vinyl acetate), poly(vinylidene chloride), poly(vinyl butyral), copolymers of vinyl chloride and vinyl acetate, polystyrenes, poly(methyl methacrylates) homopolymers or copolymers of acrylamides, copolymers of alkylacrylates and acrylic acid, etc., such as

poly(n-isopropylacrylamide)
poly(diacetone acrylamide)
copoly(acrylamide/N-isopropylacrylamide)
copoly(diacetone acrylamide/N-isopropylacrylamide)
copoly(methacrylamide/N-isopropylacrylamide)
2,3-naphthalene diol,
2-hydroxy-3-naphthnilide
2-hydroxy-2′-methyl-3-naphthanilide
copoly(N-isopropylacrylamide/1-vinyl-2-pyrrolidone)
copoly(methyl methacrylate/methacrylic acid)
copoly(butyl acrylate/acrylic acid)

as well as additional polymers such as polyphenylene oxides, terpolymers of ethylene glycol, isophthalic acid and terephthalic acid, terpolymers of p-cyclohexane dicarboxylic acid, isophthalic acid and cyclohexylenebismethanol, copolymers of p-cyclohexanedicarboxylic acid and 2,2,4,4-tetramethylcyclobutane-1,3-diol, and additional polymers such as, for example, the condensation product of epichlorohydrin and bisphenol-A.

The photographic or image-forming compositions of this invention can also include a dye-forming coupler which, it is theorized, reacts with a photolytic product of the phosphine-azide complex to form a dye in exposed regions. If used, the coupler is usually present in a molar amount substantially equivalent to the amount of phosphine-azide complex, or in a slight excess, e.g. 5–10% molar, to insure maximum dye formations.

Couplers that are advantageous herein include couplers of the type used in two-component diazotype compositions. Such couplers are described in the literature, for example in Kosar Light-Sensitive Systems, John Wiley & Sons, New York (1965), especially at pages 220–240. Especially desirable couplers are recited in U.S. Patent 3,573,052, especially at column 6, line 17 to column 7, line 20. Representative couplers of this type include

2,3-naphthalenediol
2-hydroxy-3-naphthanilide
2-hydroxy-2′-methyl-3-naphthanilide
2-hydroxy-2′,4′-dimethoxy-5′-chloro-3-naphthanilide
2-hydroxy-2′,5′-dimethoxy-4′-chloro-3-naphthanilide
2-hydroxy-1′-naphthyl-3-naphthanilide
2-hydroxy-2′-naphthyl-3-naphthanilide
2-hydroxy-4′-chloro-3-naphthanilide
2-hydroxy-3-naphthanilide
2-hydroxy-2′,5′-dimethoxy-3-naphthanilide
2-hydroxy-2′,4′-dimethyl-3-naphthanilide
1-hydroxy-2-naphthamide
N-methyl-1-hydroxy-2-naphthamide
N-butyl-1-hydroxy-2-naphthamide
N-octadecyl-1-hydroxy-2-naphthamide
N-phenyl-1-hydroxy-2-naphthamide
N-methyl-N-phenyl-1-hydroxy-2-naphthamide
N-(2-tetradecyloxyphenyl)-1-hydroxy-2-naphthamide
N-[4-(2,4-di-tert-amylphenoxy)butyl]-1-hydroxy-2-naphthamide
1-hydroxy-2-naphthopiperidide
N-(3,5-dicarboxyphenyl)-N-ethyl-1-hydroxy-2-naphthamide
N,N-dibenzyl-1-hydroxy-2-naphthamide
N-(2-chlorophenyl)-1-hydroxy-2-naphthamide
N-(4-methoxyphenyl)-1-hydroxy-2-naphthamide
1-hydroxy-2-naphthopiperizide
1,3-bis(1-hydroxy-2-naphthamidobenzene)
2-acetamido-5-methylphenol
2-acetamido-5-pentadecylphenol
2-butyramido-5-methylphenol
2-(2,4-di-tert-amylphenoxyacetamido)-5-methylphenol
2-benzamido-5-methylphenol

Still other useful couplers include those which contain a reactive methylene or methine group, such as those described in U.S. Pat. 3,062,650, especially at column 4, line 8 to column 4, line 27. This type of coupler, e.g. 3-methyl-1-phenyl-5-pyrazolone, is particularly useful when the organoazide has an amino group substituted on the organic residue, as in the case of an amino-arylazide. Preferably, such aminoarylazides are 4-amino-1-azidobenzene compounds or derivatives.

The image-forming compositions of this invention are conveniently prepared, for example, by codissolving at least one of the phosphine-transition metal complex triorganophosphine precursors and at least one organoazide. Desirable solvents include a wide range of organic media such as methyl ethyl ketone, methylene chloride, acetone, lower alkanols, dichloroethane, tetrahydrofuran, toluene, etc., either alone or in combination. In the solution, the ratio of phosphine to azide can be varied widely, but it is preferred that the phosphine be included in a slight molar excess, e.g. from 5–10%, to insure that substantially all azide is complexed. Without substantially complete azide complexing, background stabilization is impaired.

Image-forming elements utilizing the compositions of this invention are conveniently prepared by coating such compositions onto a support material. Advantageous support materials include conventional photographic film base materials like cellulose esters such as cellulose acetate, cellulose triacetate, cellulose acetate butyrate, etc.; poly-α-olefins typically having from 2 to 10 carbon atoms like polyethylene, polypropylene, and polystyrene; polyesters such as polyesters poly(ethylene terephthalate); polycarbonates as well as metals such as zinc and aluminum and paper including polyethylene and polypropylene coated papers. Other support materials that are suitably used herein are known in the art.

Coating is typically by solvent coating means, since it offers the potential for rapid, convenient, continuous operation. Coating is effected by first dissolving components of the photographic or image-forming composition in a suitable solvent, such as those described herein, along with a matrix polymer if desired. Exemplary matrix polymers are described hereinabove. The coating solution conventionally contains from about 5 to about 20 weight percent solids, and preferably from about 8 to about 15 percent sloids. In that solution, if a matrix polymer is utilized, the image-forming components are typically included in an amount of from about 20 to about 50 parts by weight per 100 parts of polymeric binder, with concentrations in the range of from about 25 to about 45 parts per 100 parts of matrix polymer being preferred. Wider variations are possible where desired, but the above-mentioned ratios are typical for most conventional preparations. After coating by such means as immersion, whirler coating, brushing, doctor blade coating, hopper coating or the like, typically at a wet thickness of from about .001 inches to about .020 inches, the coated material is dried to prepare a composite image-forming element of this invention.

The subject image-forming compositions and elements are activated to yield a triorganophosphine and form the phosphineazide complex by chemical treatment including treatment with base. Generally, any of the bases useful in initiating coupling in diazotype reproduction media, e.g. ammonia, organic amines and other organic nitrogen bases, are suitable herein to release the phosphine from its precursor. A range of such bases is described in Kosar, cited hereinabove, as well as in the patent literature, for example U.S. Pat. 3,578,452, Canadian Pat. 772,109, etc. Other Lewis bases, including water, are also useful for releasing phosphine from the phosphine-transition metal complexes. Treatment can be accomplished by immersion in a solution of the base, by fuming with vapors of the base, etc.

It is noted that the radiation-sensitivity of the phosphine-azide complexes described herein should not be equated to the known sensitivity of aryl azides such as those used in vesicular photography or other photographic systems. Such compounds are known to exhibit low photoreactivity, whereas the radiation-sensitive complexes of this invention exhibit a relative photographic speed about ten times that of a comparable non-complexed azide.

When the sensitive phosphine-azide complex of activated image-forming composition or element is exposed to activating rays, and if a coupler is included in the composition or element that is so exposed, an image forms in exposed regions. Usually, this is a readily visible dye image which can vary in optical density depending on the particular formulation. In certain cases, the image may be a latent image that is not easily visible or is not visible at all. It is theorized that the dye-forming reaction is promoted by the imagewise release of hydroxyl ions and ammonium hydroxide on exposure of the phosphine-azide complex. It is theorized further that this liberation is due to reaction of a phosphinimine anion that is formed on exposure with water that is inherently present in the composition or element.

The selection of appropriate exposing rays will depend on the spectral response for the particular phosphine-azide complex. Characterization of appropriate exposing rays can be readily determined by preparation of wedge spectrograms for the phosphine-azide complex in question. Generally, however, the region of spectral response will include ultraviolet and other actinic rays so that exposure by means of a mercury arc lamp, which is rich in UV rays, or a similar exposure source is appropriate. Numerous diazo copiers and other commercially available photocopying apparatus incorporate exposure stations which include radiation sources emitting in the UV. As a general rule these are quite satisfactory for exposing compositions and elements of this invention.

Subsequent to an image-defining exposure, the composition or element is preferably heated to a temperature sufficient to stabilize non-image regions against printup (i.e. to stabilize the photographic image). It is theorized that on heating, the phosphine-azide complex rearranges to form a stable, substantially colorless phosphinimine. Where the image after exposure either is of low optical density or is a latent image, the heat stabilization treatment simultaneously effects an image intensification such that it is readily viewable by eye. Stabilization heating is generally accomplished at temperatures of at least about 60° C., with temperatures up to about 130° C. being useful for most situations. It will be recognized that the support or any components should not be deleteriously affected by heating, but higher temperatures require shorter fixation times. The duration of the heat fixing step is variable, depending on factors like fixation temperature, etc. Usually, times of from about 5 seconds to 2 minutes are sufficient. Heating can be carried out conveniently, such as by contact with a suitably heated surface, insertion into a heated chamber or the like.

In cases where no coupler is present in the composition or element, exposure of the phosphine-azide complex is desirably followed by treatment of the composition or element with one or more couplers of the types described herein to promote image formation. A dense dye image will then form spontaneously, or an intensifiable image of the type noted herein will result. As an example of useful treatment methods, a coupler solution can be contacted against the composition or element by such means as immersing the composition or element therein, swabbing or spraying the solution over the composition or element, or by a similar means. After such treatment, the composition or element can be washed and/or dried or drying can be accomplished simultaneously with heat stabilization.

In one embodiment of the invention, a base can be included in an image-forming composition or element, in lieu of the phosphine precursor. Useful bases include, for example, N,N,N',N'-tetramethylethylene diamine, as well as a wide variety of other organic amines and nitrogen containing organic compounds. Activation to form the phosphine-azide complex is then accomplished by treatment with a phosphine precursor such as those described herein. Treatment is easily carried out by using a solution of the precursor according to methods like those discussed previously with reference to coupler treatment.

In yet another embodiment of this invention, an image-forming composition that includes a phosphine precursor, a radiation-sensitive azide of the type described in U.S. Pat. 3,062,650 wherein an amino group is present thereon, e.g. a p-disubstituted aminophenylazide, and a coupler that is reactive with such an azide, multiple images such as two-color dye images can be prepared as follows: The composition is given a first imagewise exposure with activating radiation for the azide, i.e., radiation to which the azide is sensitive. A visible dye image forms on exposure. The composition is then activated by chemical treatment such as by contact with base (e.g. by fuming with ammonia vapor) to release triorganophosphine from the precursor and form the phosphine-azide complex and thereafter is given a second imagewise exposure with activating radiation for the complex, i.e., radiation to which the complex is sensitive. Since the complex is a different chemical species from the azide, it can have a different spectral absorption envelope. Accordingly, each exposure may require the use of a different radiation source, although ultraviolet rays will generally suffice. On the second exposure, an image forms in exposed regions. It will be appreciated that this second dye image may, in certain cases, be intensifiable as discussed herein. This second image, when visible, is preferably of a different color from the image formed on the first exposure. Heat stabilization is then accomplished, and this also effects image intensification of the second dye image if it is of a low optical density. If the concentration of azide is sufficient, and the first exposure is not so intense that all azide is photolyzed in regions of exposure, then remaining azide in such regions will complex with the phosphine on activation with base and the second exposure will produce a second dye in areas that are common to each exposure.

As discussed previously, the compositions and elements of this invention are useful in preparing negative images, i.e. images corresponding to regions of irradiation. They can also be processed by thermophotographic techniques to prepare positive images, i.e. images corresponding to non-irradiated regions. A photographic composition or element, or an image-forming composition or element which has been activated to form a phosphine-azide complex therein, is given an imagewise thermal exposure to stabilize such regions against printup. Thereafter, it is overall exposed to activating radiation for the complex to prepare a visible or intensifiable dye image. If no coupler is present in the element, image development will also include treatment with a coupler solution as described elsewhere herein.

In still another embodiment of this invention, lithographic surfaces are prepared in exposed regions when the azide used is a hydrophilic polymeric azide like those described in U.S. Pat. 3,002,003 and other references cited therein. Lithographic surfaces can also be prepared when the coupler is a hydrophilic, polymeric coupler such as a polymeric pyrazolone. Desirably, the azide used with the polymeric coupler is a bis azide. After exposure and subsequent process steps as described herein, the developed surface is wet with water which is accepted in unexposed areas. Greasy printing inks are transferable from exposed regions which comprise the printing surface.

The following examples are included for a further understanding of the invention.

EXAMPLE 1

Phosphine-transition metal complexes are prepared by adding a warm (40° C.) solution of the metal salt to a boiling saturated solution of the phosphine. Upon addition, the complex forms and is thereafter recovered by either cooling and/or concentrating the solution to effect precipitation. The complexes prepared are indicated below in tabular form.

TABLE

Formulation	Solvent	Color	M.P., ° C.
$Co(\phi_3P)_2Cl_2$	Acetone	Blue	
$Co(\phi_3P)_2Cl_2$	Ethanol	do	246-250 [1] 247-251
$Co(\phi_3P)_2Br_2$	Acetone	Blue-green	235-242 234-239
$Co[(n\text{-}C_8H_{17})_3P]_2Cl_2$	[2]	Blue	Oil.
$Co[(p\text{-}CH_3OC_6H_4)_3P]_2Br_2$	Ethanol	Bright green	195-198
$Co[(p\text{-}CH_3C_6H_4)_3P]_2Br_2$	do	Green	255-260 254-257
$Co[(m\text{-}CH_3C_6H_4)_3P]_2Cl_2$	do	Bright blue	208-210
$Co[(m\text{-}CH_3C_6H_4)_2P]_2Br_2$	do	Bright green	203-206 206-208
$Co[(p\text{-}CH_3C_6H_4)_3P]_2Cl_2$	do	Blue	208-212
$Co[(p\text{-}CH_3C_6H_4)_3P]_2Cl_2$	do	do	213-218
$Co(\phi_2PC_2H_5)_2Cl_2$	do	do	178-180
$Co(\phi_2PCH_3)_2Cl_2$	do	do	175-179
$Co(\phi_2PC_2H_5)_2Br_2$	do	Light green	198-203 [1] 186-196
$Ni(\phi_3P)_2(SCN)_2$	1-butanol	Red	228-229 217-218
$Ni[(n\text{-}C_4H_9)_3P]_2Cl_2$	Ethanol	Red	43-46 48-49
$Ni[\phi(CH_3)_2P]_2Cl_2$	do	Red	148-150
$Ni[(m\text{-}CH_3C_6H_4)_3P]_2Br_2$	do	Green	191-193 168-171
$Ni[(p\text{-}CH_3OC_6H_4)_3P]_2Cl_2$	do	Dark red	[1] 180-185
$Ni[(m\text{-}CH_3C_6H_4)_3P]_2Cl_2$	do	Red-green	205-211
$Ni[(p\text{-}CH_3C_6H_4)_3P]_2Cl_2$	do	do	[1] 225-235
$Ni(\phi_2PC_2H_5)_2Cl_2$	do	Bright red	145-150 146-151
$Ni(\phi_2PCH_3)_2Cl_2$	do	Orange red	147-151

[1] Dec. [2] Acetone/ethyl acetate/benzene.

NOTE.—As used herein, the symbol ϕ indicates a phenyl group.

EXAMPLE 2

A coating is made from a mixture containing the following components: 0.2 g. $Co(\phi_3P)_2Cl_2$, 0.1 g. p-azidobenzenesulfonamide and 0.1 g. 2,3-naphthalenediol dissolved in 15 cc. 1,2-dichloroethane. This blue solution is then mixed with 15 cc. of 10% cellulose acetate butyrate in 1,2-dichloroethane and the mixture is doctor blade coated at 0.006 inch wet thickness on a poly(ethylene terephthalate) support. After drying, the resultant image-forming element is activated by 5 sec. contact with moist ammonia vapor. Thereafter, imagewise exposure is accomplished on a diazo copier using a multi-tube fluorescent light-source, and the background is stabilized by heating to 110° C. for about 10 seconds.

EXAMPLE 3

A solution of 1-azido-4-(2-benzimidazolyl)benzene (0.05 g.),

$$Ni(\phi_3P)_2Cl_2$$

(0.20 g.) and 4-methoxynaphthol(0.05 g.) is poured onto filter paper and dried. The element is then activated by contact (5 sec.) with moist ammonia vapors and thereafter exposed imagewise to an infrared lamp for 10 seconds through, and in contact with a silver negative image. The entire sheet is then irradiated with UV light to produce a dye image in the thermally unexposed areas.

EXAMPLE 4

A solution of p-morpholinophenylazide (0.15 g.), a coupler, 2,4-dichloro-6-(2,4-dipentylphenoxyacetamido)-3-methylphenol (0.2 g.) and

$$Co(m\text{-}CH_3C_6H_4)_3P_2Cl_2$$

(0.8 g.) is prepared in 15 ml. of acetone. This is added to 15 ml. of a 10 percent solution of cellulose acetate butyrate in dichloroethane and the mixture is doctor blade coated on poly(ethylene therephthalate) film support at a wet thickness of 0.006 inch. The resulting image-forming element is first exposed on a diazo copier using a mercury arc source to form a dye image in exposed areas, The element is then contacted with moist ammonia vapor at 50° C. for 10 seconds to liberate phosphine from the phosphine-transition metal complex precursor, and re-exposed in the diazo copier, but at only one-third the prior exposure, to produce a different color dye imge in the newly exposed areas. The background regions are stabilized by heating to 110° C. for 5 seconds.

Results similar to those in Examples 1 through 4 are obtained by substituting equivalent concentrations of other azides and/or other transition metal complexes described herein. Other useful concentrations and procedures can be determined by one skilled in the art using well established techniques.

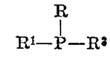
The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

There is claimed:

1. In an image forming composition in admixture comprising a radiation-sensitive aryl or heterocyclyl organoazide and a triorganophosphine precursor which, on treatment with base yields a triorganophosphine that can form a radiation sensitive complex with the organoazide, the improvement comprising having as the triorganophosphine precursor, a transition metal complex having the formula

$$(Z)_2MX_2$$

wherein Z represents a triorganophosphine group having the formula

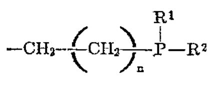


$$R^1-\overset{\displaystyle R}{\overset{|}{P}}-R^3$$

wherein each of R^1, R^2 and R^3 independently represents one of an alkyl group, an alkoxy group, an aryl group, or an amino group having the formula

$$-N\left(-R^4\right)_2$$

wherein R^4 represents either an alkyl group or an aryl group, and R^3 additionally represents a group having the formula



$$-CH_2-\left(-CH_2-\right)_n-\overset{\displaystyle R^1}{\overset{|}{P}}-R^2$$

wherein n represents a positive integer having a value of from 1 to about 18 and each of R^1 and R^2 are as previously defined, M represents cobalt or nickel and X represents a monovalent anion.

2. An image-forming composition as in claim **1** and further comprising an azo dye-forming coupler.

3. An image-forming composition as in claim **1**, and further comprising a polymeric binder material.

4. An image-forming element comprising a support having coated thereon a layer comprising an image-forming composition as described in claim **1**.

5. An image-forming composition comprising in admixture a radiation-sensitive aryl or heterocyclyl organoazide and, as a triorganophosphine precursor, a complex selected from those having the formula

$$[(Z^1)]_2MX_2$$

wherein

Z^1 represents a triorganophosphine group that is either a

triphenylphosphine group
a tri-(n-octyl)phosphine group,
a tri-(p-methoxyphenyl)phosphine group,
a tri-(p-tolyl)phosphine group,
a tri-(m-tolyl)phosphine group,
a diphenylethylphosphine group,
a diphenylmethylphosphine group,
a tri-n-butylphosphine group, or
a dimethylphenylphosphine group,

M represents a transition metal that is either cobalt or nickel, and

X represents an anion that is either a halide anion or a thiocyanate anion.

6. An image-forming composition as in claim **5** and further comprising an azo dye-forming coupler.

7. An image-forming composition as in claim **5** and further comprising a polymeric binder material.

8. An image-forming element comprising a support having coated thereon a layer comprising an image-forming composition as described in claim **5**.

9. An image-forming composition comprising in admixture a radiation-sensitive aryl or heterocyclyl organoazide, an azo dye-forming coupler, and a triorganophosphine precursor having the formula

$Co(\phi_3P)_2Cl_2$
$Co(\phi_3P)_2Br_2$
$Co[(n\text{-}C_8H_{17})_3P]_2Cl_2$
$Co[(p\text{-}CH_3OC_6H_4)_3P]_2Br_2$

$Co[(p\text{-}CH_3C_6H_4)_3P]_2Br_2$
$Co[(m\text{-}CH_3C_6H_4)_3P]_2Cl_2$
$Co[(m\text{-}CH_3C_6H_4)_3P]_2Br_2$
$Co[(p\text{-}CH_3C_6H_4)_3P]_2Cl_2$
$Co(\phi_2PC_2H_5)_2Cl_2$
$Co(\phi_2PCH_3)_2Cl_2$
$Co(\phi_2PC_2H_5)_2Br_2$
$Ni(\phi_3P)_2(SCN)_2$
$Ni[(n\text{-}C_4H_9)_3P]_2Cl_2$
$Ni[\phi(CH_3)_2P]_2Cl_2$
$Ni[(m\text{-}CH_3C_6H_4)_3P]_2Br_2$
$Ni[(m\text{-}CH_3OC_6H_4)_3P]_2Cl_2$
$Ni[(m\text{-}CH_3C_6H_4)_3P]_2Cl_2$
$Ni[(p\text{-}CH_3C_6H_4)_3P]_2Cl_2$
$Ni(\phi_2PC_2H_5)_2Cl_2$, or
$Ni(\phi_2PCH_3)_2Cl_2$

10. An image-forming element comprising a support having coated thereon a layer comprising an image-forming composition as described in claim **9**.

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CHARLES L. BOWERS, Jr., Primary Examiner

U.S. Cl. X.R.

96—33, 35.1, 36, 49, 75, 90 R, 115 R, 48 HD; 117—36.8; 250—65 T

PO-1050
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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,764,335 **Dated** October 9, 1973

Inventor(~~s~~) Norvell J. Nelson

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

Col. 12, line 45, claim 1

Delete "composition in admixture comprising" and insert -- composition comprising in admixture --; line 56, " $R^1 - \overset{R}{\overset{|}{P}} - R^3$ " should read -- $R^1 - \overset{R^2}{\overset{|}{P}} - R^3$ --.

Col. 14, line 12, claim 9

"$Ni[(m-CH_3OC_6H_4)_3P]_2Cl_2$" should read

-- $Ni[(p-CH_3OC_6H_4)_3P]_2Cl_2$ --.

Signed and sealed this 17th day of December 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents