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Publication number:

**0 186 868**  
**A2**

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## EUROPEAN PATENT APPLICATION

21 Application number: 85116272.7

51 Int. Cl.<sup>4</sup>: **G 03 C 7/32**  
**// C08F20/54**

22 Date of filing: 19.12.85

30 Priority: 02.01.85 US 688478  
02.01.85 US 688479

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43 Date of publication of application: 09.07.86  
Bulletin 86/28

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84 Designated Contracting States: **DE FR GB NL**

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54 **Photographic element and process for providing metal complex color images.**

57 A process of obtaining highly stable color dyes (e.g. color masking dyes) comprises use of an element which has a support having thereon at least one silver halide emulsion layer having associated therewith an essentially colorless, immobile, ligand-releasing compound of the structure **LIG-X**. In this structure, **LIG** is a ligand which is capable of complexing with metal ions (e.g. ferrous ions) to form a metal complex dye, and **X** is a group which, as a function of silver halide development, is cleaved from **LIG**. A color image is formed by developing the described element after imagewise exposure with a developing agent to imagewise cleave the bond between **LIG** and **X**, and treating the developed element with metal ions (e.g. ferrous ions) to form a metal complex dye image.

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PHOTOGRAPHIC ELEMENT AND PROCESS FOR PROVIDING  
METAL COMPLEX COLOR IMAGES

This invention relates to color  
photography. In particular, it relates to  
5 photographic elements containing essentially  
colorless, immobile, ligand-releasing compounds, and  
to processes of using such elements to provide color  
images.

It is well known in the photographic arts to  
10 record color images with photographic elements  
containing dye-providing materials which can be used  
to provide color images. Although the properties of  
dyes commonly used to provide such images (e.g. azo  
or azo-methine dyes) have been optimized over the  
15 years, there is a continued search in the art for  
dyes which provide images having improved stability  
to heat, light, humidity and chemical reagents.

It is known that dye stability can be  
enhanced by forming metal-dye complexes. For  
20 example, U. S. Patent 4,142,891 (issued March 6, 1979  
to Baigrie et al) relates to imaging in diffusion  
transfer assemblages with metal-complexed azo dyes.

Although metal-dye complexes are favorably  
regarded for their improved stability, most known  
25 metallized dyes or dye precursors are already colored  
at the time of imagewise exposure. If such dyes and  
silver halide are incorporated in the same layer of a  
photographic element, the dye will act as an unwanted  
filter, absorbing a portion of the incident radiation  
30 which otherwise would reach the silver halide. This  
results in a loss of sensitivity (i.e. photographic  
speed). Further, such colored dyes or dye precursors  
cannot be used in white photographic papers.

One way to eliminate the unwanted filtering  
35 effect is to have the silver halide and the dye in

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separate layers while maintaining them in reactive association. While this is a useful and practical solution, it increases the number of layers in the element, making it thicker and presenting  
5 manufacturing and imaging inefficiencies.

It would, therefore, be desirable to form highly stable color images using dye precursors which are essentially colorless prior to imagewise exposure and development and can be placed in any layer in the  
10 element.

The present invention overcomes the problems noted above with a photographic element which comprises a support having thereon at least one silver halide emulsion layer. This element is  
15 characterized by having associated with the silver halide emulsion layer an essentially colorless, immobile, ligand-releasing compound of the structure LIG-X. In this structure, LIG is a ligand which is capable of complexing with metal ions to form a metal  
20 complex dye, and X is a group which, as a function of silver halide development, is cleaved from LIG.

This invention also provides a process of forming a dye image in the element described above which has been imagewise exposed. This process  
25 comprises the steps of a) developing the element to imagewise cleave the bond between LIG and X as a function of development, and b) treating the element with metal ions to form a metal complex dye with LIG and the metal ions.

30 The photographic elements of this invention of this invention can be used to obtain color images of exceptional stability. Further, these elements and the process of using same provide desirable versatility in the placement of the dye-providing  
35 materials described herein because they are

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essentially colorless until development with development compositions after imagewise exposure and until treatment with metal ions. Hence, the problems of placement often encountered with known metallized or metallizable dyes can be avoided. The dye-providing materials can also be used to provide color masking dyes.

The LIG-X compounds are essentially colorless, meaning that prior to complexation of the LIG moiety with metal ions to form a visible dye, LIG-X exhibits essentially no observable color. That is, LIG-X exhibits a low optical density (i.e. less than 0.05), although it may emit or reflect electromagnetic radiation in the non-visible portions of the electromagnetic spectrum. Therefore, the LIG moiety and the metal ions form a colored dye from a colorless precursor, as opposed to compounds which are merely shifted in their absorption  $\lambda_{\text{max}}$  upon complexation with a metal ion to provide a dye of a different color.

LIG is a moiety, which when complexed with one or more metal ions, forms a visible dye. Depending on the way LIG and X are joined, this complexation can occur either while LIG and X are joined or after LIG is cleaved from X. In certain embodiments, LIG and X are joined such that LIG is incapable of complexing with metal ions until LIG and X are cleaved. In other words, the metal chelating site on LIG is blocked with X. In other embodiments, LIG and X are joined such that metal-LIG complexation can occur without LIG-X cleavage. Imagewise release and removal of LIG then allows metal complexation with the remaining LIG moiety still attached to X. In either case, complexation of metal ions with the LIG moiety provides a dye image as a function, either directly or inversely, of silver halide development.

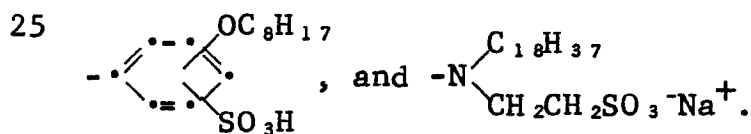
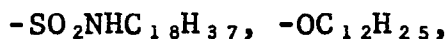
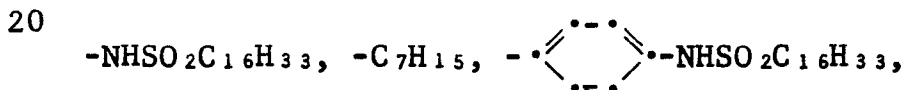
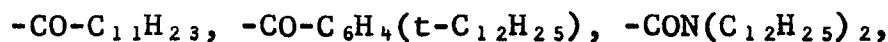
Generally, the dyes formed upon complexation of the LIG moiety and metal ions are visibly colored dyes. That is, they absorb electromagnetic radiation in the visible portion of the electromagnetic spectrum, i.e. between 400 and 700 nm. More than one molecule of a LIG moiety can be complexed with one metal ion. For example, there may be two or three LIG molecules complexed with a single metal ion. Representative dyes which can be formed are cyan, yellow and magenta dyes.

Useful LIG moieties can be obtained from ferriin type compounds such as hydrazones, tetrazolylpyridines, pyridylquinazolines, bis-isoquinolines, imines, phenanthrolines, bipyridines, terpyridines, bidiazines, pyridyldiazines, pyridylbenzimidazoles, diazyltriazines, o-nitrosoanilines and phenols, tetrazines, triazines described by Schilt et al in the journal Talanta, 15, pp. 475-478 (1968), pyridine derivatives of phenazine and quinoxaline described by Schilt et al in Talanta, 15, pp. 852-855 (1968), substituted benzimidazole derivatives as described by Schilt et al, Talanta, 15, pp. 1055-1058 (1968), oximes of substituted methyl and phenyl 2-pyridyl ketones as described by Schilt et al, Talanta, 16, pp. 448-452 (1969), and the like. Other ligand-providing compounds are described in the following Talanta literature articles: 16, pp. 519-522 (1969), 13, pp. 895-902 (1966), 17, pp. 649-653 (1970), 19, pp. 1025-1031 (1972), 21, pp. 831-836 (1974), 22, pp. 915-917 (1975), 23, pp. 543-545 (1976), 24, pp. 685-687 (1977), 26, pp. 85-89 (1979), pp. 863-865 (1981), 36, pp. 373-376 (1979), 55, pp. 55-58 (1980), 29, pp. 129-132 (1982), and in Blandamer et al, J. Chem. Soc. Dalton, pp. 1001-1008

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(1978), and Case, J. Org. Chem., 31, pp. 2398-2400 (1966). The terpyridines are particularly useful for obtaining magenta dyes.

In certain embodiments, LIG can have a ballast group which renders LIG nondiffusible in the photographic element during processing. This type of ligand-releasing compound can be illustrated as BALL-LIG-X wherein LIG and X are as defined above, and BALL is an organic nonpolymeric or polymeric group of such molecular size and configuration as to render the compound nondiffusible in a photographic element during development in an alkaline processing composition. Particularly useful ballast groups include long chain alkyl groups (e.g. 6 to 30 carbon atoms), as well as aromatic groups (phenyl, naphthyl) along with alkyl groups. Representative ballast groups include

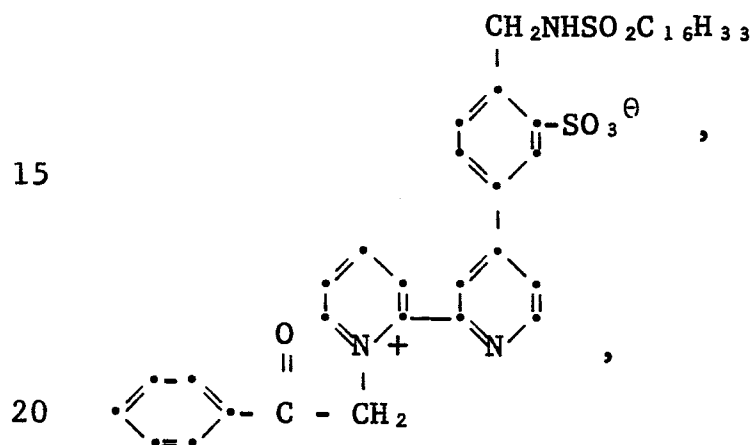
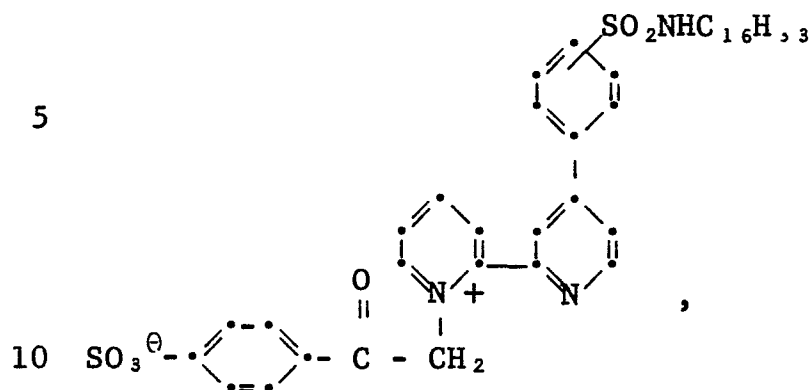


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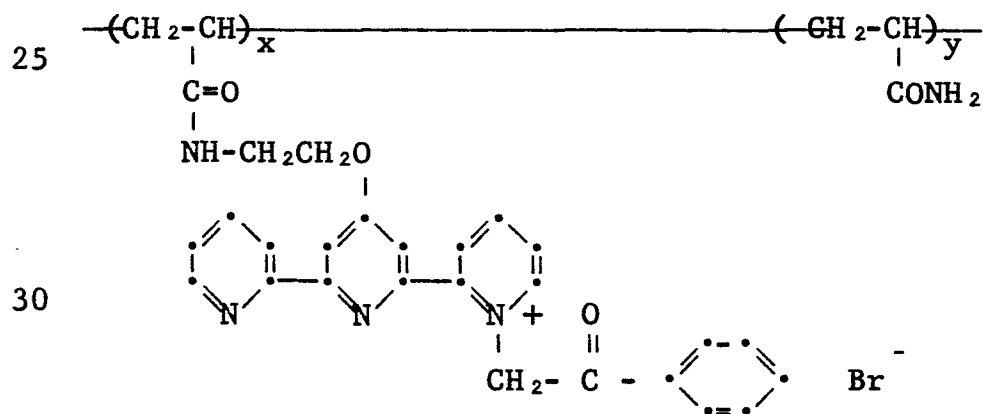
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Examples of useful BALL-LIG-X compounds include:



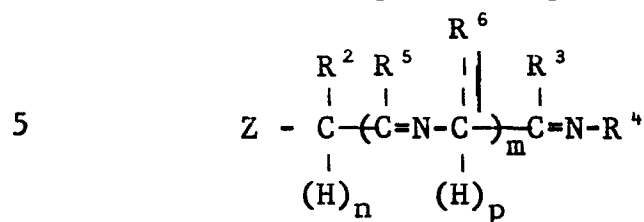
and a polymer having recurring units represented by the structure:



wherein x is from 10 to 100 weight percent, and y is from 0 to 90 weight percent.

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Particularly useful LIG moieties are those derived from compounds represented by the structure:



wherein m is 0 or a positive integer of 1 to 3, n and p are independently 0 or 1, and -- represents a single or double bond.

Z is R<sup>1</sup>-N=, O=, S=, R<sup>1</sup>-P=, (R<sup>1</sup>)<sub>2</sub>P- or (R<sup>1</sup>)<sub>3</sub>P=, and when Z is (R<sup>1</sup>)<sub>2</sub>P-, n is 1, otherwise n is 0. Preferably, m is 0 or 1 and Z is R<sup>1</sup>-N=.

R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> are independently hydrogen, amino (primary, secondary or tertiary), hydroxy, mercapto, alkoxy (preferably of 1 to 20 carbon atoms, e.g. methoxy, chloromethoxy, ethoxy, octyloxy, alkoxy substituted with imino, etc.), alkyl (preferably of 1 to 20 carbon atoms in the nucleus, e.g. methyl, ethyl, chloromethyl, isopropyl, t-butyl, heptyl, alkyl substituted with imino, etc.), aryl (preferably of 6 to 14 carbon atoms, e.g. phenyl, naphthyl, xylyl, p-methoxyphenyl, aryl substituted with imino, etc.), or a heterocyclic moiety (preferably having 5 to 20 carbon, nitrogen, sulfur or oxygen atoms in the nucleus, e.g. pyridyl, quinolyl, a heterocycle substituted with imino, etc.).

When R<sup>6</sup> is a group defined above, p is 1 and -- is a single bond.

Alternatively, if m is 0, R<sup>1</sup> and R<sup>2</sup>, R<sup>2</sup> and R<sup>3</sup>, and R<sup>3</sup> and R<sup>4</sup>, taken together, can independently represent the carbon and heteroatoms (e.g. nitrogen, oxygen, sulfur, selenium, etc.) necessary to complete a substituted or unsubstituted



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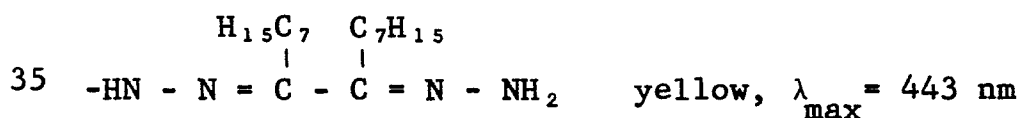
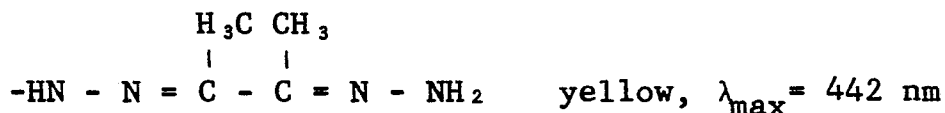
5 to 20 membered mono- or polycyclic carbocyclic or heterocyclic group (e.g. pyridine, quinolyl, triazinyl, phenanthrolinyl, pyrimidyl, etc.). The heterocyclic nucleus so formed can be substituted with one or more oxo, alkyl, amino, imino, aryl, phosphino (e.g. diphenylphosphino), alkoxy, amide, sulfonamide, thio or sulfo groups as defined above, or a heterocyclic group (e.g. pyridyl, pyrimidyl, thiazolyl, imidazolyl, thienyl, etc.).

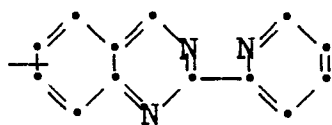
- 10            If m is 1, 2 or 3, R<sup>1</sup> and R<sup>2</sup>, R<sup>5</sup> and R<sup>6</sup>, and R<sup>3</sup> and R<sup>4</sup>, taken together, can independently represent the carbon and heteroatoms (e.g. nitrogen, oxygen, sulfur, selenium, etc.) necessary to complete a substituted or unsubstituted
- 15    5 to 20 membered mono- or polycyclic heterocyclic nucleus as defined above where m is 0. When R<sup>5</sup> and R<sup>6</sup> are so defined, p is 0 when -- is a double bond, and p is 1 when -- is a single bond.

          If desired, LIG or a ballast group attached to it can contain one or more solubilizing groups, e.g. sulfate, sulfonate, carboxylate, hydroxy or phosphate groups.

          Examples of useful LIG moieties which form color dye complexes with ferrous ions are shown below. In these structures, the point of attachment to X is represented by an unsatisfied bond. The approximate  $\lambda_{\max}$  of each resulting ferrous ion complex dye is also noted, however, the  $\lambda_{\max}$  can be shifted slightly (e.g. 10-15 nm) depending upon

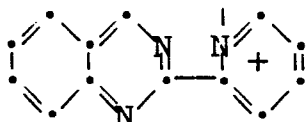
30    the moiety to which LIG is attached.





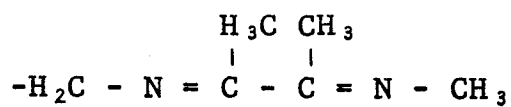
yellow,  $\lambda_{\max} = 441 \text{ nm}$

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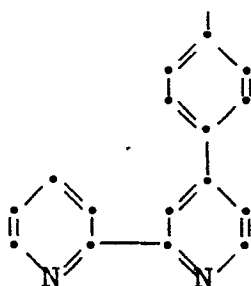
yellow,  $\lambda_{\max} = 441 \text{ nm}$

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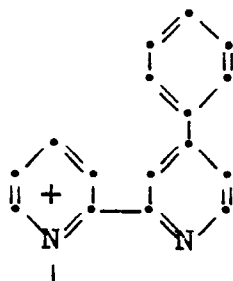
magenta,  $\lambda_{\max} = 564 \text{ nm}$

15



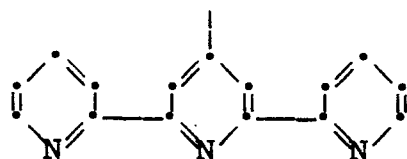
magenta,  $\lambda_{\max} = 536 \text{ nm}$

20



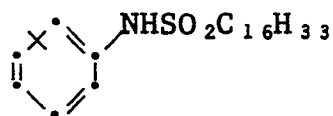
magenta,  $\lambda_{\max} = 536 \text{ nm}$

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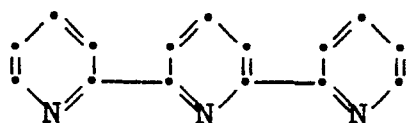


magenta,  $\lambda_{\max} = 555 \text{ nm}$

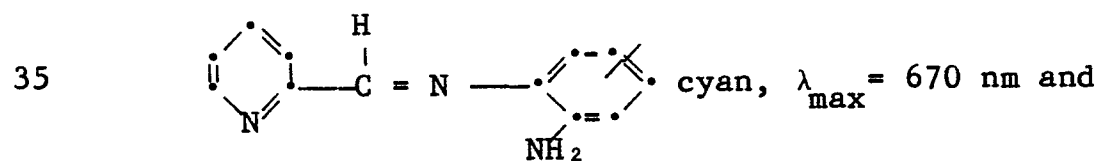
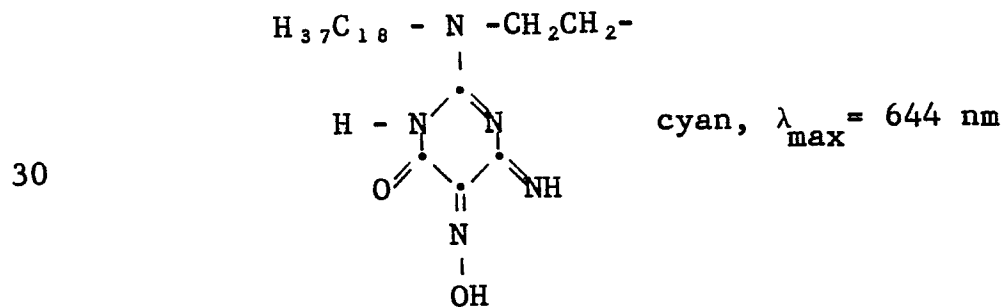
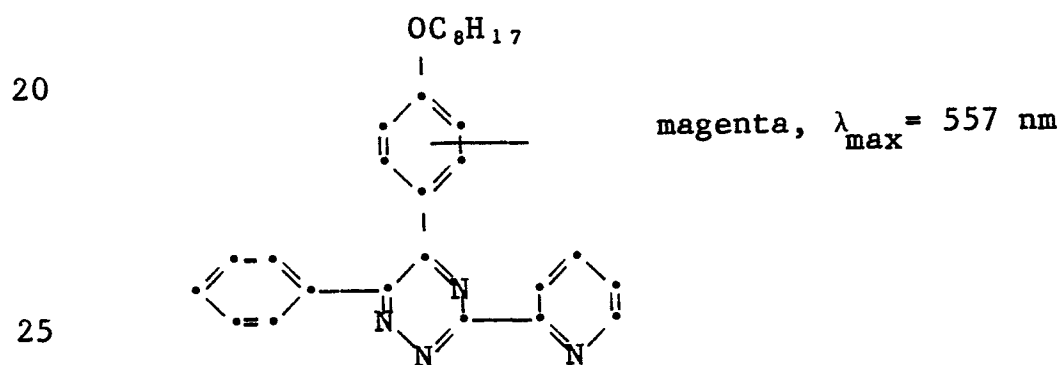
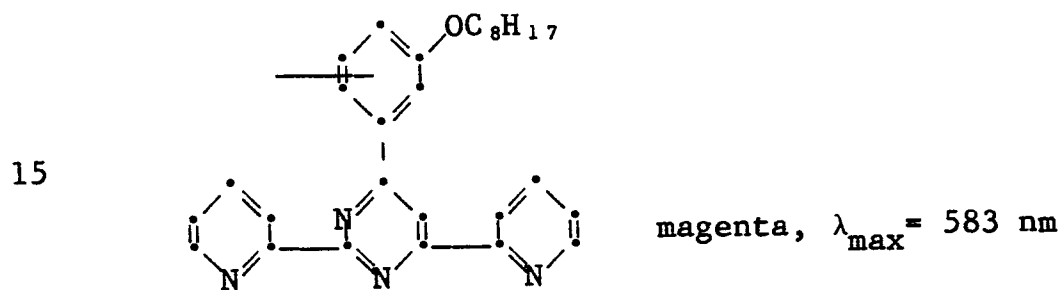
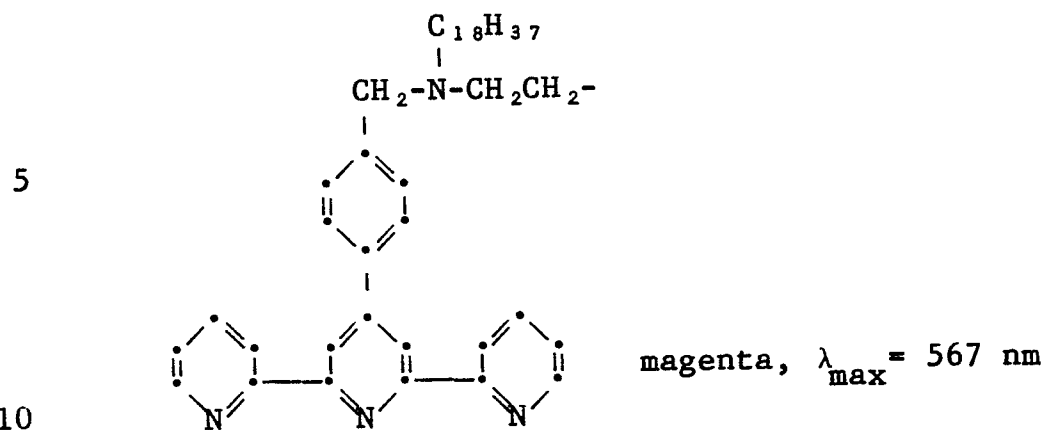
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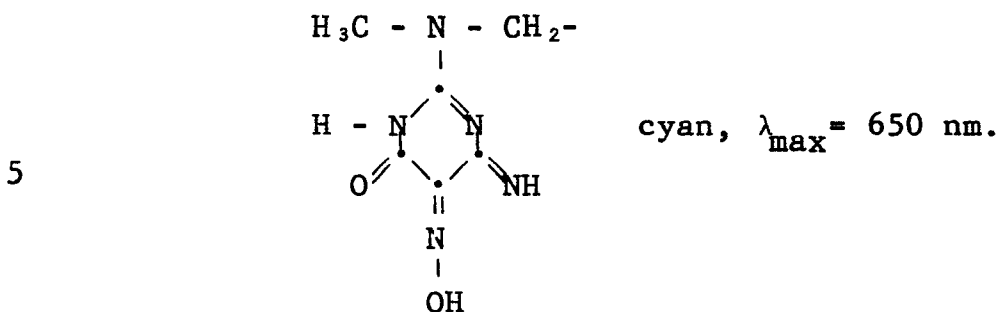


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magenta,  $\lambda_{\max} = 571 \text{ nm}$





X is any moiety which will react with  
 10 oxidized developing agent (e.g. oxidized color  
 developing agent). In preferred embodiments, it is a  
 coupler moiety employed in known color-forming  
 couplers which yields a colored product on reaction  
 with oxidized color developing agents or which yields  
 15 a colorless product on reaction with oxidized color  
 developing agents. Both types of coupler moieties  
 are well known to those skilled in the photographic  
 art and described, for example, in Research  
Disclosure, publication 17643, paragraph VII,  
 20 December, 1978, and references noted therein.

However, useful results can be obtained with  
 this invention when X is another moiety known in the  
 art to release dyes, or other photographically useful  
 fragments as a result of silver halide development.  
 25 Such moieties include redox dye releasers and similar  
 compounds as described, for example, in U. S. Patents  
 4,053,312, 4,055,429, 4,076,529, 4,139,379,  
 4,139,389, 4,199,354, 4,199,355, and 4,232,107.

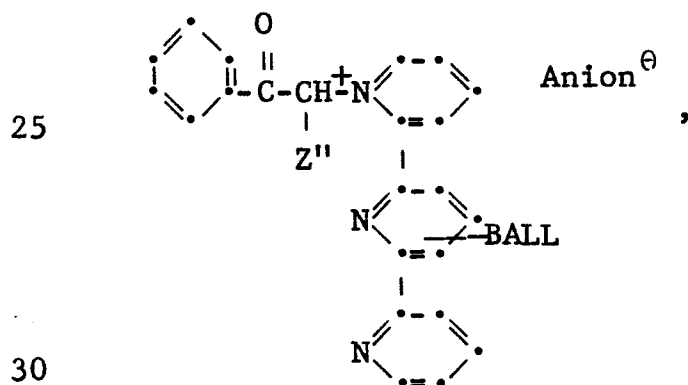
X can be unballasted or ballasted with an  
 30 organic ballasting group as described above for LIG.  
 X can be monomeric, or it can form part of a dimeric,  
 oligomeric or polymeric coupler.

The LIG moiety is joined to X at any of the  
 positions from which groups cleaved from couplers by  
 35 reaction with oxidized developing agent can be

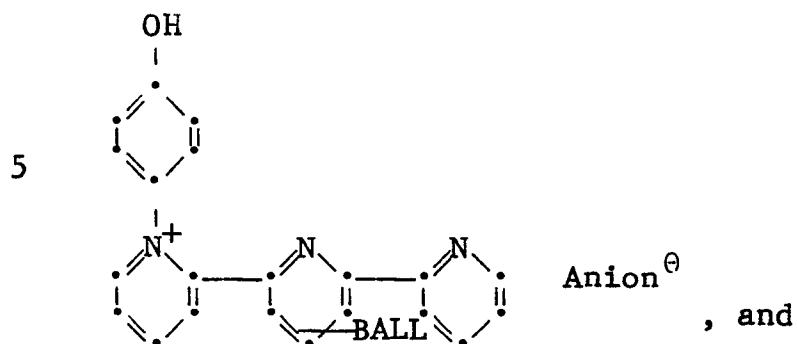
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attached. Preferably, LIG is attached to X in a coupling position so that upon reaction of the coupler with oxidized developing agent, LIG will be cleaved from X. However, LIG can be in a non-coupling position of X, from which position it will be cleaved as a result of reaction of X with oxidized developing agent. In the case where the LIG moiety is in a non-coupling position, other groups can be in the coupling position, including the known coupling off groups or the same or a different LIG moiety. Accordingly, the LIG-X compounds useful in this invention can provide more than one mole of LIG per mole of compound. The LIG moieties can be the same or different and can be cleaved at the same or different times or rates.

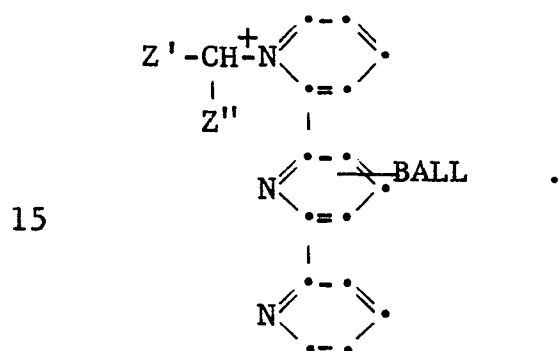
In a preferred embodiment of this invention, there is no linking group between X and LIG. The LIG moiety is blocked by X preventing complexation with metal ions, and cleavage by oxidized developer produces only the coupled product resulting from the coupling reaction with the oxidized developer and LIG. Examples of such preferred LIG-X compounds are:



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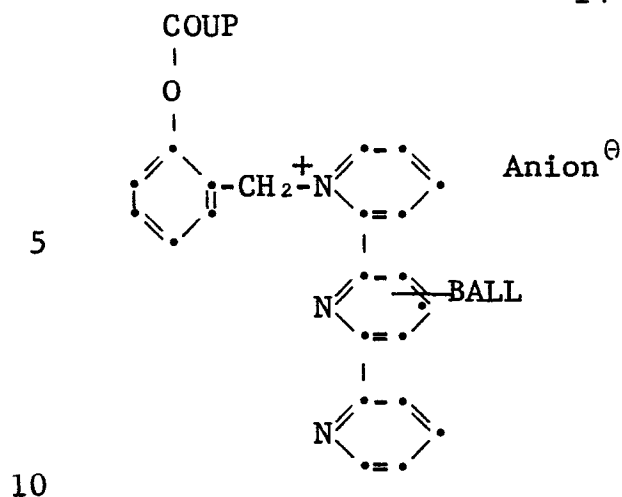
20 In these structures, Z' is an electron withdrawing group, Z'' is an electron withdrawing group, hydrogen, alkyl or aryl, BALL is a suitable ballasting group as defined above, and Anion<sup>-</sup> is a suitable anion.

25 Alternatively, release of LIG and X moieties linked with an organic blocking group (BL) can occur in several steps wherein the BL-LIG fragment is coupled off from the X moiety upon reaction with oxidized developer. The BL-LIG fragment is then capable of releasing the LIG moiety by an intramolecular reaction. The compounds are resistant

30 to unblocking under storage conditions and in the absence of oxidized developer, but are unblocked upon release from the coupler during the coupling reaction.

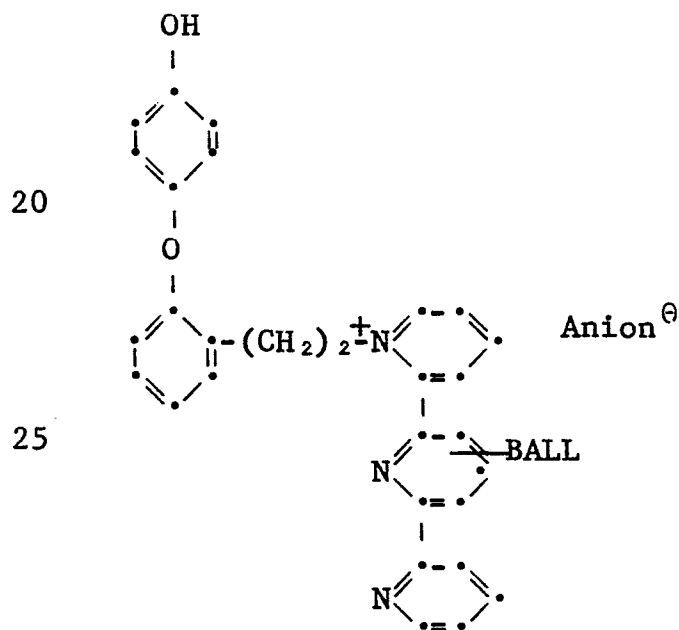
The intramolecular reaction which results in release of the LIG moiety can be an elimination

35 reaction such as occurs with



wherein COUP is any suitable coupler moiety. This concept is described in U.S. Patent 4,409,323.

Alternatively, the intramolecular release can occur by a nucleophilic displacement reaction, as occurs with



30 This concept is described in U.S. Patents 4,248,962 and 4,310,612.

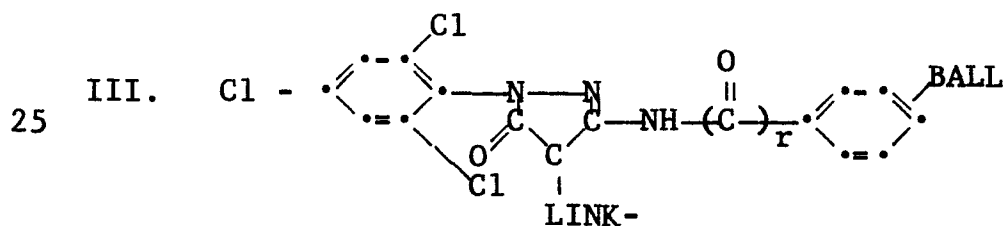
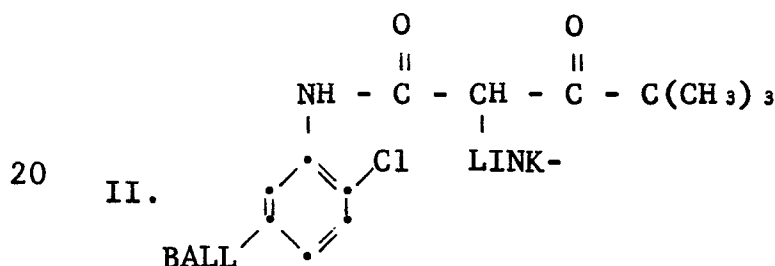
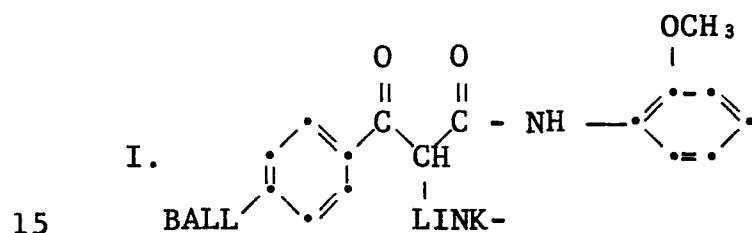
In yet another embodiment, LIG and X are connected with a single bond or with an organic linking moiety which generally remains with LIG when

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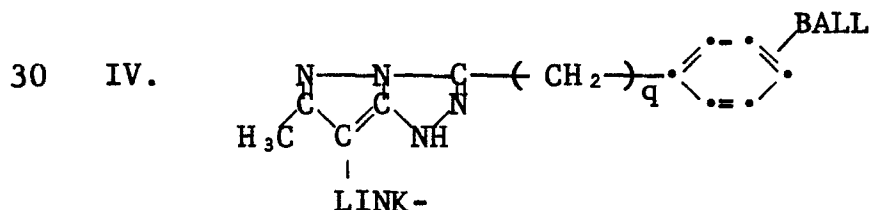
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it is cleaved and is protonated or ionized depending upon the pKa of the group. Useful organic linking moieties include -COO-, -CONH-, -O-, -S-, -SO<sub>2</sub>-, -SO<sub>2</sub>NH-, -CH<sub>2</sub>CO-, -SO<sub>2</sub>N(Alkyl)- and the like as well as the timing groups described in U.S. Patent 4,248,962. A particularly useful linking group is a single bond or -O-.

Examples useful in the practice of this embodiment of the invention as X moieties are the following color coupler moieties:



wherein r is 0 or 1,

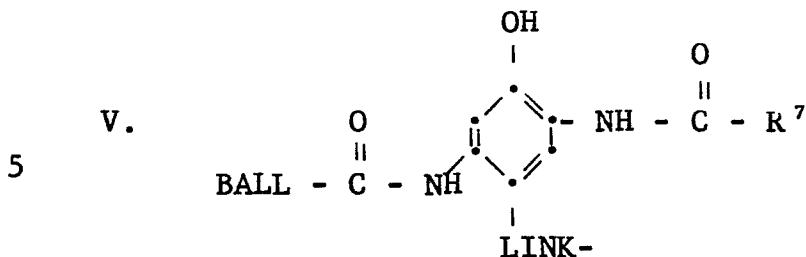


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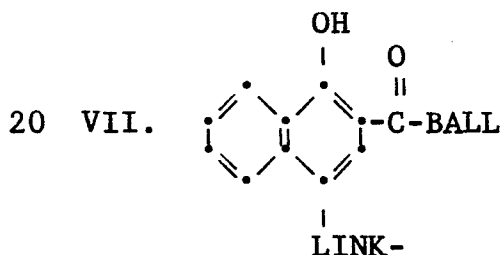
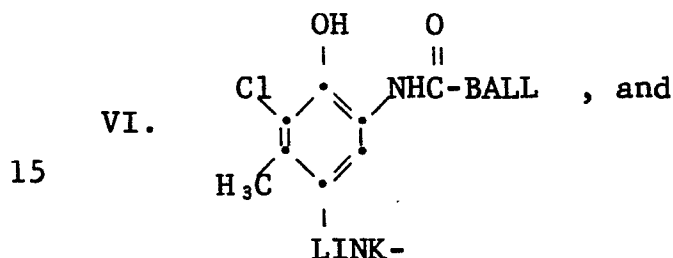


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wherein q is an integer of 1 to 20,



wherein R<sup>7</sup> is substituted or unsubstituted alkyl (preferably of 1 to 20 carbon atoms) or substituted or unsubstituted aryl (preferably of 6 to 14 carbon atoms),



In these formulae, BALL is any suitable ballast group as described above (e.g. -NHSO<sub>2</sub>C<sub>16</sub>H<sub>33</sub>, -NHCO-alkylene-oxy-aryl, alkyl of 1 to 20 carbon atoms, aryl of 6 to 14 carbon atoms in the nucleus, etc.), and LINK is a suitable linking moiety, as described above, which links X and LIG prior to reaction with oxidized developing agent. BALL can also be a suitable polymer backbone.

Representative LIG-X compounds useful in the practice of this invention include the following:

N-{{4-chloro-3-{4,4-dimethyl-3-oxo-2-[4'-(2,2':6',2''-terpyridyl)oxy]pentanamido}-phenyl}}hexadecanesulfonamide, a magenta dye-providing compound,

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1-hydroxy-N-[4-(2,4-di-t-pentylphenoxy)butyl]-  
4-[4'-(2,2':6',2''-terpyridyl)oxy]-2-naphthamide, a  
magenta dye-providing compound,

4-{{4,4-dimethyl-3-oxo-2-{3-[4'-(2,2':6',2''-  
5 terpyridyl)]phenoxy}pentanamido}}-N-methyl-N-  
octadecylbenzenesulfonamide, a magenta dye-providing  
compound,

1-hydroxy-4-{{{4-nitro-2-{N-isopropyl-N-{4-  
[6-phenyl-3-(2-pyridyl)-1,2,4-triazin-5-yl]phenoxy-  
10 carbonyl}aminomethyl}}phenoxy}}}N-(2-tetra-  
decyloxyphenyl)-2-naphthamide, a magenta  
dye-providing compound, and

1-hydroxy-N-[4-(2,4-di-t-pentylphenoxy)butyl]-4-  
{{{4-{N-{2-[4'-(2,2':6',2''-terpyridyl)oxy]-  
15 ethyl}sulfamoyl}}phenoxy}}}2-naphthamide, a  
magenta dye-providing compound.

The LIG-X compounds useful in the practice  
of this invention can be readily prepared using  
chemical reactions known to one skilled in  
20 photographic chemistry. Generally, a compound from  
which the LIG moiety is derived is reacted with a  
compound (e.g. a color coupler) from which X can be  
derived. Detailed syntheses of exemplary LIG-X  
compounds are provided below.

25 In certain embodiments, the following  
general preparatory techniques can be used:

a) Reaction of a LIG moiety containing a  
hydroxy group with a color coupler containing a  
leaving group (e.g. halogen, tosylate, mesylate,  
30 sulfonium salt, etc.) in the coupling off position to  
produce a LIG-X compound of the invention having the  
LIG moiety bonded to the X coupler moiety through an  
-O- linkage. Alternatively, a LIG moiety having a  
mercapto group could be used to obtain a LIG-X  
35 compound having the LIG and X moieties linked through  
an -S- linkage.

b) Reaction of a color coupler having a hydroxy group with a LIG moiety containing a leaving group (as defined above) to produce the same kind of LIG-X compound as described in a).

5 In other embodiments, LIG-X compounds useful in this invention can be prepared by condensation of a LIG-containing carboxylic acid halide or sulfonic acid halide with a color coupler containing a hydroxy, mercapto or amino group in the coupling  
10 position to produce LIG-X compounds having LIG and X moieties joined by an ester, amide, sulfonamide or thioester linkage.

The LIG-X compounds preferred for use in this invention can be prepared, in general, by the  
15 reaction of a ballasted and optionally solubilized LIG moiety with a coupler moiety containing a leaving group in the coupling-off position. This results in quaternization of LIG by the coupler to form LIG-X where the chelation site of LIG is blocked.  
20 Alternatively, the LIG moiety can contain an ethylenically unsaturated polymerizable monomer group (such as acrylamide, acrylate, etc.). The LIG-X compound resulting from reaction with a coupler moiety can be polymerized to yield a polymeric LIG-X  
25 compound.

As noted above, LIG is a moiety capable of complexing with metal ions to provide desired dyes in one or more layers of photographic elements. A variety of metal ions can be so used as long as the  
30 complex of the LIG moiety with the metal ion is stable, or in other words, the complex is likely to remain in complexed form for a substantial period of time. In general, the log of the formation constant of such complexes should be in the range of from 10  
35 to 30, and preferably from 15 to 25. Useful metal

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ions include  $\text{Fe}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Cu}^+$ ,  $\text{Cu}^{++}$ ,  $\text{Ru}^{++}$  and  $\text{Os}^{++}$ . Ferrous ions are preferred in the practice of this invention.

In the practice of this invention, cleavage  
5 of LIG from X results from reaction of oxidized developing agent with the LIG-X compound. Any suitable developing agent can be used in the practice of this invention, which when oxidized from silver halide development, can react with LIG-X.  
10 Particularly useful developing agents are color developing agents, including aminophenols, phenylenediamines, tetrahydroquinolines and the like as described, for example, in Research Disclosure, publication 17643, paragraph XX, noted above. Other  
15 useful developing agents include hydroquinones, catechols and pyrazolidones.

In a preferred embodiment of this invention, a negative image can be generated in an element. This is done by incorporating in the element a LIG-X  
20 compound wherein X is a moiety which yields a colorless or diffusible reaction product with oxidized developer, and X is attached to LIG in such a manner that it is incapable of complexation with metal ions prior to the reaction with oxidized  
25 developer. LIG is appropriately ballasted as outlined above to prevent diffusion. Upon imagewise development with a developing agent, the LIG-X bond is cleaved in exposed areas, and the coupled product may be washed out of the element if desired.  
30 Subsequent treatment of the element with metal ions (e.g. ferrous ions) either during the bleach step or in a separate metallization step provides dyes in the exposed areas, resulting in a negative image.

In another embodiment of this invention, LIG  
35 and X are joined such that LIG is capable of

complexing with metal ions without cleavage of the  
 5   LIG-X bond. In other words, the metal chelating site  
    in LIG is not blocked by X. In the exposed areas of  
    the element, a suitable color dye image is formed  
    with a known color coupler and the LIG-X bond is  
    cleaved as a function of silver halide development to  
    yield a soluble ligand which diffuses out of the  
    element during processing so that it is unavailable  
    to form a metal complex dye. The reaction product of  
 10   X and the oxidized developing agent can be colorless  
    or diffusable, in which case it will not contribute  
    to image density, or colored in which case it can  
    augment or modify the principal dye image (e.g. in  
    color correction). In the unexposed areas, the  
 15   unreacted LIG-X compound is treated with metal ions  
    (e.g. ferrous ions) to provide a visually colored dye  
    which acts as a masking dye in those areas.

The present invention can also be used to  
 generate a reversal image in an element using what  
 20   are known in the art as universal couplers. This can  
    be done by incorporating a LIG-X compound in the  
    element wherein X is a moiety which yields a  
    colorless or diffusible reaction product with  
    oxidized developing agent and LIG is a moiety capable  
 25   of complexing with metal ions to provide a dye while  
    still linked to X. Upon imagewise development with a  
    developing agent, the LIG-X bond in exposed areas is  
    cleaved and fragments washed out of the element.  
    Subsequent treatment of the element with metal ions  
 30   (e.g. ferrous) provides dyes in unexposed areas to  
    provide a reversal image.

In still another embodiment, the  
 photographic element of this invention can provide a  
 diffusion transfer image. This element comprises a  
 35   support and a plurality of layers including one or

more image-recording layers and an image-receiving layer. A LIG-X compound is incorporated in or adjacent an image-recording layer, and the LIG-X bond is cleaved as a function of development either via  
5 coupling off chemistry or redox release chemistry. Redox release chemistry is described, e.g. in U.S. Patents 4,108,850 and 4,139,379, whereupon reduction of a hydroquinone compound releases a dye fragment. In either case, the released LIG moiety diffuses to  
10 the image-receiving layer which contains mordanted metal ions. These ions complex with the LIG moiety to provide the desired dye image.

The photographic elements and film units of this invention can be processed by known techniques  
15 in which the processing solutions or compositions are incorporated in the element or film unit or are separately applied in a solution or process sheet. These solutions or compositions contain developing agents (e.g. color developing agents) and other  
20 suitable processing addenda, as well as metal ions to complex with LIG, if desired. Alternatively, the metal ions can be incorporated within the element in the same or different layer as the LIG-X compound. More specifically, processing of the elements of this  
25 invention can be accomplished by suitable silver development, either color or black and white, for example, by treatment with a phenylenediamine or hydroquinone developer, followed by bleaching with an  $\text{Fe}^{+3}$  salt bleach, or simply by treatment of the  
30 imagewise distribution of LIG with ferrous ions. Electron transfer agents can be used in redox release processes. The ferrous or other ions can be included in the bleach solution for complexation with the LIG moiety.

Photographic elements of this invention in which the described LIG-X compounds are incorporated can comprise a support and one or more silver halide emulsion layers and associated dye-forming layers.

5 The LIG-X compounds can be incorporated in the silver halide emulsion layer or in another layer, such as an adjacent layer, where they will come into reactive association with oxidized color developing agent which has developed silver halide in the emulsion  
10 layer. The silver halide emulsion layer can contain, or have associated with it, photographic coupler compounds, such as color forming couplers, colored masking couplers, etc. These coupler compounds can form dyes of the same or different color or hue as  
15 the dyes formed by complexation of LIG and metal ions. Additionally, the silver halide emulsion layer can contain other addenda generally contained in such layers.

A multilayer, multicolor photographic  
20 element of this invention can comprise a support having thereon a red-sensitive silver halide emulsion unit having associated therewith a cyan dye image providing material, a green-sensitive silver halide emulsion unit having associated therewith a magenta  
25 dye image providing material and a blue-sensitive silver halide emulsion unit having associated therewith a yellow dye image-providing material, at least one of the silver halide emulsion units having associated therewith a LIG-X compound. Each silver  
30 halide emulsion unit can be composed of one or more layers and the various units and layers can be arranged in different locations with respect to one another as is known in the art. The LIG-X compounds described herein can be incorporated into or  
35 associated with one or more units or layers of the

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element. Preferably, the LIG-X compound is in or associated with the green-sensitive silver halide emulsion unit.

5 The light sensitive silver halide emulsions can include coarse, regular or fine grain silver halide crystals or mixtures thereof and can be comprised of such silver halides as silver chloride, silver bromide, silver bromiodide, silver chlorobromide, silver chloriodide, silver  
10 chlorobromiodide and mixtures thereof. The emulsions can be negative-working or direct-positive emulsions. They can form latent images predominantly on the surface of the silver halide grains or predominantly on the interior of the grains. They  
15 can be chemically and spectrally sensitized. The emulsions generally are gelatin-containing emulsions although other natural or synthetic hydrophilic colloids, soluble polymers or mixtures thereof can be used if desired.

20 The element support can be any suitable substrate used in photographic elements. Generally, a flexible paper or resinous film support is used, and a paper support is particularly useful. Paper supports can be acetylated or coated with baryta  
25 and/or an  $\alpha$ -olefin polymer such as polyethylene, polypropylene, ethylene-butene copolymer and the like.

Further details regarding silver halide emulsions and photographic elements, including diffusion transfer elements, are well known in the  
30 art as described, for example, in Research Disclosure, publication 17643, noted above, as well as in Research Disclosure, publication 15162, November, 1976 and U. S. Patent 4,358,525.



Preparation 1

A useful magenta dye-forming LIG-X compound is 1-hydroxy-N-[4-(2,4-di-t-pentylphenoxy)butyl]-4-[4'-(2,2':6',2''-terpyridyl)oxy]-2-naphthamide which  
5 was prepared in the following manner.

To a solution of 12.25 g (25 mmole) of 1,4-dihydroxy-N-[4-(2,4-di-t-pentylphenoxy)butyl]-2-naphthamide and 3.1 g (10 mmole) of 2,6-di-2-pyridyl-4-methylsulfonopyridine in 100 ml of dry  
10 N,N-dimethylformamide (DMF) under N<sub>2</sub> was added in portions 2.4 g (50 mmole) of 50% NaH. After hydrogen evolution was complete, the solution was heated to 90°C for two hours. Thin layer chromatography analysis (9/1 CH<sub>3</sub>CN/MeOH) revealed that all of  
15 the sulfone was consumed. The reaction mixture was poured into 2 l of dilute KH<sub>2</sub>PO<sub>4</sub> buffer, and the product solidified upon stirring. After removal of the solvent, the crude product was triturated several times with cyclohexane to remove unreacted  
20 naphthamide. The resulting purified LIG-X compound was isolated by filtration as a tan solid (9 g). Analysis by mass spectroscopy showed the compound to be consistent with the assigned structure.

Preparation 2

25 The monomer 1-benzoylmethyl-2-[4-(2-acrylamidoethoxy)-6-(2,2'-bipyridyl)]pyridinium bromide was prepared in the following manner.

A mixture of 10.00 g (20 mmole) of N-[2-[2,6-di(2-pyridyl)-4-pyridyloxy]ethyl]acrylamide  
30 and 5.79 g (29 mmole) of α-bromoacetophenone in 10.0 ml DMF was stirred at 80°C under argon for 3.5 hours. Upon cooling to room temperature, the resulting solid mass was triturated with CH<sub>2</sub>Cl<sub>2</sub> to remove unreacted starting  
35 materials. The crude product was filtered, washed

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with  $\text{CH}_2\text{Cl}_2$  and taken up in methanol. The methanol solution was evaporated in vacuo to a clear oil. Addition of  $\text{CH}_2\text{Cl}_2$  followed by trituration yielded 6 g of a white solid. Elemental and nuclear magnetic resonance (NMR) analyses showed the resulting compound to be consistent with the assigned structure.

### Preparation 3

A useful magenta dye-forming polymeric LIG-X compound is poly{acrylamide-co-1-benzoylmethyl-2-[4-(2-acrylamidoethoxy)-6-(2,2'-bipyridyl)]-pyridinium bromide} which is prepared in the following manner.

To a solution of acrylamide (24.0 g, 0.34 mole) and 1-benzoylmethyl-2-[4-(2-acrylamidoethoxy)-6-(2,2'-bipyridyl)]pyridinium bromide (6.0 g, 0.011 mole) in water (300 ml) and ethanol (50 ml) was added 2,2'-azobis(2-methylpropionitrile) (0.60 g) as an initiator. The mixture was maintained under a nitrogen atmosphere and heated to  $65^\circ\text{C}$ . After 1.5 hour, degassed water (nitrogen gas bubbled into the water for 15 minutes) (200 ml) was added and heating at  $65^\circ\text{C}$  was continued for 4.5 hours. The resulting polymer solution was then purified by dialysis in distilled water to give, after concentration, 10.3% solids (27 g, 89% yield).

### Preparation 4

A useful magenta dye-forming LIG-X compound is N-{[4-chloro-3-{4,4-dimethyl-3-oxo-2-[4'-(2,2':6',2''-terpyridyl)oxy]pentanamido}-phenyl]}hexadecanesulfonamide which was prepared in the following manner:

The following were added to a 25 mL flask equipped with a stirrer: 0.5 g (2 mmole) of 2,6-di-2-pyridyl-4-hydroxypyridine, 0.43 g (3.75

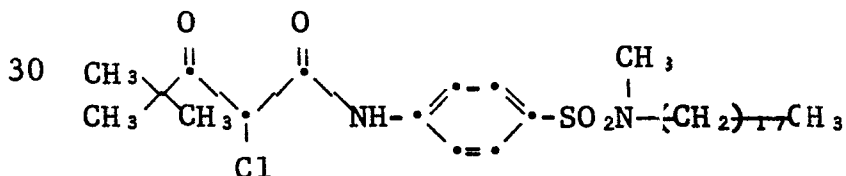
-26-

mmole) of tetramethylguanidine, 5 ml of CH<sub>3</sub>CN and 1.5 g (2.7 mmole) of N-[4-chloro-3-(2-chloro-3-oxo-4,4-dimethylpentanamido)phenyl]hexadecanesulfonamide. The resulting mixture was heated at 40°C with stirring for one hour. A thin layer chromatography analysis (10% EtOAc/CH<sub>3</sub>CN) revealed that starting terpyridine remained, so another 0.3 g of the hexadecanesulfonamide and 0.1 g of tetramethylguanidine were added to the mixture. The reaction mixture was stirred an additional five hours whereupon the solvent was removed. The residue was chromatographed on silica gel. Nonpolar degradation products of the coupler were eluted with 10% cyclohexane/CH<sub>2</sub>Cl<sub>2</sub> up to CH<sub>2</sub>Cl<sub>2</sub>. The desired LIG-X compound was eluted with 10% EtOAc/CH<sub>2</sub>Cl<sub>2</sub> up to 50% CH<sub>2</sub>Cl<sub>2</sub>/EtOAc. Removal of the solvent left 0.8 g of a glassy solid identified as the desired magenta dye by mass spectroscopy.

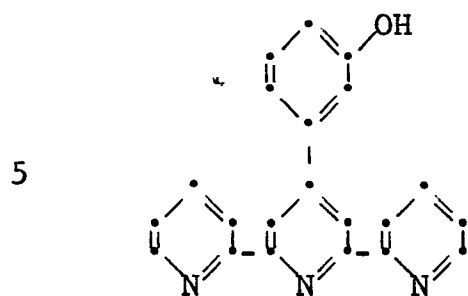
# Preparation 5

A useful magenta dye-forming LIG-X compound is 4-{{4,4-dimethyl-3-oxo-2-{{3-[[4'-(2,2':6',2''-terpyridyl]phenoxy]pentanamido}}}-N-methyl-N-octadecylbenzenesulfonamide which was prepared in the following manner.

To a solution of 1.4 ml of triethylamine (2 equivalents) in 100 ml of dry acetonitrile were added 3 g of



and 1.63 g of

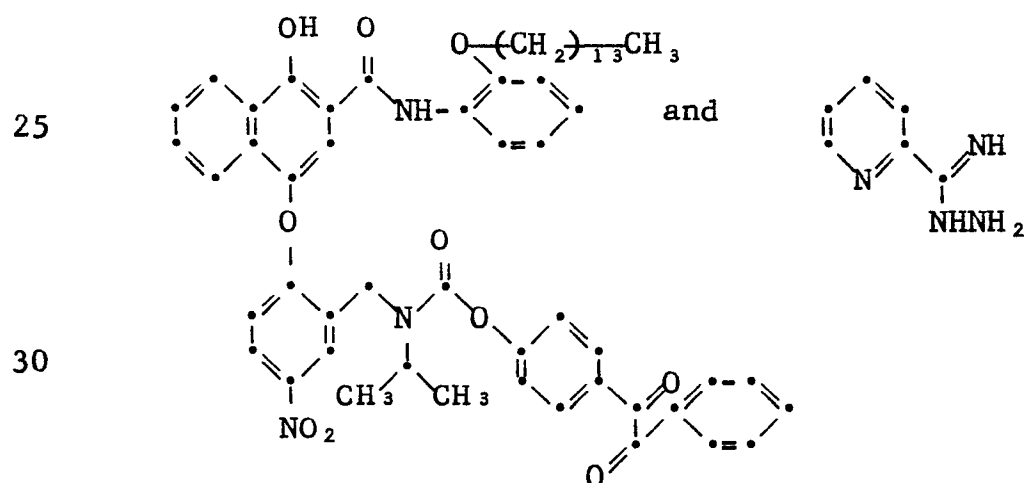


The resulting reaction mixture was refluxed under  
 10 argon for 24 hours. Upon cooling, 2.5 g of a white  
 solid was collected by filtration. The material  
 showed one spot on thin layer chromatography and  
 possessed infrared, NMR and mass spectra consistent  
 with the assigned structure.

15 Preparation 6

Another useful magenta dye-forming LIG-X  
 compound is 1-hydroxy-4-{{4-nitro-2-  
 {{N-isopropyl-N-{4-[6-phenyl-3-(2-pyridyl)-1,2,4-  
 triazin-5-yl]phenoxy}carbonyl}aminomethyl}}-  
 20 phenoxy}}-N-(2-tetradecyloxyphenyl)-2-naphthamide  
 which was prepared in the following manner.

The reactants



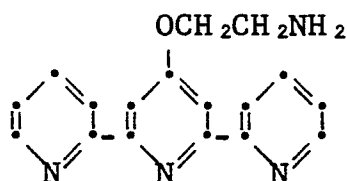
were combined (2.5 g and 0.37 g, respectively) in 100  
 35 ml of ethanol and refluxed under argon overnight.

Upon cooling to room temperature, the product oiled out. Slow evaporation of the solvent and grinding with a stirring rod caused the product to solidify. Recrystallization from isopropanol afforded 1.70 g of buff yellow solid showing a one spot thin layer chromatography with a very slight trace of the first reactant and infrared, NMR and mass spectra consistent with the assigned structure.

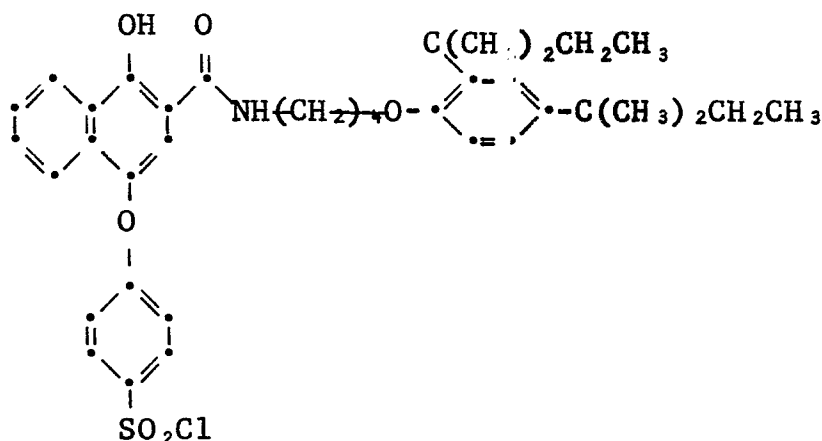
# Preparation 7

Another useful magenta dye-forming LIG-X compound is 1-hydroxy-N-[4-(2,4-di-t-pentylphenoxy)butyl]-4-{{{4-{{N-{2-[4'-(2,2':6',2''-terpyridyl)oxy]ethyl}sulfamoyl}}phenoxy}}}-2-naphthamide which was prepared in the following manner.

To a solution of 0.584 g of



and 0.4 g of dry triethylamine in 100 ml of tetrahydrofuran, was added a solution of 1.33 g of



in 20 ml of tetrahydrofuran. After total addition, the reaction mixture was stirred at room temperature for two hours. The resulting  $\text{Et}_3\text{N} \cdot \text{HCl}$  was

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filtered off, 0.5 ml of glacial acetic acid was added and the filtrate was reduced to dryness. The residue was taken up in  $\text{CH}_2\text{Cl}_2$ , washed with 1 normal acetic acid, water, and brine and then dried over

5  $\text{Na}_2\text{SO}_4$ . The  $\text{CH}_2\text{Cl}_2$  was removed in vacuo and the resulting material redissolved in ether and evaporated to dryness to afford 1.69 g of a fluffy white solid having infrared, NMR and mass spectra consistent with the assigned structure.

10 The following examples are provided to illustrate the practice of this invention.

Example 1 - Photographic Element Containing Polymeric LIG-X Compound which Provides a Magenta Dye Complex with Ferrous Ions

15 To a warm stirred solution of poly{acryl-  
amide-co-1-benzoylmethyl-2-[4-(2-acrylamidoethoxy)-6-(2,2'-bipyridyl)pyridinium bromide]} (10.3% solids, 58.04 g solution), was added 12.5% gel solution (30.6  
20 g), 10% Alkanol XC<sup>™</sup> surfactant solution (3.8 g), a spreading agent solution (4.3 g), and distilled water (41.0 g). A coating composition was prepared by adding 6.3 ml of silver halide emulsion containing 160 mg Ag/ml and 60 mg gelatin/ml to the above  
25 solution. The emulsion was then coated on a cellulose acetate support at about 129 ml/m<sup>2</sup> laydown. An overcoat solution containing 1.07 g gelatin/m<sup>2</sup> and 85 mg of 2% bis(vinylsulfonyl-methyl) ether hardener solution/m<sup>2</sup> was coated over  
30 the emulsion at about 54 ml/m<sup>2</sup> laydown.

The resulting photographic element was imagewise exposed, developed with pH 11 phenylenediamine color developing solution to cleave LIG from X (polymeric backbone), bleached with ferric  
35 ethylenediaminetetraacetic acid bleach solution, and fixed. The element was then placed into a dilute

ferrous ammonium sulfate solution (0.1 molar) which provided ferrous ions which complexed with the free LIG moiety to form a magenta dye image in imagewise exposed areas.

5      Example 2 - Photographic Element Containing  
                                          LIG-X Compound as Masking Dye

This example illustrates the use of LIG-X compounds to provide masking dyes in a photographic element.

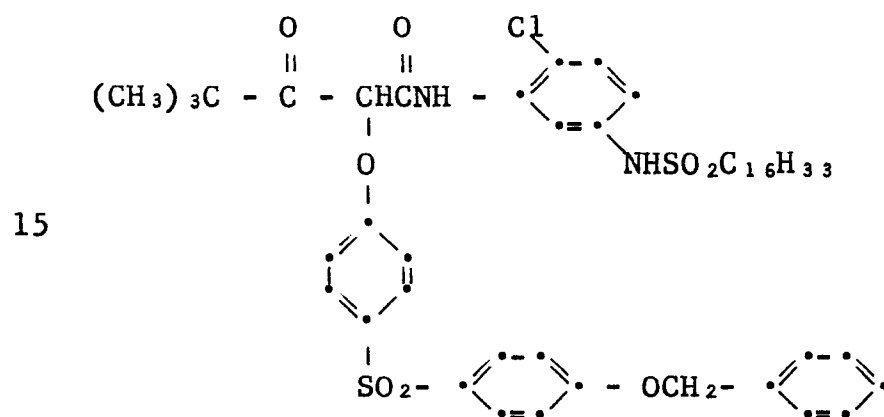
10            A 1:1 molar ratio of a known cyan dye-providing coupler, N-[N'-(4-cyanophenyl)ureido-3-hydroxyphenyl]-2-(2,4-di-t-pentylphenoxy)hexanoic acid amide and a colorless magenta dye-providing LIG-X compound, 1-hydroxy-N-[4-(2,4-di-t-pentylphenoxy)butyl]-4-[4'-(2,2':6',2''-terpyridyl)oxy]-2-  
 15 naphthamide dissolved in half their weight of dibutyl phthalate and three times their weight of ethyl acetate was dispersed in a silver bromide emulsion on a cellulose acetate support. The coating  
 20 levels were 0.48 g/m<sup>2</sup> of magenta dye-providing LIG-X compound, 0.58 g/m<sup>2</sup> of the cyan dye-providing color coupler, 0.9 g/m<sup>2</sup> of Ag and 3.8 g/m<sup>2</sup> of gelatin.

The resulting element was imagewise exposed,  
 25 developed with a phenylenediamine color developing solution (pH 10) and bleached using a ferricyanide-based bleach solution. This process provided a cyan dye image in the exposed areas and cleaved the terpyridyl LIG moiety from the X moiety  
 30 in those areas. The free LIG moiety was washed out of the element in the processing solutions. The element was then placed into a dilute ammonium ferrous sulfate solution (10<sup>-3</sup> molar), providing  
 35 the uncoupled LIG-X compound, generating a magenta color correcting dye image in the unexposed areas of the element.

Example 3

This example illustrates the use of a LIG-X compound to correct for undesired green absorption of a yellow dye in a photographic element.

- 5 A 1:3 molar ratio of a magenta dye-providing LIG-X compound, N-{{4-chloro-3-{4,4-dimethyl-3-oxo-2-[4'-(2,2':6',2''-terpyridyl)oxy]pentan-amido}phenyl}}hexadecanesulfonamide, and a known  
10 structure:



- 20 were coated in a silver halide emulsion on a cellulose acetate support after being dissolved in half their weight of dibutyl phthalate and three times their weight of ethyl acetate. The coating levels were 1.8 g/m<sup>2</sup> of magenta dye-providing LIG-X  
25 compound, 5.9 g/m<sup>2</sup> of the yellow dye-providing color coupler, 2.5 g/m<sup>2</sup> of Ag and 12.4 g/m<sup>2</sup> of gelatin.

- The resulting element was imagewise exposed, developed and bleached as described in Example 2 to  
30 provide a cyan dye image. Uncoupled LIG moiety was washed out of the exposed areas. The element was then treated with ferrous ions as in Example 2. The ferrous ions complexed with the LIG moiety of the uncoupled LIG-X compound, generating a magenta color  
35 correcting dye in the unexposed areas of the element.

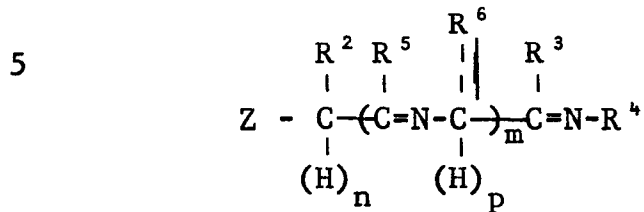


CLAIMS:

1. A photographic element comprising a support having thereon at least one silver halide emulsion layer, the element characterized by having associated with the silver halide emulsion layer an  
5 essentially colorless, immobile, ligand-releasing compound of the structure LIG-X wherein LIG is a ligand which is capable of complexing with metal ions to form a metal complex dye, and X is a group which, as a function of silver halide development, is  
10 cleaved from LIG.
2. The element as claimed in claim 1 wherein X is a coupler moiety and LIG is joined to the coupling position thereof so that, upon reaction of the coupler moiety with oxidized developing agent,  
15 LIG is cleaved from X.
3. The element as claimed in claim 1 wherein LIG and X are joined such that LIG is incapable of complexing with the metal ions until LIG is cleaved from X.
- 20 4. The element as claimed in any of claims 1 to 3 wherein X is a coupler moiety which forms a colorless reaction product upon reaction with oxidized developing agent.
5. The element as claimed in any of claims  
25 1 to 3 wherein X is a coupler moiety which forms a diffusible reaction product upon reaction with oxidized developing agent.
6. The element as claimed in any of claims  
30 1 to 5 wherein LIG and X are joined such that LIG is capable of complexing with the metal ions while LIG is joined to X, and upon cleavage from X, LIG is capable of diffusing out of the element.

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7. The element as claimed in any of claims 1 to 6 wherein LIG is derived from a compound represented by the structure:



wherein m is 0 or a positive integer of 1 to 3, n and p are independently 0 or 1, -- represents a single or double bond,

Z is R<sup>1</sup>-N=, O=, S=, R<sup>1</sup>-P=, (R<sup>1</sup>)<sub>2</sub>P- or (R<sup>1</sup>)<sub>3</sub>P=, and when Z is (R<sup>1</sup>)<sub>2</sub>P-, n is 1, otherwise n is 0,

15 R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> are independently hydrogen, amino, hydroxy, mercapto, alkoxy, alkyl, aryl or a heterocyclic moiety, and when R<sup>6</sup> is so defined, p is 1 and -- is a single bond,

20 if m is 0, R<sup>1</sup> and R<sup>2</sup>, R<sup>2</sup> and R<sup>3</sup>, and R<sup>3</sup> and R<sup>4</sup>, taken together, can independently represent the carbon and heteroatoms necessary to complete a substituted or unsubstituted carbocyclic or heterocyclic nucleus, or, if m is 1 to 3, R<sup>1</sup> and R<sup>2</sup>, R<sup>5</sup> and R<sup>6</sup>, and R<sup>3</sup> and R<sup>4</sup>, taken together, can independently represent the carbon and heteroatoms necessary to complete a substituted or unsubstituted heterocyclic nucleus, and when R<sup>5</sup> and R<sup>6</sup> are so defined, p is 0 when -- is a double bond, 25 and p is 1 when -- is a single bond.

8. The element as claimed in claim 7 wherein m is 0 or 1 and Z is R<sup>1</sup>-N=.

9. The element as claimed in any of claims 1 to 8 comprising a support having thereon, in order,

a red-sensitive emulsion unit which has associated therewith a color coupler compound which is capable of forming a cyan dye,

a green-sensitive silver halide  
5 emulsion unit which has associated therewith a magenta dye image-providing material, and

a blue-sensitive silver halide emulsion unit which has associated therewith a color coupler compound which is capable of forming a yellow dye,  
10 the element having the LIG-X compound associated with at least one of the units.

10. The element as claimed in any of claims 1 to 9 which is a photographic paper product.

11. A process of forming a dye image in an  
15 imagewise exposed element as claimed in any of claims 1 to 10 comprising the steps of

a) developing the element to imagewise cleave the bond between LIG and X as a function of development, and  
20 b) treating the element with metal ions to form a metal complex dye with LIG and the metal ions.

12. The process as claimed in claim 11 wherein the metal ions are ferrous ions.

25 13. The process as claimed in either of claims 11 and 12 which is color correction in an imagewise exposed element.

30

35