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3,629,336

LIGANDS WHICH ARE ALSO SILVER HALIDE DEVELOPING AGENTS

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No Drawing. Continuation-in-part of application Ser. No. 487,054, Sept. 13, 1965. This application Dec. 1, 1969, Ser. No. 881,323

Int. Cl. C07c 49/82

U.S. Cl. 260—590

9 Claims

ABSTRACT OF THE DISCLOSURE

Ligands or co-ordinating agents which will form a co-ordination complex with a metal and which also include a silver halide developing function particularly a paradihydroxyphenyl silver halide developing function or a substituted derivative thereof, thereby making them additionally useful in photography.

This application is a continuation-in-part of application Ser. No. 487,054, filed Sept. 13, 1965, and now abandoned.

This invention relates to novel compounds and, more particularly, to a novel class of ligands containing a silver halide developing radical or a radical which, upon hydrolysis, will provide a silver halide developing radical.

As is well known in the art, ligands are co-ordinating agents which will form a co-ordination complex with a metal. Those atoms of the ligand which are linked directly to the metal cation are called co-ordinating or donor atoms and each metal ion requires several of these atoms to make up its co-ordination number. According to the number of co-ordinating atoms which it contains, the complex-forming agent or ligand is said to be uni-dentate (one "tooth") or multi-dentate, e.g., bi-dentate, ter-dentate, etc. Ligands are further classified as organic or inorganic. In organic ligands, the co-ordination atoms (generally O, N or S) are attached to the carbon skeleton of an organic molecule. One particularly useful application of such compounds is in the field of dye technology to form a stable metal-dye complex, also commonly referred to as a metallized dye.

The present invention is directed to a novel class of substantially colorless organic ligands which are useful in photography.

A primary object of this invention therefore is to provide a novel class of ligands.

Another object of this invention is to provide a novel class of ligands which contain a silver halide developing radical and hence are useful photographic developers.

Still another object is to provide a novel class of ligands of the foregoing description which are particularly useful as intermediates in the preparation of metallized dyes, which in turn may be employed in photographic products, processes and compositions for forming color images.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the products and processes involving the several steps and the relation and order of one or more of such steps with respect to each of the others, and the product possessing the fea-

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tures, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a further understanding of the nature and objects of the invention, reference should be had to the following detailed description.

As was mentioned previously, the novel ligands of this invention contain a silver halide developing radical or a radical which upon hydrolysis will provide a silver halide developing radical, e.g., a protected dihydroxyphenyl radical. These compounds may be represented by the following formula:

(A) $Y-Z$

wherein Y is a radical comprising a silver halide developing substituent or a protected derivative thereof, and Z is a ligand radical, i.e., a radical of a substantially colorless compound containing one or more co-ordinating or donor atoms for forming a metal complex.

As examples of silver halide developing substituents, mention may be made of phenyl or naphthyl nuclei containing at least a hydroxy and/or amino substituent ortho or para to another such substituent. Silver halide developing substituents of the foregoing description are per se well known in the field of photography (see, for example, Photography, Its Materials and Processes, 6th edition, by Neblette, published by D. Van Nostrand Company, Inc. 1962), pp. 231-234). A preferred group of developing substituents are the hydroquinonyls, including substituted derivatives thereof, e.g., chloro, methyl, phenyl, and/or methoxy-substituted derivatives of hydroquinone. As examples of useful substituted hydroquinones, mention may be made of the following: methylhydroquinone; p-methylphenyl hydroquinone; chlorohydroquinone; methoxy-hydroquinone; 2,6 - dimethylhydroquinone; 2,6 - dimethoxy-hydroquinone; 2-methoxy-6 - methylhydroquinone; 2,3 - dimethylhydroquinone; 2,5,6-trimethylhydroquinone, etc.

As examples of protected derivatives, mention may be made of protected dihydroxyphenyl radicals such as p-diacetoxyphenyl, p-dicathyloxyphenyl, p-dimethoxyphenyl, p-dibenzoyloxyphenyl, etc. These protected dihydroxyphenyl radicals are also per se well known in the art.

In addition to the above-mentioned substituents contributing to the silver halide developing function, the benzene or naphthalene nucleus may contain other substituents for linking the developing moiety to the ligand moiety. As examples of such linking substituents, mention may be made of aminophenalkyl-thio substituents such as disclosed in U.S. Patent No. 3,009,958; aminoalkylamino substituents such as disclosed in U.S. Patent No. 3,002,997; aminophenalkyl substituents such as disclosed in U.S. Patent No. 3,019,107; alkyl-thio substituents such as disclosed in U.S. Patent No. 3,043,690; aminoalkyl substituents such as described in U.S. Patent No. 3,062,884; aminophenyl substituents such as disclosed in U.S. Patent No. 3,134,811; the acyl substituents such as disclosed in U.S. Patent No. 3,142,564; the aminophenoxy substituents such as disclosed in U.S. Patent No. 3,061,434, etc., as well as the various linking substituents disclosed in the application of Elkan R. Blout and Howard G. Rogers, Ser. No. 485,840 filed Feb. 3, 1955, now U.S. Patent 3,255,001.

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The ligand moiety may be selected from the various groups of organic ligands heretofore known in the art.

As examples of such ligands, mention may be made of amines such as:

diethylene triamine	8-hydroxyquinoline
2,2'-dipyridyl	1,2,3-triaminopropane
ethylenediamine	triaminotriethylamine
9,10-phenanthroline	triethylenetetramine
1,2-propylenediamine	diguanide;
pyridine	

organic acids such as:

citric acid	malic acid
glycolic acid	oxalacetic acid
glyceric acid	phthalic acid
gluconic acid	salicylic acid
lactic acid	succinic acid
kojic acid	tartaric acid
malonic acid	mercaptoacetic acid;

amino acids such as:

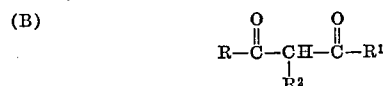
asparagine	N,N-dihydroxyethylglycine
aspartic acid	glycyl-glycine
ethylenediaminetetraacetic acid	proline
glycine	anthranilic acid;

and diketones and aldehydes such as:

acetylacetone	salicylaldehyde
tropolone	α -isopropyltropolone
β -methyltropolone	

These and other useful ligands are described, for example, in "Instability Constants of Complex Compounds," Yatsimirskii and Vasilev, Pergamon Press Inc., 1960 (Library of Congress Card No. 60-10220).

One preferred class of ligands comprises the diketones and di-aldehydes. These may be defined as β -hydroxy- α - β -unsaturated carbonyl compounds, or compounds capable of tautomerizing to such a structure, and they may also be represented by the following formulae:

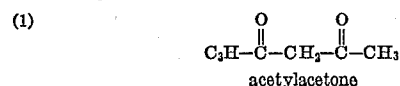
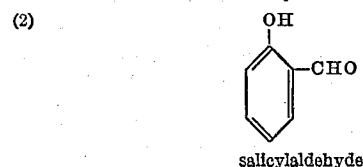


and

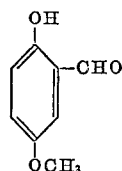


wherein R and R¹ are hydrogen, an alkyl, preferably lower alkyl, alkoxyalkyl, alkylamino, aryl, e.g., phenyl, or a phenylamino radical, or a substituted derivative of these radicals, and may be the same or different; R² may be hydrogen, lower alkyl or a phenyl radical; R³ may be a lower alkyl radical, hydroxy or hydrogen; and X represents the atoms necessary to complete an aliphatic, aromatic or heterocyclic ring. Any of the said R, R¹, R², R³ and/or the ring containing the atoms designated by X may also contain an appropriate radical for linking the developing moiety, e.g., the linking groups heretofore noted.

As examples of this class of ligands (including those previously listed), mention may be made of the following:

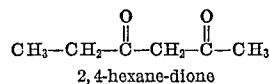


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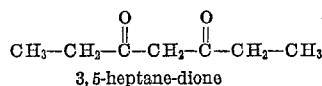
p-methoxy salicylaldehyde

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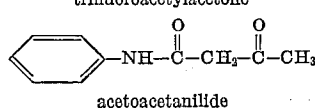
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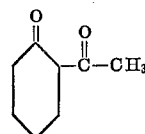


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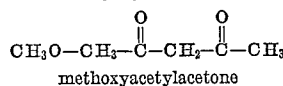


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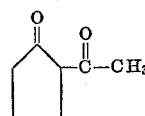


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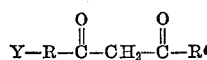
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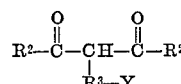
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The preferred ligands of this invention which contain a ligand moiety within the scope of Formulae B and C, e.g., a ligand of Formulae 1-9a, may be represented by one of the following formulae:

(D)

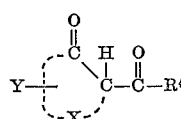


50 (E)



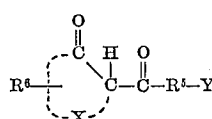
(F)

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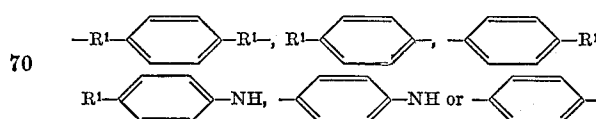
(G)

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65 wherein:

R is an alkylene radical having from 1-6 carbon atoms or a substituted chosen from the group consisting of



and

75 R¹ is an alkylene radical having from 1-6 carbon atoms;

Each R^2 is hydrogen or an alkyl radical having from 1-6 carbon atoms;

R^3 is an alkylene radical having from 1-6 carbon atoms;

R^4 is hydrogen or an alkyl radical having 1-6 carbon atoms;

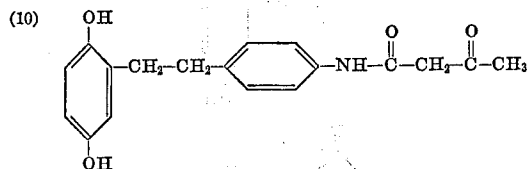
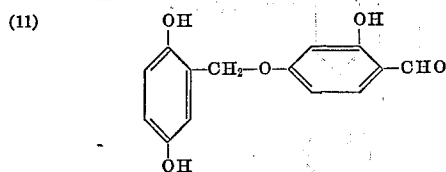
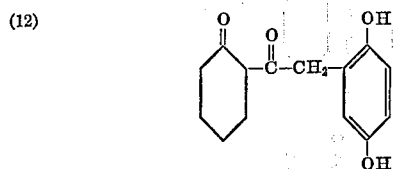
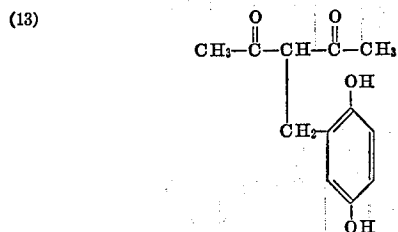
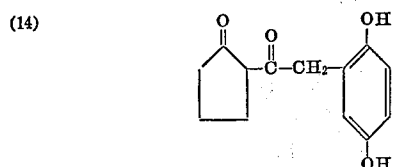
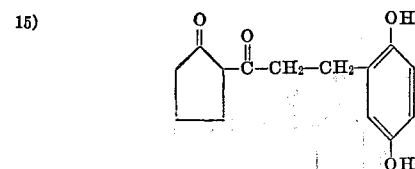
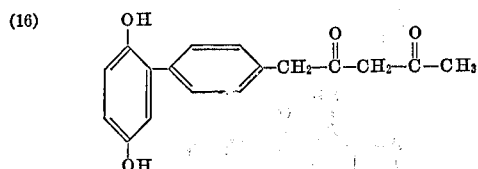
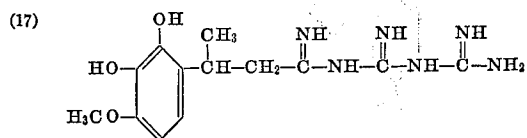
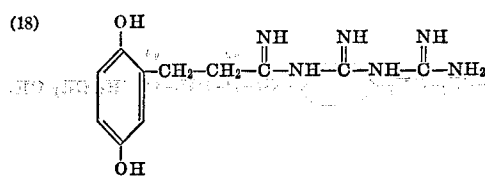
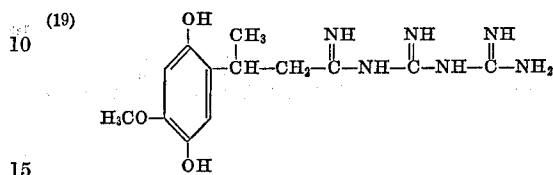
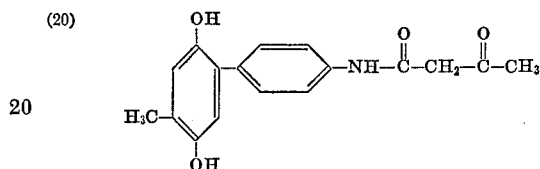
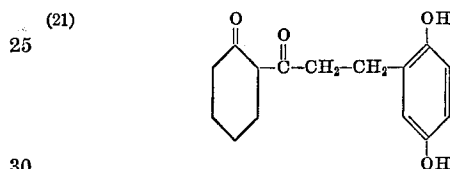
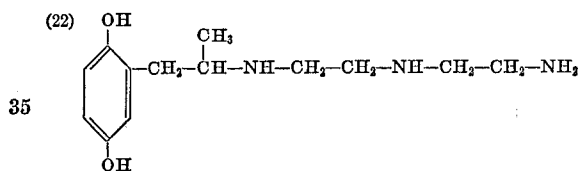
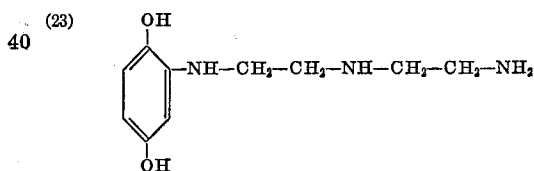
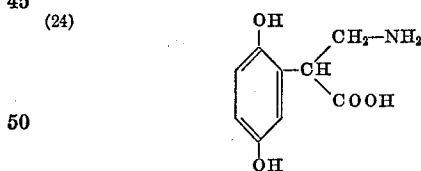
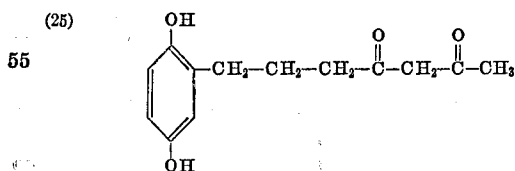
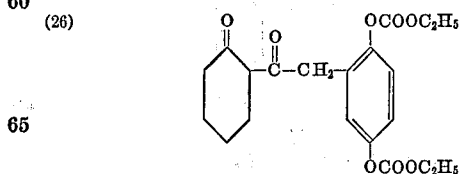
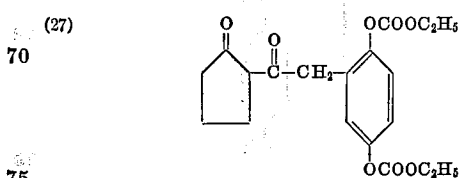
R^5 is an alkylene radical having from 1-6 carbon atoms;

R^6 is an alkyl radical having from 1-3 carbon atoms, an alkoxy radical having from 1-3 carbon atoms or H;

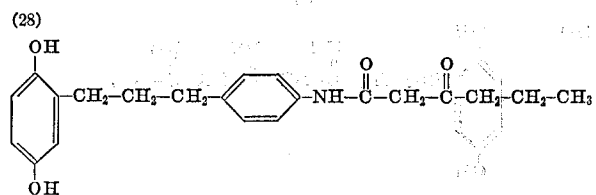
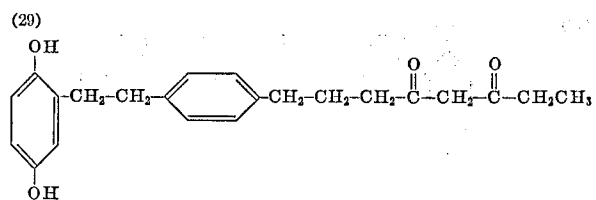
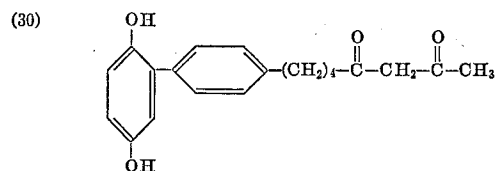
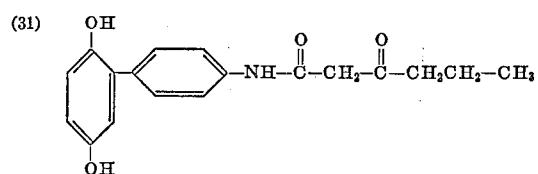
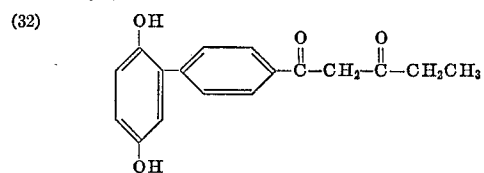
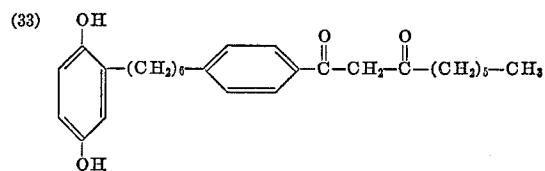
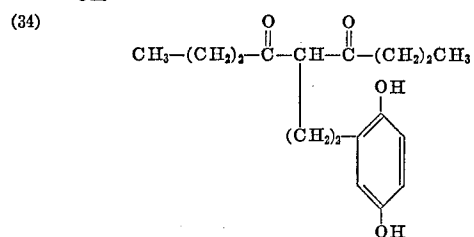
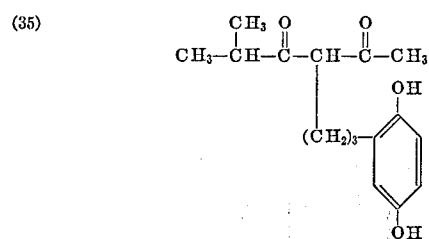
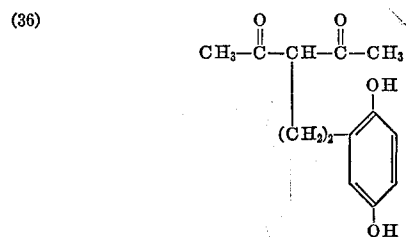
X represents the atoms necessary to complete a cyclopentane, cyclohexane or a benzene ring; and

Y is ortho or paradihydroxyphenyl or methyl or methoxy substituted derivatives thereof.

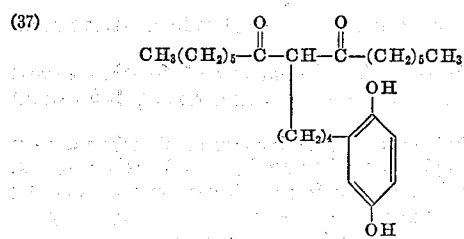
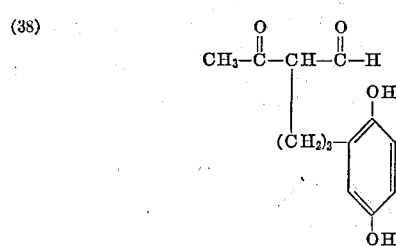
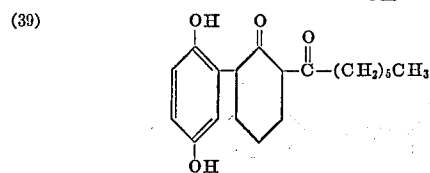
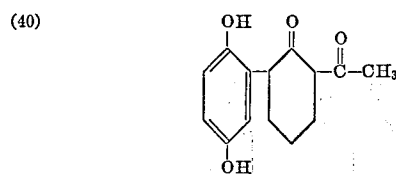
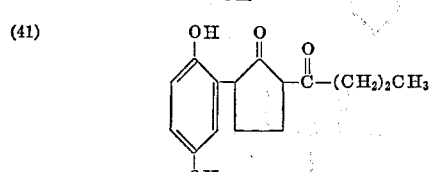
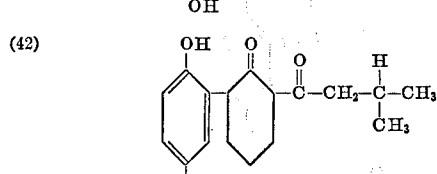
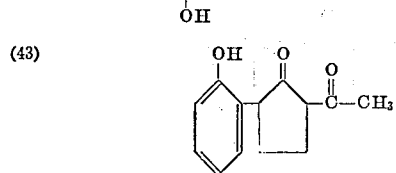
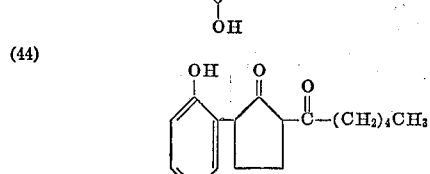
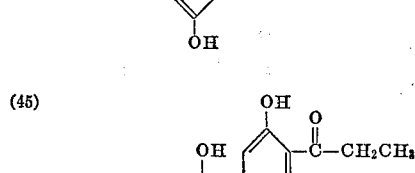
As examples of ligands contemplated by the present invention, mention may be made of the following compounds:



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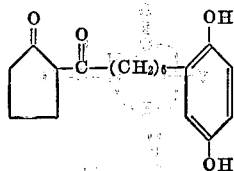


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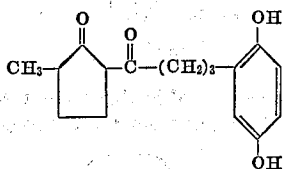


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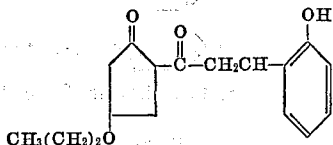
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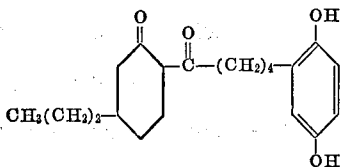
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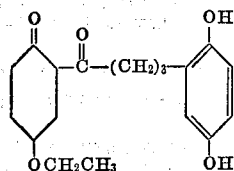
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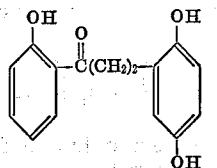
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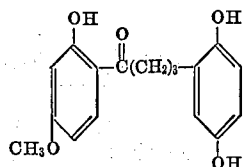
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(52)



The preparation of the novel ligands of this invention will be readily apparent to those skilled in the art in the light of the foregoing disclosure and illustrative examples.

In general, these ligands can be prepared by appropriate reactions between compounds providing the Y and Z moieties. In the case of hydroxy-containing developing substituents, e.g., dihydroxyphenyl substituents such as hydroquinonyl, it may be advisable or necessary to protect the hydroxy groups during this reaction, e.g., by alkylation, benzylation or acylation. The preparation of such protected developing substituents is per se known in the art. The protective groups may be removed subsequently by hydrolysis in known manner to provide the corresponding developer substituent.

By way of illustration, compounds such as the ligand of Formula 10 may be prepared by a substitution reaction involving replacement of an alkoxy group on the compound providing the ligand moiety with the designated amino group of a compound providing the developer moiety.

By way of further illustration, ligands such as that represented by Formula 11 may be prepared by appropriate reaction between a bromoalkyl substituent on a protected dihydroxyphenyl radical and the phenolic hydroxyl group

on the compound providing the ligand moiety, e.g., by reacting 2-bromomethyl-1,4-diacetoxy-benzene with 2,4-dihydroxybenzaldehyde, followed by hydrolysis with sodium hydroxide to remove the protective groups.

The following examples show by way of illustration and not by way of limitation the preparation of the novel ligands of this invention.

EXAMPLE 1

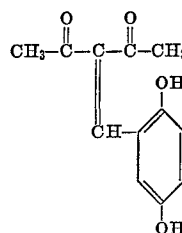
- 21.6 g. of aminophenethylhydroquinone and 50 ml. of ethyl acetoacetate were heated on a steam bath overnight and then refluxed for 2½ hours at 130° C. The excess ester was distilled off at 100° C. under vacuum. The residue was then triturated with 1:1 ethyl acetate and ligroin. Three recrystallizations from nitromethane gave 4.45 g. of the ligand of Formula 10, M.P. 145.5–146.5° C.

EXAMPLE 2

- To a mixture of 33.4 g. of 1-N-morpholinocyclohexene in 150 ml. of benzene was added 33 g. of 2,5-bis-cathyloxy-phenylacetyl chloride. The mixture was stirred for one hour and then refluxed for one and one-half hours. The resulting solid was filtered and washed with ether. The filtrates were then shaken with dilute hydrochloric acid and the solvents were evaporated. The copper chelate of the resulting β-diketone product was formed in 95% ethanol with 20 g. of cupric acetate at about 60° C. The mixture was cooled and the solid copper complex was collected. This complex was then decomposed by stirring with methylene chloride and 10% sulfuric acid. Evaporation of the solvent left 15.4 g. of an oil which crystallized to a solid (Formula 26) melting at 58–65° C. Hydrolysis of the cathyloxy groups with sodium hydroxide under nitrogen yielded the free ligand-developer, M.P. 200–201° C. of Formula 12.

EXAMPLE 3

- 33.4 g. of gentisaldehyde were condensed with 24.2 g. of acetylacetone in 150 ml. of benzene, using 7 ml. of piperidine as catalysts to form gentisylidene acetylacetone, M.P. about 180° C., having the following structural formula:



- 5.0 g. of the latter compound was hydrogenated in 100 ml. of methanol over a Raney nickel catalyst until the theoretical amount of hydrogen was absorbed to yield the developer-ligand of Formula 13.

EXAMPLE 4

- To a mixture of 16.7 g. of 1-N-morpholinocyclopentene and 16.7 g. of triethylamine in 150 ml. of benzene was added 16.5 g. of 2,5-bis-cathyloxy-phenylacetyl chloride. Formation of the copper complex followed by decomposition with methylene chloride and evaporation of the solvent, all in the manner described in Example 2, yielded 9.2 g. of the ligand of Formula 27.

- The free ligand-developer (Formula 14) may be obtained by hydrolysis of the cathyloxy groups with sodium hydroxide under a blanket of nitrogen.

As was mentioned previously, the novel class of ligands of this invention and the protected derivatives thereof are particularly useful as intermediates in the preparation of metallized dyes which in turn may be employed in photographic products, processes and compositions for forming color images.

These metallized dyes and the preparation thereof utilizing the novel ligands of this invention are described

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and claimed in the copending application of Elbert M. Idelson, Ser. No. 798,438, filed Feb. 11, 1969.

The ligands of Formulae D, E, F, and G may also be employed in the preparation of the 1:1 chromium-complexed dyes which are described and claimed in the application of Elbert M. Idelson, Ser. No. 486,853, now U.S. Patent No. 3,453,107.

The compounds of this invention may further be employed in the various processes for developing a photo-exposed silver halide emulsion to form a visible image. For example, they may be employed in diffusion transfer processes wherein an aqueous alkaline processing composition containing a silver halide developing agent and a silver halide solvent is applied to an exposed silver halide emulsion to reduce exposed areas of the emulsion to image silver while forming in terms of unexposed areas in imagewise distribution of a soluble silver complex which is transferred, by imbibition, to a superposed silver-receptive stratum to form a positive silver image thereon.

The following examples illustrate this use of the compound of this invention.

EXAMPLE 5

A standard silver iodobromide emulsion was exposed and the thus exposed negative was then developed with a processing composition comprising:

Water—100.0 cc.
Potassium hydroxide—11.2 g.
Hydroxyethyl cellulose—3.9 g.
Ligand of Formula 10—0.94 g.

After one minute development was stopped by immersing the emulsion in an acetic acid bath for two minutes to provide a negative image.

EXAMPLE 6

A standard silver iodobromide emulsion was exposed and the thus exposed negative was then developed by spreading between the emulsion and a superposed image-receiving element at a gap of 0.0026" a processing composition, comprising:

Water—830 cc.
Hydroxyethyl cellulose—36.6 g.
Sodium sulfite—26 g.
Sodium thiosulfate—74 g.
6-nitrobenzimidazole—10 g.
Sodium hydroxide—42.5 g.
Ligand of Formula 10—41.5 g.

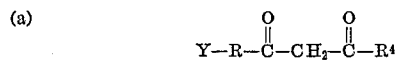
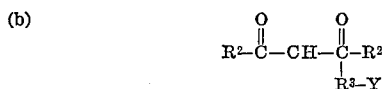
After 10 seconds, the image-receiving element was separated to reveal a positive silver transfer image.

In the photographic processes of Examples 5 and 6, the ligand was employed in its free developer form. However, it will be appreciated that it may be added to the processing composition in its protected form, in which case hydrolysis in situ in the alkaline composition provides the free dihydroxyphenyl developing function.

Since certain changes may be made in the above product and process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

I claim:

1. A compound selected from the group consisting of compounds of the formulae:



12

(c)

5

(d)

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wherein:

R is an alkylene radical having from 1-6 carbon atoms or a radical chosen from the group consisting of

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and

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wherein:

each R² is hydrogen or an alkyl radical having from 1-6 carbon atoms;

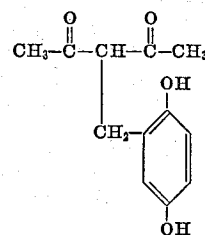
R³ is an alkylene radical having 1-6 carbon atoms; and

Y is paradihydroxyphenyl.

4. A compound of claim 3 of the formula:

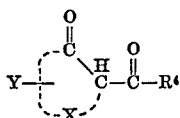
70

75



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5. A compound of claim 1 corresponding to the formula:



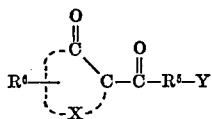
wherein:

R⁴ is hydrogen or an alkyl radical having from 1-6 carbon atoms;

X represents the atoms necessary to complete a cyclopentane ring or a cyclohexane ring; and

Y is paradihydroxyphenyl.

6. A compound of claim 1 corresponding to the formula:



wherein:

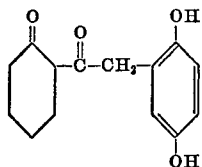
R⁵ is an alkylene radical having 1-6 carbon atoms;

R⁶ is an alkyl radical having 1-3 carbon atoms, an alkoxy radical having 1-3 carbon atoms or hydrogen;

X represents the atoms necessary to complete a cyclopentane ring or a cyclohexane ring; and

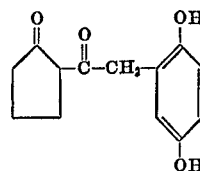
Y is paradihydroxyphenyl.

7. A compound of claim 6 of the formula:

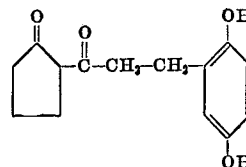


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8. A compound of claim 6 of the formula:



9. A compound of claim 6 of the formula:



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DANIEL D. HORWITZ, Primary Examiner

U.S. Cl. X.R.

260-283 R, 290 R, 463, 469, 479 S, 521 R, 562 K, 564 B, 600; 96-3, 29 D, 63, 66 HD, 93
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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,629,336

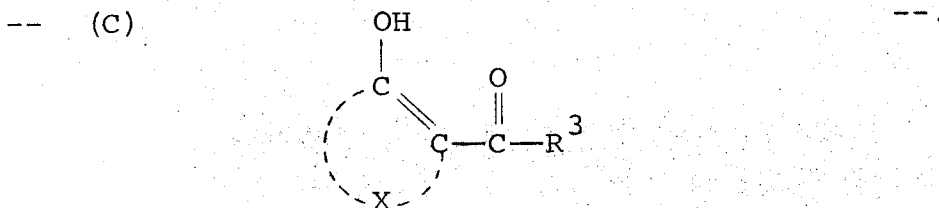
Dated December 21, 1971

Inventor(s) Elbert M. Idelson

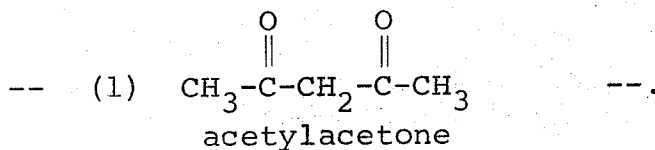
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 54 delete "or" and insert --of--.

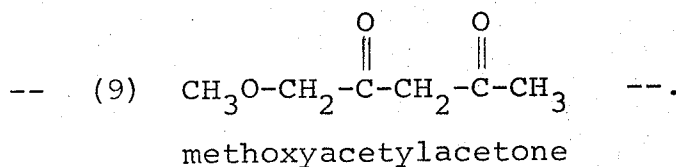
Column 3, line 45 Formula C should read as



Column 3, line 65 Formula 1 should read as



Column 4, line 33 Formula 9 should read as



Signed and sealed this 2nd day of January 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patent