

1

2

3,551,406 CHROMIUM COMPLEXES OF A MONOAZO COM- POUND AND A COLORLESS LIGAND

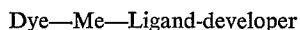
Elbert M. Idelson, Newton, Mass., assignor to Polaroid Corporation, Cambridge, Mass., a corporation of Delaware

No Drawing. Continuation-in-part of application Ser. No. 487,033, Sept. 13, 1965. This application Mar. 4, 1969, Ser. No. 804,315

Int. Cl. C07c 107/00; C09b 45/16; G03e 5/24
U.S. Cl. 260—147 8 Claims

ABSTRACT OF THE DISCLOSURE

Photographic products, processes and compositions for forming dye images employing a metal-complexed dye having bonded to the metal-complexing atom by at least one coordinating atom a substantially colorless ligand containing a silver halide developing function, which complexes may be illustrated schematically as follows:



This application is a continuation-in-part of copending U.S. application Ser. No. 487,033, filed Sept. 13, 1965, and now abandoned.

The invention relates to photography and more particularly to products, processes and compositions for the development of photosensitive silver halide emulsions.

One object of this invention is to provide novel metal-complexed dyes useful in the preparation of color images.

Another object is to provide novel metal complexes which are useful in the development of an exposed silver halide emulsion.

A further object is to provide novel products, processes and compositions for preparing color images wherein a metal complex containing both a dye moiety and a silver halide developing function is employed to develop an exposed silver halide emulsion and to form a reversed or positive dye image on a superposed dyeable stratum.

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

The invention accordingly comprises the process 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 features, 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 fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

In U.S. Pat. No. 2,983,606, issued to Howard G. Rogers, diffusion transfer processes are disclosed wherein dye developers are utilized to develop an exposed photosensitive element and to form a color transfer image on a superposed image-receiving layer. Dye developers are dyes which contain, in the same molecule, a silver halide developing function and a chromophoric system of a dye. A particularly useful class of dye developers are those containing a hydroquinonyl developing function.

In processes of this type, an exposed photosensitive element containing at least one silver halide emulsion is wetted by a liquid processing composition, for example, by immersing, coating, spraying, flowing, etc., in the dark, and the exposed photosensitive element may be superposed prior to, during, or after wetting, on a sheet-like image-receiving element containing a dyeable stratum for receiving a dye transfer image. In a preferred embodiment, the photosensitive element contains a layer of dye developer associated with each of one or more silver halide

emulsions (depending upon whether monochromatic or multicolor images are contemplated) and the liquid processing composition is applied to the photosensitive element in a uniform layer as the photosensitive element is brought into superposed relationship with the image-receiving element. As is disclosed in the aforementioned patent, the processing composition may be confined in a rupturable container which is capable, upon rupturing, of spreading its contents in a substantially uniform layer between the superposed elements. Where monochromatic images are desired, the dye developer may also be present initially in the liquid processing composition. The processing composition permeates the emulsion to initiate development and as a function thereof, the dye developer is oxidized and rendered less mobile and diffusible, at least in the processing composition which is alkaline. In undeveloped and partially developed areas of the emulsion, the dye developer is unreacted and diffusible, thus providing as a function of the point-to-point degree of development of the silver halide emulsion, an imagewise distribution of unoxidized dye developer diffusible in the liquid processing composition. At least part of this imagewise distribution of unoxidized dye developer is transferred, by inhibition, to the superposed image-receiving element to form a dye image.

As is disclosed in the aforementioned patent, the developing function may be attached to the dye moiety through a covalent bond or it may be insulated from the dye moiety by means of an achromophoric bond or bivalent linking group. This latter concept is described with more particularity and claimed in U.S. Pat. No. 3,255,001, issued to Elkan R. Blout and Howard G. Rogers. The developing function may also be a part of the dye itself, as, for example, the amino naphthol group in the dye developer, 1-amino-2-naphthol-4-azobenzene.

The present invention is directed to another means of associating a developing function with a dye moiety to provide a substance which is both a dye and a silver halide developing agent and hence may be employed in the aforementioned procedures for preparing color images.

This objective is accomplished by providing a metal-complexed dye in which the developing function is contained on a substantially colorless ligand contributing at least one and preferably two of the coordinating or donor atoms necessary to form the desired complex.

Thus, the objects of this invention are accomplished by providing a novel class of metal-complexed dyes which may be defined as metal-complexed dyes having bonded to the metal atom of the complex by at least one and preferably two coordinating atoms, a substantially colorless ligand of the formula:



wherein Y is a radical comprising a silver halide developing substituent and Z is a ligand radical, i.e., a radical of a compound containing one or more coordinating or donor atoms for forming a metal complex.

The novel complexes of this invention may be illustrated schematically as follows:



wherein "Dye" is a chelatable or complexable dye, "Me" is a metal-complexing atom, and "Ligand-Developer" is a substantially colorless ligand contributing at least one and preferably two of the coordinating or donor atoms necessary to form the desired complex, which ligand contains a silver halide developing agent or substituent.

As examples of useful metals contemplated by the "Me" moiety, mention may be made of the transition metals, particularly those of the first transition series, i.e., chromium, copper, cobalt, nickel, iron, zinc, manganese, scandium, titanium, and vanadium. Other useful metals,

e.g., aluminum, silver, palladium, platinum, etc. will be readily suggested to those skilled in the art.

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-dimethyl-hydroquinone; 2,6-dimethoxyhydroquinone; 2 - methoxy-6-methyl-hydroquinone; 2,3-dimethyl-hydroquinone; 2,5,6-trimethyl-hydroquinone, etc.

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. Pat. No. 3,009,958; aminoalkylamino substituents such as disclosed in U.S. Pat. No. 3,002,997; aminophenalkyl substituents such as disclosed in U.S. Pat. No. 3,043,690; aminoalkyl substituents such as described in U.S. Pat. No. 3,062,884; aminophenyl substituents such as disclosed in U.S. Pat. No. 3,134,811; the acyl substituents such as disclosed in U.S. Pat. No. 3,142,564; the aminophenoxy substituents such as disclosed in U.S. Pat. No. 3,061,434, etc., as well as the various linking substituents disclosed in U.S. Pat. No. 3,255,001

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
2,2'-dipyridyl
ethylenediamine
9,10-phenanthroline
1,2-propylenediamine
pyridine
8-hydroxyquinoline
1,2,3-triaminopropane
triaminotriethylamine
triethylenetetraamine
diguamide;

organic acids such as:

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

amino acids such as:

asparagine
aspartic acid
ethylenediaminetetraacetic acid
glycine
N,N-dihydroxyethylglycine
glycyl-glycine

proline

anthranilic acid;

and diketones and aldehydes such as:

acetylacetone
tropolone
 β -methyltropolone
salicylaldehyde
 α -isopropyltropolone.

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 dialdehydes. 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:

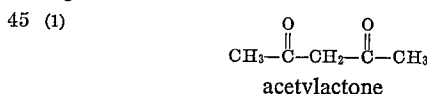


and

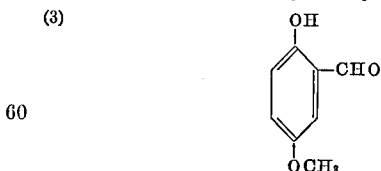


wherein R and R¹ are each hydrogen, or an alkyl, preferably lower alkyl, lower alkoxyalkyl, lower alkylamino, aryl, e.g., phenyl, or a phenylamino radical, or a substituted derivative of these radicals, and may be the same or different; R² may be hydrogen, or a lower alkyl or a phenyl radical; R³ may 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.

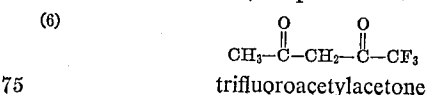
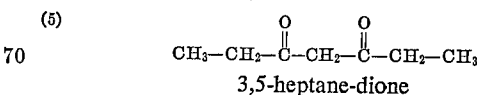
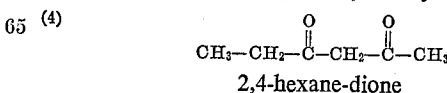
As examples of this class of ligands, (including those previously listed), mention may be made of the following:

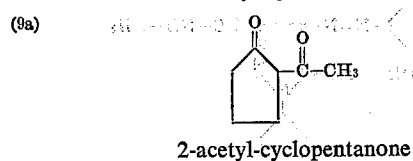
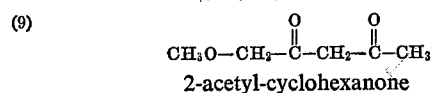
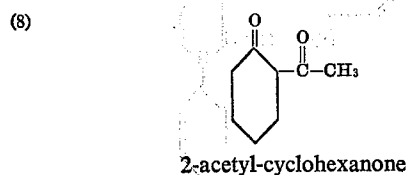
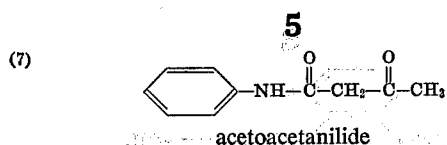


salicylaldehyde

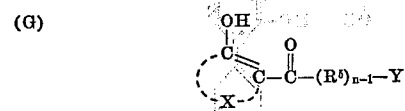
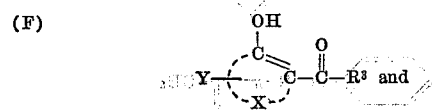
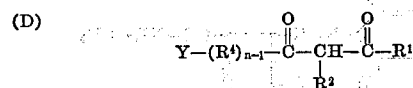


p-methoxy salicylaldehyde



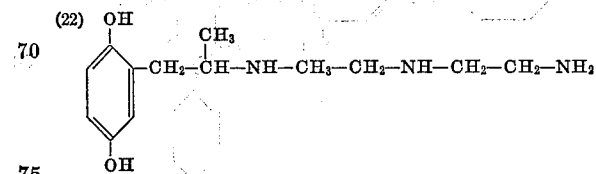
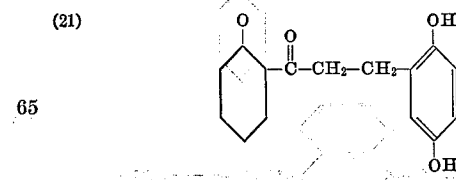
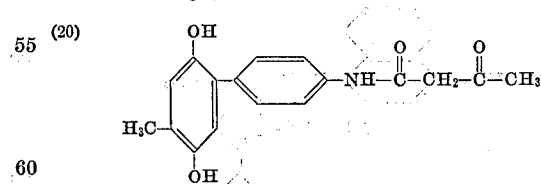
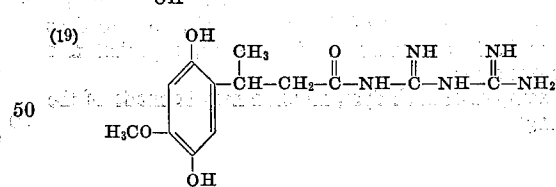
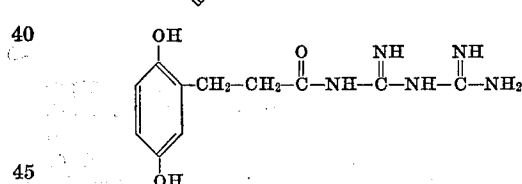
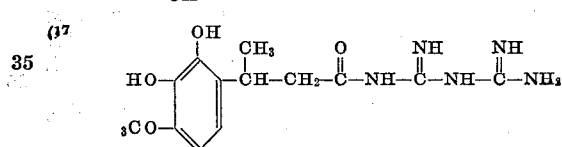
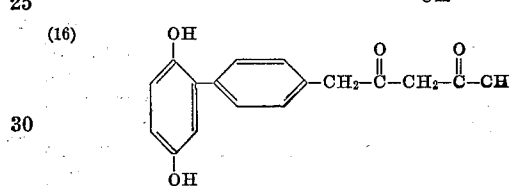
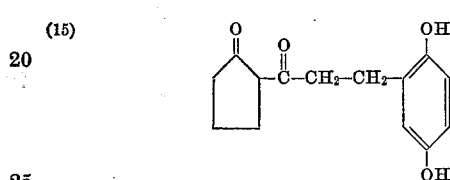
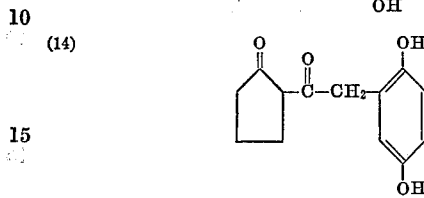
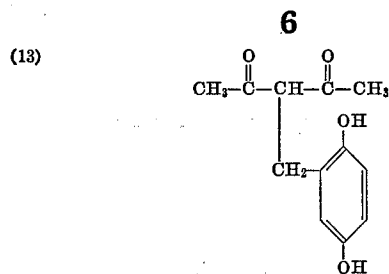
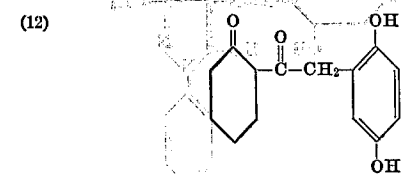
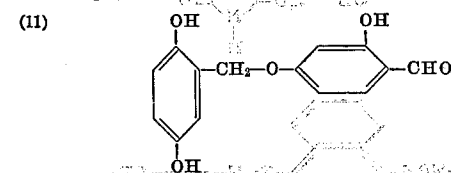
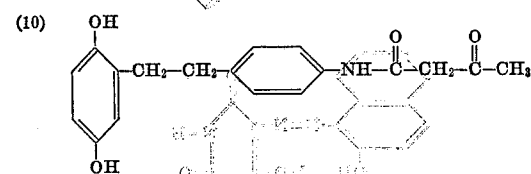


The preferred ligands of this invention which contain a ligand moiety within the scope of Formulae B and C, e.g., a ligand of Formulae 1-9a, may be represented by one of the following formulae:

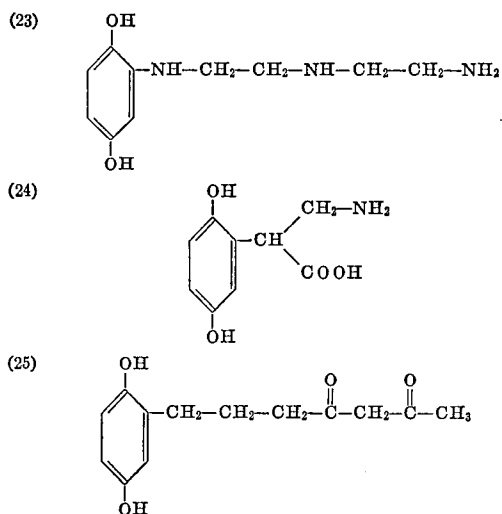


wherein Y, R, R¹, R², R³ and X have the meanings heretofore noted; R⁴ is an alkylene radical, preferably lower alkylene, an arylene, e.g., a phenylene radical, a phenyl-amino radical, or a substituted derivative of these radicals; R⁵ is an alkylene radical; an n is 1 or 2.

As examples of these ligands, mention may be made of the following compounds:



7



Developer ligands of the foregoing description, i.e., ligands of the Formula Y-Z, and the preparation thereof are described and claimed in the copending application of Elbert M. Idelson, Ser. No. 487,054, filed Sept. 13, 1965.

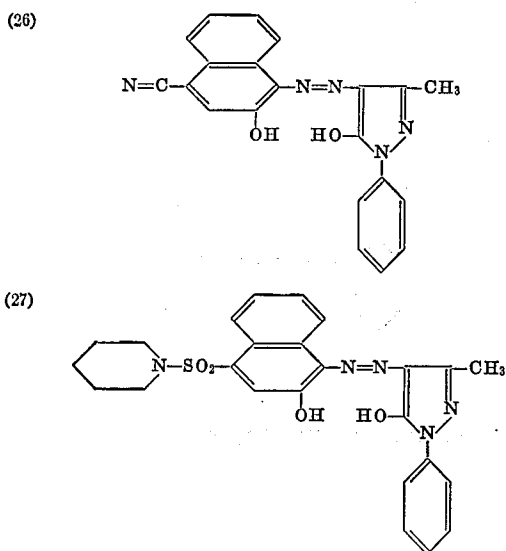
As examples of suitable dyes useful in the preparation of the novel metallized dyes of this invention, mention may be made of azo dyes and, in particular, monoazo dyes having hydroxy and/or carboxy substituents ortho, ortho' to the azo linkage. Such dyes and metal complexes formed therefrom are per se known in the art. (See, for example, "Synthetic Dyes" by Venkataraman, vol 1, chapter XIV, pp. 551-569 (1952).)

A particularly useful class of dyes are the ortho, ortho'-dihydroxy-azo dyes of the formula:

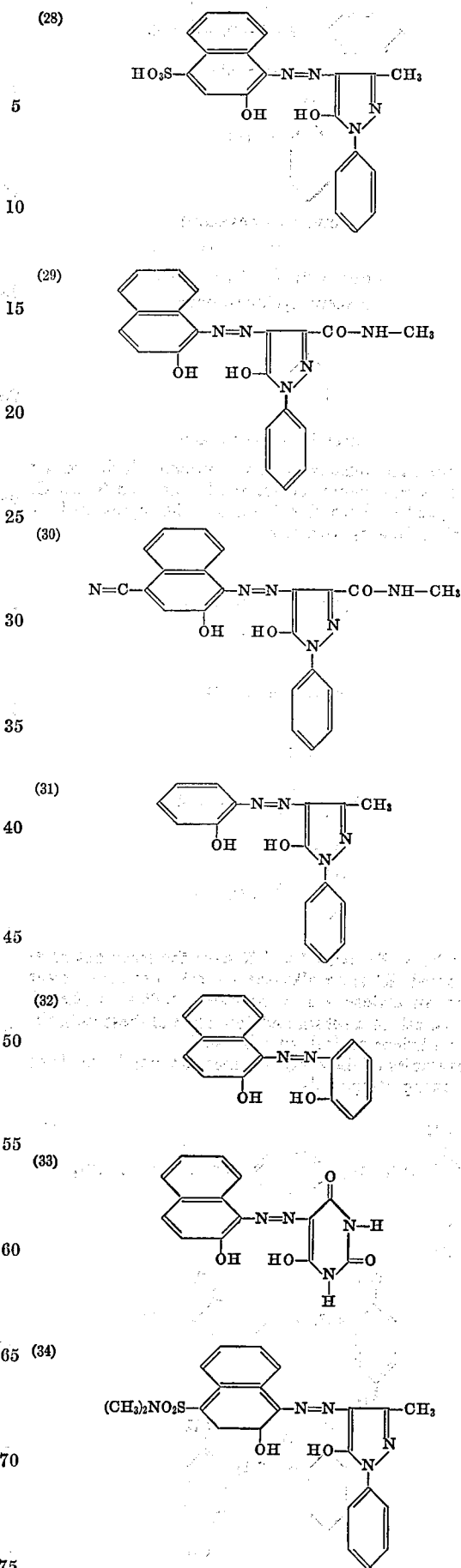


wherein A is an aromatic radical, e.g., a phenyl or naphthyl radical; B is an aromatic or heterocyclic radical, e.g., a phenyl, naphthyl or pyrazolone radical; and each of the hydroxy groups is bonded to one of the A or B moieties in a position ortho to the azo linkage. Included within the scope of the large number of azo dyes of Formula H are those of the phenol, naphthol and pyrazolone series.

As examples of such dyes, mention may be made of the following:

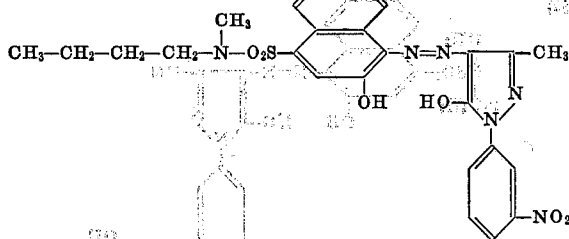


8



9

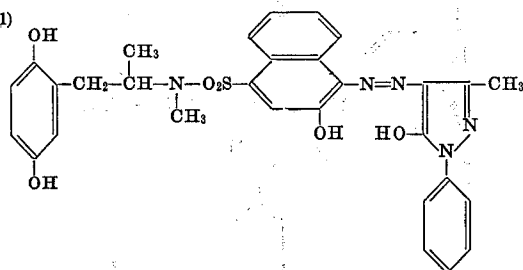
(35)



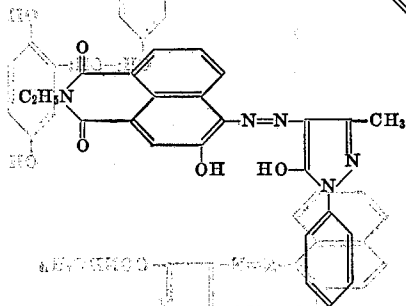
5

10

(41)



(36)



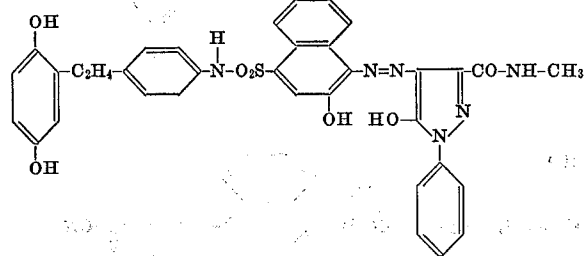
10

01

15

01

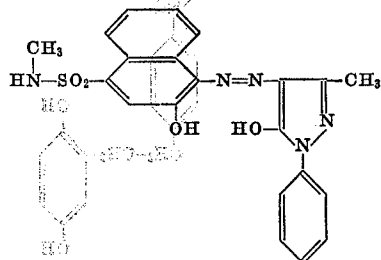
(42)



20

01

(37)



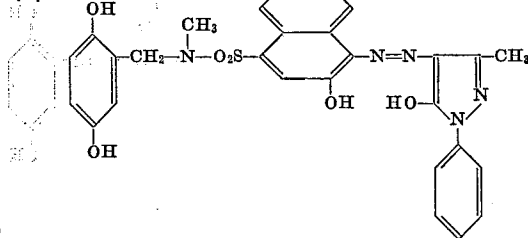
25

01

30

01

(43)



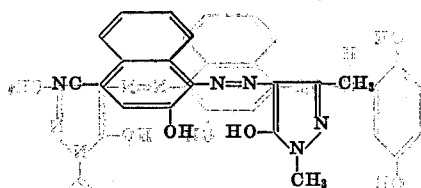
35

01

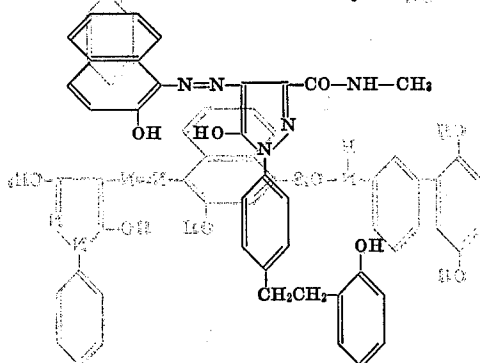
40

01

(38)



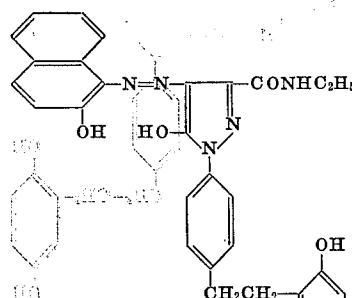
(39)



45

01

(44)



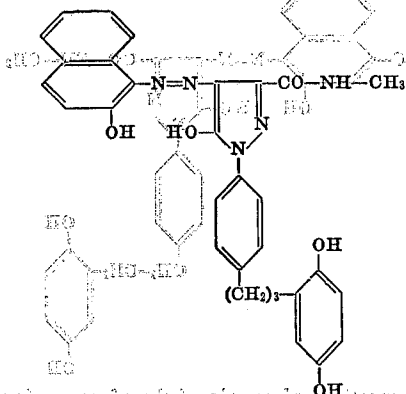
50

01

55

01

(40)



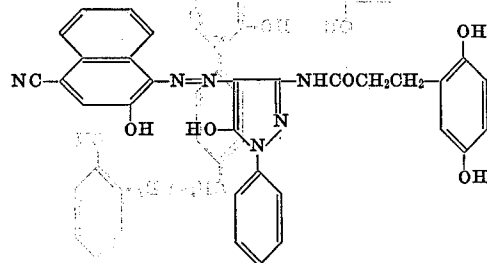
60

01

65

01

(45)



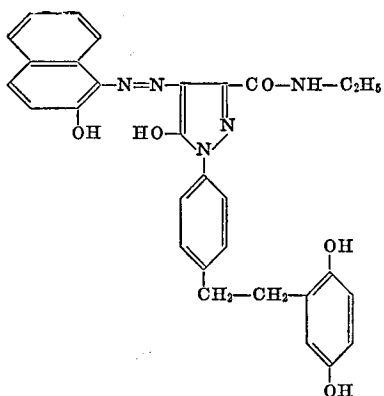
70

01

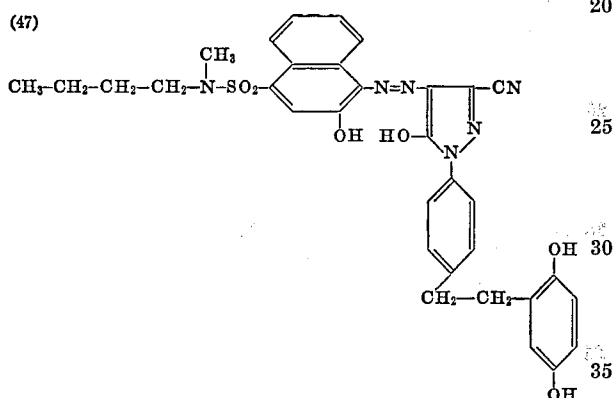
75

11

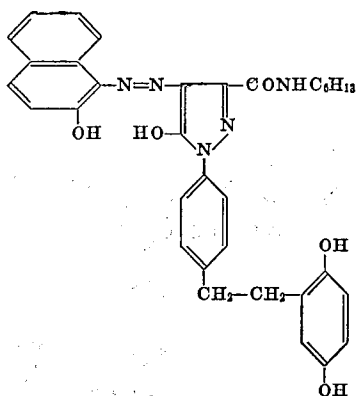
(46)



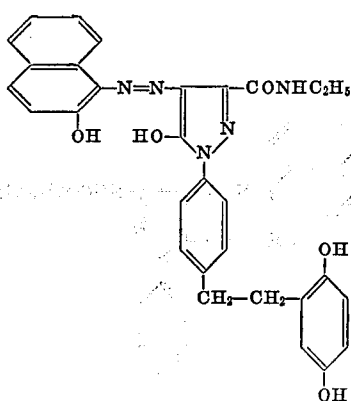
(47)



(48)

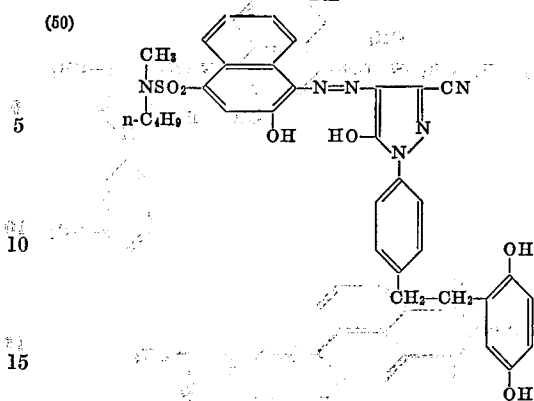


(49)

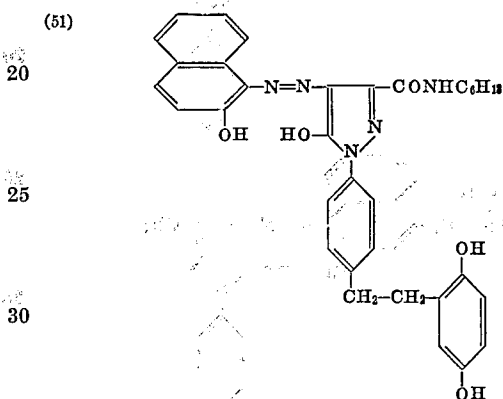


12

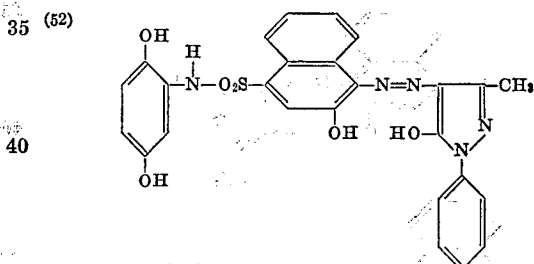
(50)



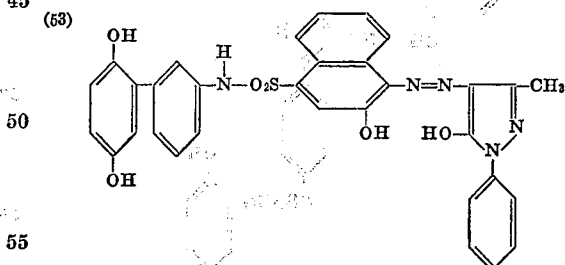
(51)



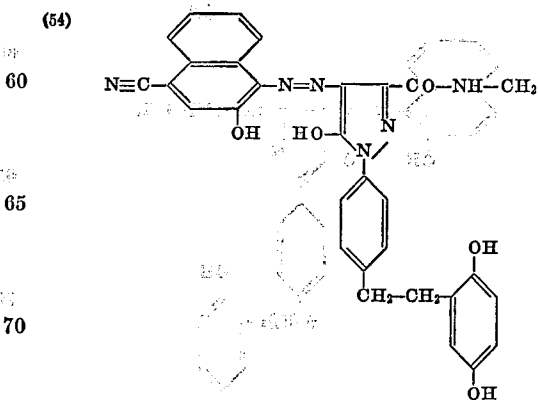
(52)



(53)

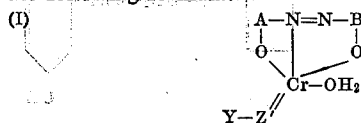


(54)

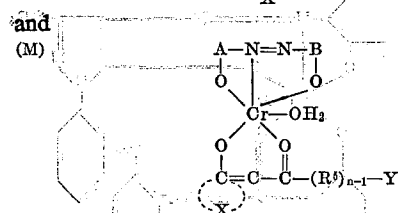
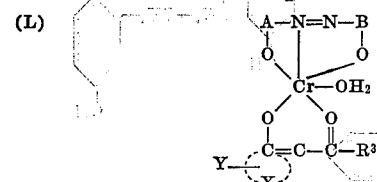
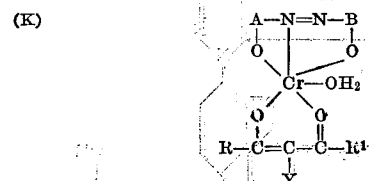
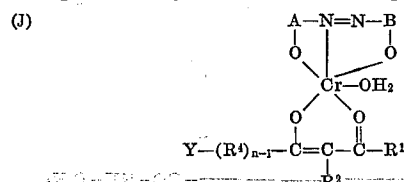


The preparations of certain of the aforementioned azo
75 dyes are disclosed in the copending application of Elbert

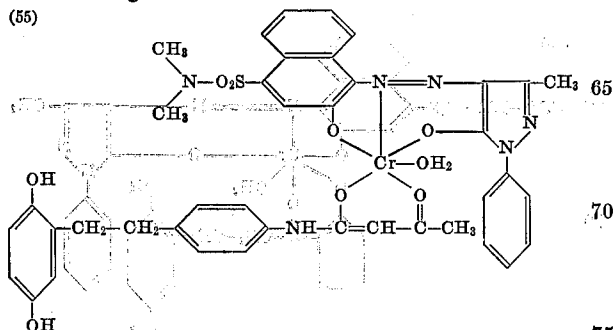
The preferred metal is chromium, in which case this preferred class of metallized dyes may be represented by the following formula:



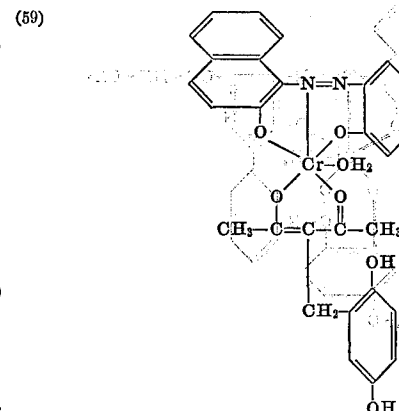
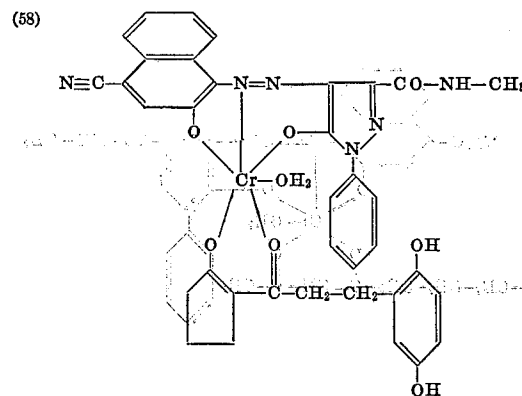
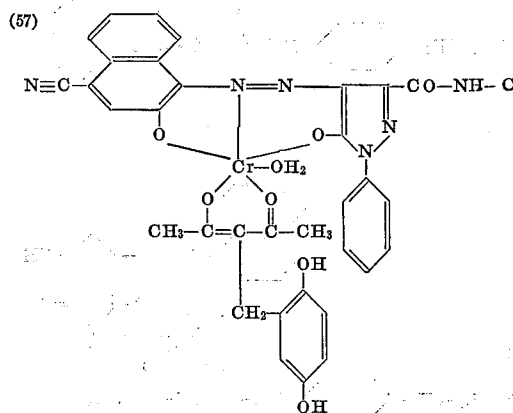
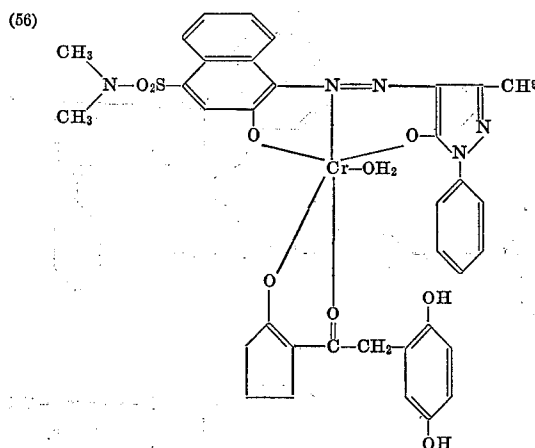
The most preferred class of metallized dyes may thus be represented by one of the following formulae:



(55)

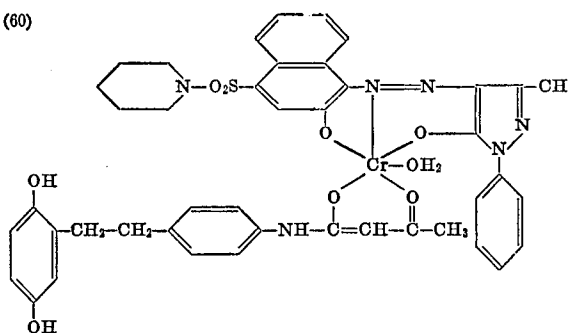


14

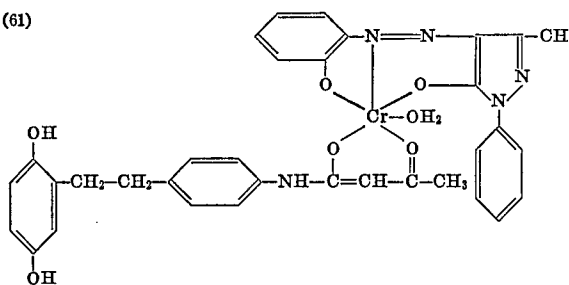


15

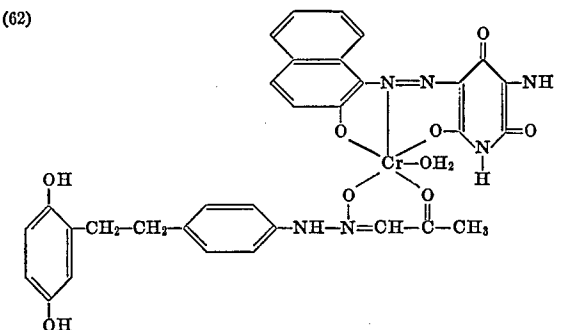
(60)



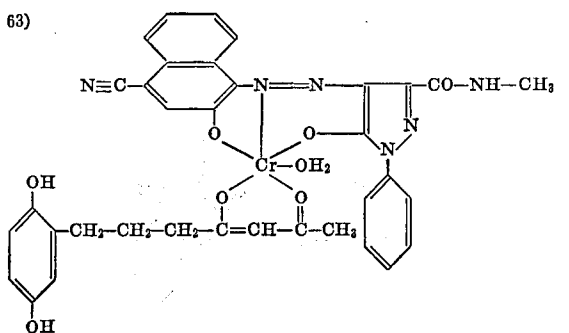
(61)



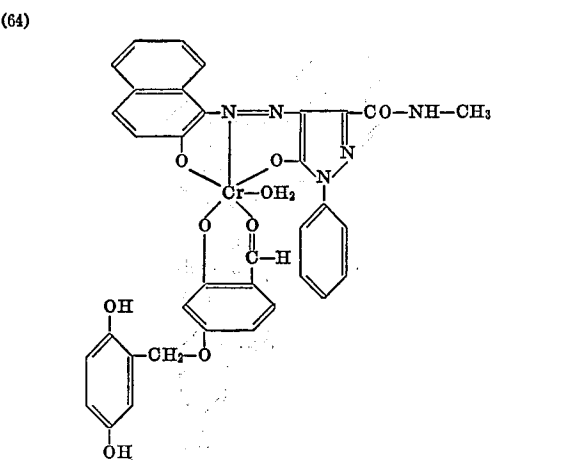
(62)



63)

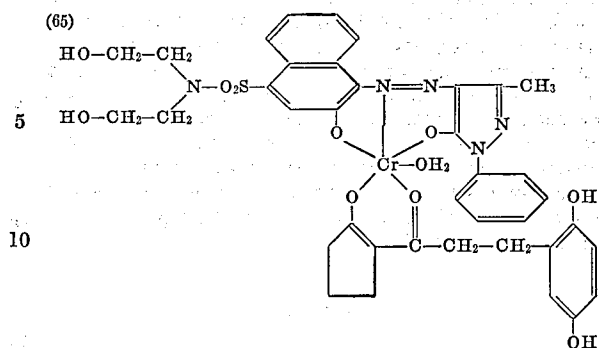


(64)



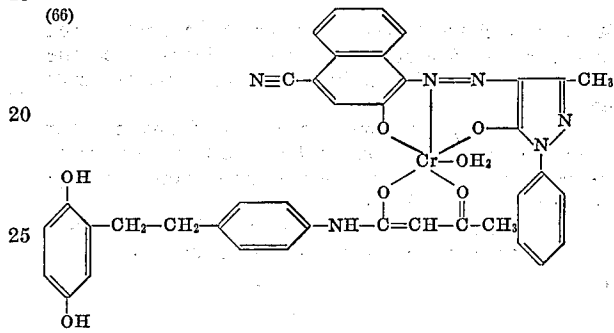
16

(65)



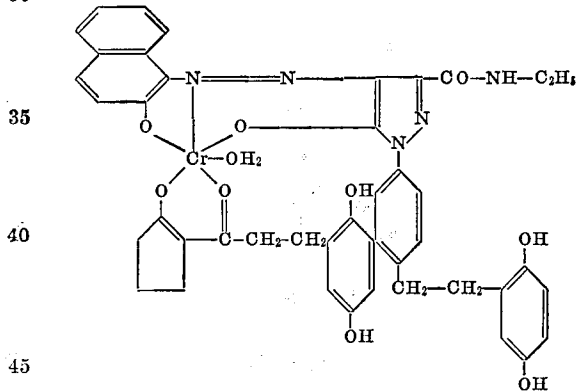
15

(66)

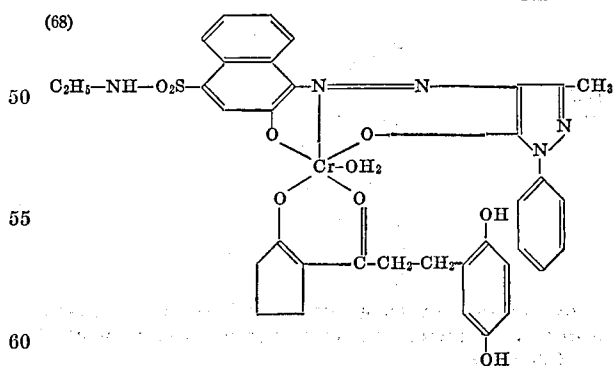


30

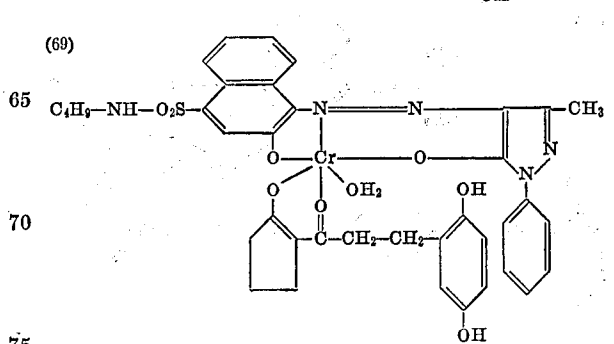
(67)



(68)

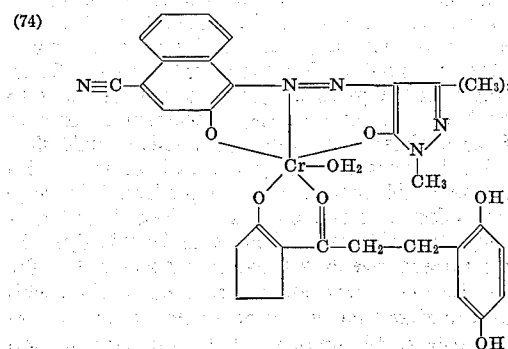
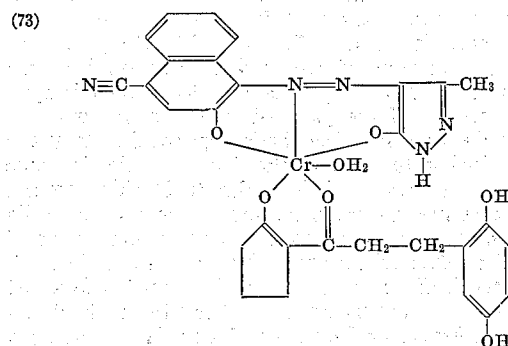
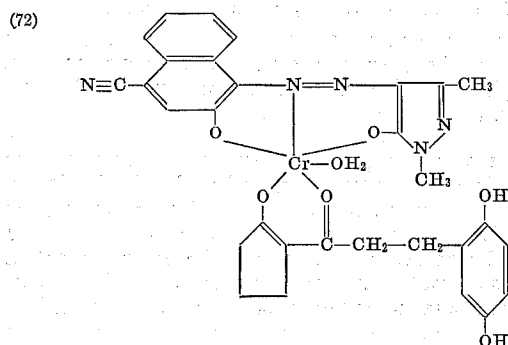
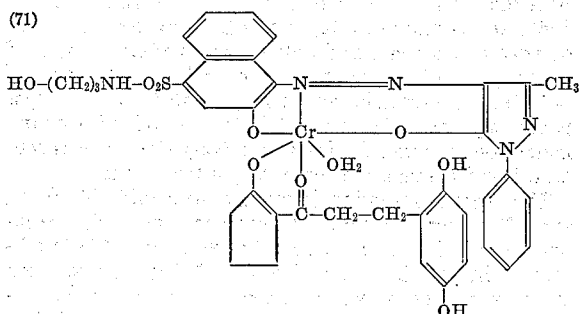
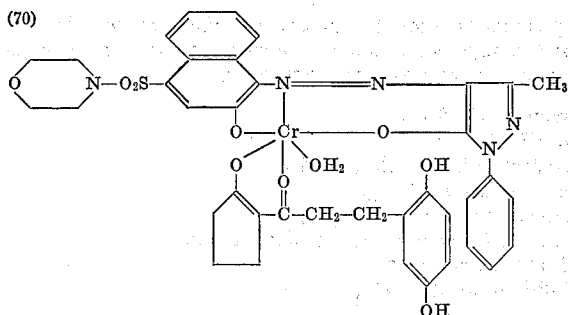


(69)

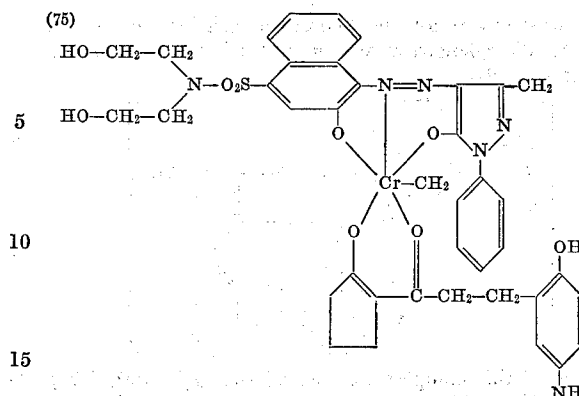


75

17



18



A preferred method of preparing the novel metal-complexed dyes of this invention comprises first forming a complex of a dye having the desired chemical and/or physical properties, e.g., the desired spectral absorption characteristics, and then substituting in this complex a developer-ligand such as described previously.

In some instances it may be desired to convert a metal-complexed dye, e.g., Inochrome Pink N (CI 18761) to a metal-complexed dye having the desired chemical and/or physical properties before or after substitution of the developer-ligand.

The metal-complexed dyes of this invention may also be prepared by reacting the non-complexed dye with the desired developer-ligand and a suitable inorganic salt of the desired metal.

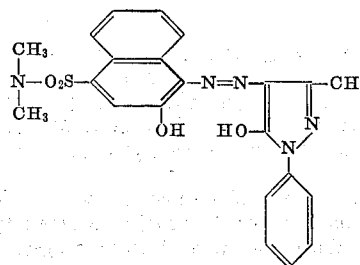
It may also be desirable in some instances to form the complexed dye with the ligand Z and substitute the radical Y on this ligand subsequent to complexing.

In any event, the preparation should be carried out under conditions which preclude oxidation of the dihydroxyphenyl developing function. This may be accomplished by providing an inert atmosphere such as a blanket of nitrogen. In some instances it may be necessary or desirable to protect the hydroxy groups during the reaction, e.g., by alkylation, benzylation or acrylation. As examples of protected dihydroxyphenyl radicals, mention may be made of diacetoxypheyl, dicathoxyphenyl, dimethoxyphenyl, dibenzoyloxyphenyl, etc. 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 desired developer substituent.

The following examples show by way of illustration and not by way of limitation the preparation of the metal-complexed dyes of this invention.

EXAMPLE 1

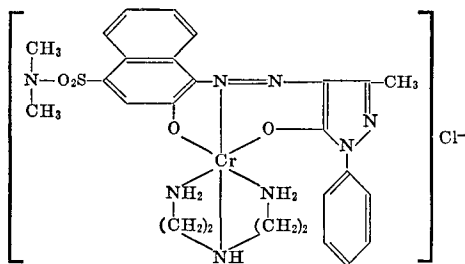
41.6 g. of:



1-phenyl-3-methyl-4-([4',-N,N-dimethylsulfonamido-2'-naphthol-1'-azo]-pyrazolone

was refluxed overnight with 50 g. of $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$ in 1700 ml. of anhydrous ethanol. Half of the solution was stirred for four hours with 85 ml. of diethylenetriamine. It was then poured into a saturated salt solution to precipitate the dye. After standing overnight the solid was collected, dried and extracted with acetone to separate it from the salt. The acetone was evaporated and the solid

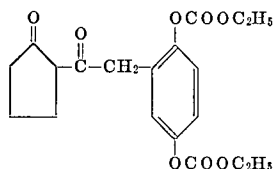
was washed with toluene, filtered and dried to yield 27.4 g. of the diethylenetriamine complex of the 1:1 chrome-complexed dye:



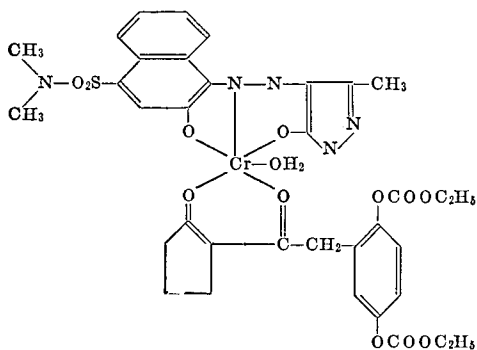
2.0 g. of this complex was heated overnight with 2.0 g. of p - (2,5 - dihydroxyphenethyl)-acetoacetanilide (Formula 10) in 16 ml. of dimethylformamide. The mixture was then refluxed for two hours, after which it was poured into dilute hydrochloric acid, collected and washed with boiling water to yield the chrome complex of Formula 55 which exhibited a $\lambda_{\max}$ of 528 m μ and 563 m μ in methyl Cellosolve; $\epsilon=20,000$ and 19,800.

EXAMPLE 2

5.0 g. of the diethylenetriamine complex [as prepared in Example 1] was heated for 1½ hours in 50 ml. of dimethylformamide with 7.7 g. of 2-(2',5'-bis-cathyloxy-homogentisoyl)-cyclopentanone:



which was prepared in the manner described in Example 4 of the aforementioned copending application, Ser. No. 487,054. The dye solution was precipitated into dilute hydrochloric acid, collected, washed and dried. Trituration with 25 ml. of nitromethane yielded 3 g. of:



which exhibited $\lambda_{\max}$ at 532 m μ and 569 m μ in methyl Cellosolve; $\epsilon=19,600$ and 21,000. Hydrolysis of the latter complex with sodium hydroxide in methyl Cellosolve, and water yielded to complex of Formula 56, having $\lambda_{\max}$ at 530 m μ and 567 m μ in methyl Cellosolve; $\epsilon=21,000$ and 21,600.

The following example shows by way of illustration the photographic use of the novel complexed dyes of this invention in the preparation of color images.

EXAMPLE 3

A photosensitive element was prepared by coating a gelatin subcoated film base at a speed of 10 ft./minute with a solution comprising 0.68 g. of the chrome-complexed dye of (Formula 55) prepared in Example 1, dissolved in 10 cc. of 2% cellulose acetate hydrogen phthalate in acetone. After this coating dried, a green-sensitive silver iodobromide emulsion was coated on at a speed of 5 ft./minute and allowed to dry. This photo-sensitive element was exposed for 1/100 of a second and processed by

spreading between the thus exposed photosensitive element and a superposed image-receiving element, an aqueous processing composition comprising:

- Water—100.0 cc.
- 5 KOH—11.2 g.
- Hydroxyethyl cellulose—3.9 g.
- Benzotriazole—3.5 g.
- Potassium thiosulfate—0.5 g.
- N-benzyl- α -picolinium bromide—2.0 g.
- 10 Zinc nitrate—0.5 g.
- Lithium nitrate—0.5 g.

The image-receiving element was prepared in accordance with the disclosure of Pat. No. 3,362,819, issued Jan. 9, 1968, and comprised a layer of a 2:1 mixture, by weight of polyvinyl alcohol and poly-4-vinylpyridine, a layer of polyvinyl alcohol, and a layer of a half-butyl ester of poly-(ethylene/maleic anhydride) coated on a baryta paper support. After an imbibition period of approximately one minute, the image-receiving element was separated and contained a magenta positive image.

The present invention is readily distinguishable from, and offers certain significant advantages over, the invention described and claimed in U.S. Pat. No. 3,128,164 issued to Milton Green and Leon E. Rubin. The patented invention relates to forming a metal complex of a chelatable dye developer, i.e., a dye containing a silver halide developing substituent bonded to the dye moiety, and employing this metal complex in photographic systems to form a dye image. As distinguished therefrom, the essence of the present invention is the provision of a developing function on the ligand moiety, thereby providing a novel means for obtaining "dye developers" useful in the disclosed photographic systems. Thus, in accordance with the present invention, one may employ chelatable dyes containing no silver halide developing function and which per se are not dye developers, the developing function being supplied by complexing in the disclosed manner. In other words, the present invention provides a novel means for preparing dye developers useful in photographic products, processes and compositions such as are described and claimed in the aforementioned U.S. Pat. No. 2,983,606.

The present invention provides certain significant advantages over the complexed dye developers disclosed in the aforementioned U.S. Pat. No. 3,218,164, chief of which is simplicity of preparation. Whereas both the patent and the instant application employ chelatable dyes, in the practice of the patented invention one must go through the sequence of synthesis steps required to attach the developing function to the dye molecule. In some instances this may be difficult due to blocking groups, inherent competing reactions, etc. Moreover, generally speaking, each reaction step necessary to preparation of the final product affords something less than 100% yield, frequently significantly less, so that the overall yield would not be as great as in the present system wherein the developing function is supplied by complexing. Moreover, when one considers multicolor systems embodying the present invention, e.g., wherein two or three complexes of this invention are employed, it would be apparent that the present invention is more adaptable to large scale production of the final product than the patented system. Thus, for example, in the patented system, one would have to go through the sequence of steps necessary to prepare each of the chelatable dye developers which would then be complexed; whereas in the practice of the present invention, one could prepare a developer-ligand in large scale production, and employ this developer-ligand in a complexing step with each of the complexable dyes. In short, the present invention provides a novel system for preparing dye developers. Moreover, in comparison with the metal-complexed dye developers disclosed in the aforementioned patent, the complexes of the present invention are appreciably more versatile, being easier to synthesize,

affording a greater variety in selection of dye moieties, and being more adaptable to large scale production.

Apart from providing a novel means of associating a developing function with a dye moiety to provide a substance which is both a dye and a silver halide developing agent, the metallized dyes of this invention possess certain other advantages in color photography.

These complexes exhibit greater stability against the color degradation effects of actinic radiation, humidity and/or heat than do the non-complexed dyes. In other words, color images prepared from these complexes may be appreciably more stable than will images prepared from analogous non-complexed dyes.

In addition, the preferred 1:1 complexes are purer in hue than the corresponding 2:1 complexes. Their particularly sharp spectral absorption characteristics with minimal absorption in unwanted regions of the spectrum make it possible to obtain accurate color reproductions of the subject matter.

It will be noted that the dyes contemplated in the preparation of the complexes of this invention include dyes such as those of Formulae 39-54 containing a silver halide developing function. Thus, complexes formed therefrom in accordance with this invention will contain two developing function. In some instances this may be desirable, since it serves to increase the developing potential per unit of complexed dye.

The dye complexes of this invention are also useful in integral multilayer photosensitive elements for use in multicolor diffusion transfer processes. As an example of such photosensitive elements, mentioned may be made of the photosensitive elements disclosed and claimed in U.S. Pat. No. 3,345,163, issued to Edwin H. Land and Howard G. Rogers, wherein at least two selectively sensitizer photosensitive strata are superposed on a single support and are processed, simultaneously and without separation, with a single common image-receiving element. A suitable arrangement of this type comprises a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum, said emulsions having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer. In one of the preferred embodiments of photosensitive elements of this type, the dye developers are disposed in separate alkali-permeable layers behind the photosensitive silver halide emulsion stratum with which they are associated.

The photosensitive elements within the scope of this invention may be used in film units which contain a plurality of photosensitive frames. The photosensitive elements of this invention are especially useful in composite film pack and roll film structures intended for use in a "Polaroid Land Camera," or a similar camera structure such, for example, as the film pack type camera shown in U.S. Pat. No. 2,991,702, issued to Vaito K. Eloranta on July 11, 1961, or the roll film type camera forming the subject matter of U.S. Pat. No. 2,435,717, issued to Edwin H. Land on Feb. 10, 1948. In general, such composite roll films comprise a photosensitive roll, a roll of image-receiving material and a plurality of pods containing an aqueous alkaline processing solution. The rolls and pods are so associated with each other that, upon processing, the photosensitive element may be superposed on the image-receiving element and the pods may be ruptured to spread the aqueous alkaline processing solution between the superposed elements. The nature and construction of the pods used in such units are well known to the art. See, for example, U.S. Pat. Nos. 2,543,181 and 2,634,886, issued to Edwin H. Land.

It will be noted that the liquid processing composition may contain one or more auxiliary or accelerating silver halide developing agents, such as p-methylaminophenol (Metol); 2,4-diaminophenol (Amidol); benzylaminophenol; hydroquinones; a substituted hydroquinone such as tolhydroquinone, phenylhydroquinone, or 4'-methyl-

phenylhydroquinone; or a 3 - pyrazolidone such as 1-phenyl-3-pyrazolidone. These silver halide developing agents are substantially colorless, at least in their unoxidized form. It is possible that some of the dye developer oxidized in exposed areas may be oxidized by an energy transfer reaction with oxidized auxiliary developing agent.

In addition, development may be effected in the presence of an onium compound, particularly a quaternary ammonium compound, in accordance with the processes disclosed and claimed in U.S. Pat. No. 3,173,786, issued to Milton Green and Howard G. Rogers on Mar. 16, 1965, and/or with a color coupler in accordance with the processes disclosed and claimed in the copending application of Howard G. Rogers, Ser. No. 455,302, filed May 12, 1965.

The dye complexes of this invention may be used also in conventional photographic processes, such as tray or tank development of conventional photosensitive films, plates or papers to obtain black-and-white, monochromatic or toned prints or negatives. By way of example, a developer composition suitable for such use may comprise an aqueous solution of approximately 1-2% of the dye, 1% sodium hydroxide, 2% sodium sulfite and 0.05% potassium bromide. After development is completed, any unreacted dye is washed out of the photosensitive element, preferably with an alkaline washing medium or other medium in which the unreacted dye is soluble. The expression "toned" is used to designate photographic images wherein the silver is retained with the precipitated dye, whereas "monochromatic" is intended to designate dye images free of silver.

It should be noted that the dye complexes of this invention are self-sufficient to provide the desired color image and do not depend upon coupling reactions to produce the desired color.

It will be apparent that, by appropriate selection of the image-receiving element from among suitable known opaque and transparent materials, it is possible to obtain either a colored positive reflection print or a colored positive transparency. Likewise, the inventive concepts herein set forth are adaptable for multicolor work by the use of special photographic materials, for example, film materials of the type containing two or more photosensitized elements associated with an appropriate number of image-receiving elements and adapted to be treated with one or more liquid processing compositions, appropriate dye developers suitable to impart the desired subtractive colors being incorporated in the photosensitized elements or in the liquid processing compositions. Examples of such photographic materials are disclosed in U.S. Pat. No. 2,647,049 to Edwin H. Land.

As examples of useful image-receiving materials, mention may be made of nylon, e.g., N-methoxymethyl-polyhexamethylene adipamide, polyvinyl alcohol, and gelatin, particularly polyvinyl alcohol or gelatin containing a dye mordant such as poly-4-vinylpyridine. The image-receiving element also may contain a development restrainer, e.g., 1-phenyl-5-mercaptotetrazole, as disclosed in U.S. Pat. No. 3,265,498 issued to Howard G. Rogers and Harriet W. Lutes.

The dye complexes herein set forth are also useful in the formation of colored images in accordance with the photographic products and processes described and claimed in U.S. Pat. No. 2,968,554, issued to Edwin H. Land on Jan. 17, 1961.

The novel complexes herein disclosed are also suitable for use as dyes for textile fibres, such as nylon.

In the preceding portions of the specification, the expression "color" has been frequently used. This expression is intended to include the use of a plurality of colors to obtain black.

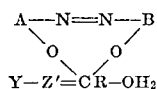
Since certain changes may be made in the above products, compositions and processes without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description

23

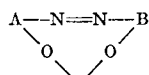
shall be interpreted as illustrative and not in a limiting sense. and

What I claimed is:

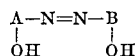
1. A chromium-complexed dye of the formula:



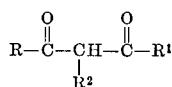
wherein



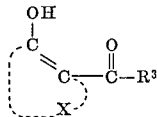
is the radical of an ortho, ortho'-dihydroxy-azo dye of the formula:



A is an aromatic radical selected from the group consisting of phenyl and naphthyl radicals; B is a member of the group consisting of phenyl, naphthyl and pyrazolone radicals; Y is ortho or para-dihydroxyphenyl or ortho or para-dihydroxyphenyl substituted by chloro, methyl, phenyl or methoxy which may be bonded directly or linked indirectly to the remainder of the molecule through a divalent linking group selected from the group consisting of amino-phenalkyl-thio, aminoalkylamino, aminoalkyl, aminophenalkyl, alkyl in said groups being lower alkyl, aminophenyl and aminophenoxy; and Z' is a substantially colorless bi-dentate ligand within the formulae:

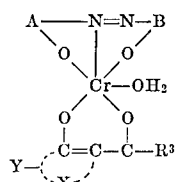
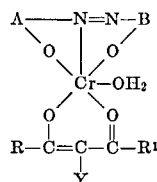
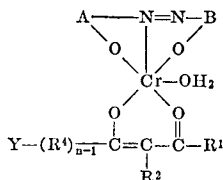


or

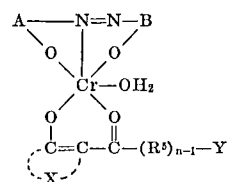


wherein R and R¹ are each selected from the group consisting of hydrogen, alkyl, lower alkoxyalkyl and alkyl-amino wherein each of said alkyl moieties is lower alkyl, phenyl and phenylamino; R² is selected from the group consisting of hydrogen, lower alkyl and phenyl; R³ is selected from the group consisting of hydrogen, hydroxyl and lower alkyl; X represents the atoms necessary to complete a member of the group consisting of cyclopentyl, cyclohexyl and phenyl.

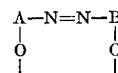
2. A chrome-complexed dye selected from the group consisting of those of the formulae:



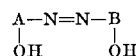
24



wherein

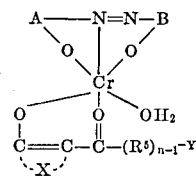


is the radical of an ortho, ortho'-dihydroxy-azo dye of the formula:

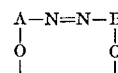


A is selected from the group consisting of phenyl and naphthyl radicals; B is selected from the group consisting of phenyl, naphthyl and pyrazolone radicals; R and R¹ are each selected from the group consisting of hydrogen, alkyl, lower alkoxyalkyl, alkylamino, wherein each of said alkyl moieties is lower alkyl, phenyl and phenyl-amino; R² is selected from the group consisting of hydrogen, lower alkyl and phenyl; R³ is selected from the group consisting of hydrogen, hydroxyl and lower alkyl; R⁴ is selected from the group consisting of lower alkylene, phenylene and phenylamino; R⁵ is lower alkylene; Y is ortho or para-dihydroxyphenyl or ortho or para-dihydroxyphenyl substituted by chloro, methyl, phenyl or methoxy which may be bonded directly or linked indirectly to the remainder of the molecule through a divalent linking selected from the group consisting of amino-phenalkylthio, aminoalkylamino, aminoalkyl, aminophenalkyl, alkyl in said groups being lower alkyl, aminophenyl and aminophenoxy; X represents the atoms necessary to complete a member of the group consisting of cyclopentyl, cyclohexyl and phenyl, and n is a positive integer from 1 to 2.

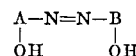
3. A chromium-complexed dye of the formula



wherein



is the radical of an ortho, ortho'-dihydroxy-azo dye of the formula:

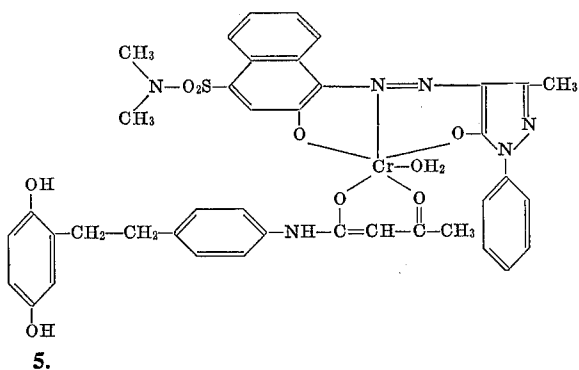


A is selected from the group consisting of phenyl and naphthyl radicals; B is selected from the group consisting of phenyl, naphthyl and pyrazolone radicals; R⁵ is lower alkylene; X represents the atoms necessary to complete a

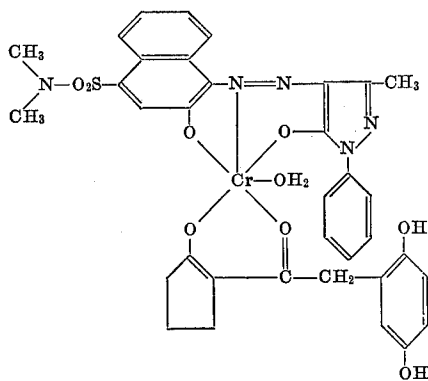
25

member of the group consisting of cyclopentyl, cyclohexyl and phenyl; Y is paradihydroxyphenyl; and n is two.

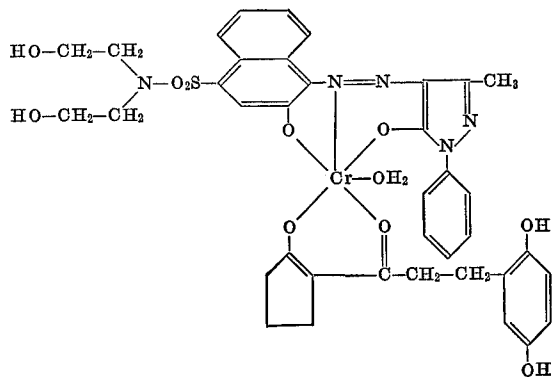
4.



5.

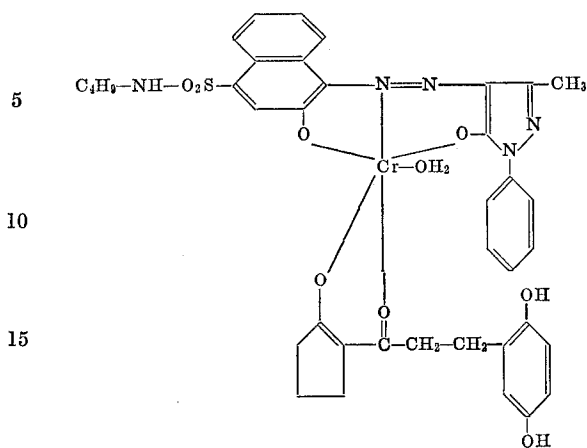


6.

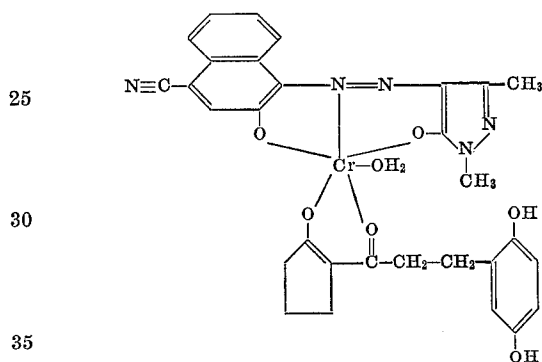


26

7.



8.



References Cited

UNITED STATES PATENTS

40	2,708,193	5/1955	Pfitzner et al.	260—147
	2,871,232	1/1959	Csendes	260—147
	3,301,845	1/1967	Hasokawa et al.	260—146
	3,356,671	12/1967	Johnson et al.	260—145

45 FLOYD D. HIGEL, Primary Examiner

U.S. Cl. X.R.

8—41; 96—63, 64, 66; 260—154, 162, 463, 519, 559, 562, 570.5, 590, 592, 600

50