United States Patent Office 3,752,836 Patented Aug. 14, 1973



3,752,836

# CHROME COMPLEXED AZOMETHINE DYE

Elbert M. Idelson, Newton, Mass., assignor to Polaroid Corporation, Cambridge, Mass.

No Drawing. Original application June 4, 1969, Ser. No. 830,499, now Patent No. 3,597,200. Divided and this application Oct. 23, 1970, Ser. No. 83,595
Int. Cl. C07f 11/00
U.S. Cl. 260—438.5 R 3 Claims

## ABSTRACT OF THE DISCLOSURE

Novel metal-complexed azomethine dyes which are also silver halide developing agents, novel non-complexed azomethines useful in the preparation of the same, and novel photographic systems and procedures employing the aforementioned metal complexes to obtain color images, particularly systems and procedures for preparing color images by diffusion transfer.

This application is a divisional of U.S. patent application Ser. No. 830,499 filed June 4, 1969, now U.S. Pat. No. 3,597,200.

## BACKGROUND OF THE INVENTION

U.S. Pat. No. 2,983,606, issued to Howard G. Rogers, discloses diffusion transfer processes for forming color images wherein a photographic element comprising an exposed silver halide emulsion is developed in the presence of a dye developer (dye which is also a silver halide developing agent) to impart to a superposed image-receiving layer a reversed or positive dye image of the developed image. To obtain multicolor images, use is made of an integral multilayer photosensitive element comprising at least two selectively sensitized emulsion layers superposed on a single support, each emulsion layer having a dye developer associated therewith. A suitable arrangement of this type for forming multicolor images 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, the emulsions having associated therewith, respectively, a cyan dye developer, a magenta dye deveolper and a yellow dye developer. Multilayer photosensitive elements of this nature are described with more particularity and claimed in U.S. Pat. No. 3,345,163 issued to Edwin H. Land and Howard G. Rogers.

U.S. Pat. No. 3,218,165, issued to Milton Green and Leon E. Rubin, discloses that dye developers which form stable coordination complexes with metals may be complexed to provide for use in the aforementioned systems dye developers exhibiting increased stability against the color degradation effects of actinic radiation, humidity and/or temperature variations.

The copending application of Elbert M. Idelson, Ser. No. 486,853, filed Sept. 13, 1965, now U.S. Pat. No. 3,453,107, discloses a class of 1:1 chrome-complexed azo dye developers for use in the aforementioned processes for forming color transfer images. A preferred group of these dyes are 1:1 chromium-complexed hydroxynaphthyl-azo-pyrazolones which have been found to be particularly useful magenta dye developers to be associated with a green-sensitive emulsion layer in the aforementioned multilayer elements.

The present invention is directed to another class of metal-complexed dyes for use in diffusion transfer color processes such as are described in the aforementioned U.S. patents.

## SUMMARY OF THE INVENTION

The present invention is directed to 1:1 chrome-complexed azomethine dye developers for use in preparing monochromatic or multicolor diffusion transfer images.



The preferred complexes constitute yellow dye developers which may be used in association with the blue-sensitive emulsion in the aforementioned multilayer elements.

As was mentioned previously, this invention relates to color photography, and more particularly, to metal-complexed azomethine dyes which are also silver halide developing agents and to photographic products, processes and compositions employing the same to obtain color transfer images.

A primary object of this invention, therefore, is to provide novel metal-dye complexes.

Another object is to provide novel 1:1 chromium-complexed dyes.

Still another object is to provide novel metal-complexed azomethine dyes containing a single coordinated metal atom per molecule of dye.

Yet another object is to provide novel photographic products, processes and compositions utilizing the aforementioned dyes to obtain images in color.

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

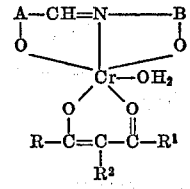
The invention accordingly comprises the several steps and the relation and order of one or more of such steps with respect to each of the others, and the product possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope 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.

The metal-dye complexes to which this invention is directed are 1:1 chromium-complexed azomethine dyes, i.e., dyes containing a single coordinated chromium atom per molecule of dye, the dye complexes being further characterized by containing a silver halide developing function, preferably a p-dihydroxyphenyl silver halide developing function, as either a part of the dye molecule, i.e., an azomethine dye developer; or contained on the ligand moiety employed in preparing the dye complex; or both, as will be more apparent hereinafter.

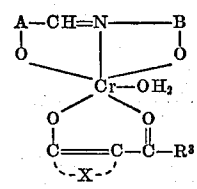
The novel dye complexes of this invention may be represented as being 1:1 chromium-complexed azomethine dyes within one of the following formulae:

(A)

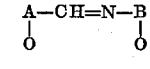


and

(B)

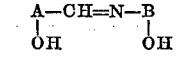


wherein: A is a phenyl or naphthyl radical; B is a phenyl, naphthyl or heterocyclic radical, e.g., a pyrazolyl radical, said



comprising the radical of an ortho, ortho'-dihydroxy-azomethine dye of the formula:

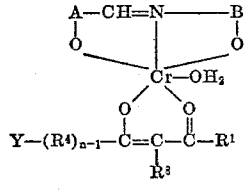
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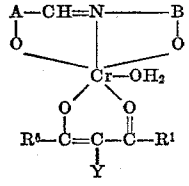
including azomethine dye developers, i.e., azomethine dyes wherein the A and/or B moieties contain a silver halide developing substituent; X represents the atoms necessary to complete an aliphatic, aromatic or heterocyclic ring, preferably the atoms necessary to complete a 5- or a 6-membered aliphatic ring or a benzene ring, which benzene ring may be substituted and may contain a radical comprising a silver halide developing function; R is alkyl, fluoroalkyl, alkoxyalkyl, the alkyl moiety preferably being lower alkyl, phenyl, phenylamino, or a radical comprising a silver halide developing function; $R^1$ is alkyl, fluoroalkyl, alkoxyalkyl, the alkyl moiety preferably being lower alkyl, phenyl, or phenylamino; $R^2$ may be hydrogen, lower alkyl, phenyl, or a radical comprising a silver halide developing function; and $R^3$ may be lower alkyl, hydroxyl, hydrogen, or a radical comprising a dihydroxyphenyl silver halide developing function, provided that where X represents the atoms necessary to complete an aromatic ring, $R^3$ cannot be hydroxyl; and provided further that at least one of said moieties which may contain or comprise a dihydroxyphenyl silver halide developing function does so, i.e., that at least one developing function is contained on the dye molecule and/or the ligand moiety contributing the two oxygen atoms bonded to the chromium atom.

In a preferred embodiment of the invention, the ligand moiety contains a silver halide developing function. The preferred 1:1 complexes of this invention may, therefore, be defined as being complexes within one of the following formulae:

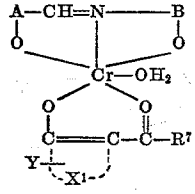
(D)



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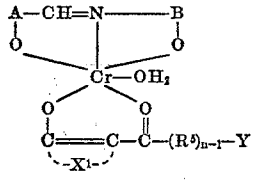


(F)



and

(G)



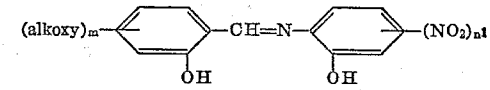
wherein A, B, and $R^1$ have the meanings heretofore given (the A and/or B moiety may also contain a silver halide developing function, as heretofore mentioned), $R^4$ is alkylene, preferably lower alkylene, phenylene, phenylamino, or a substituted derivative thereof; $R^5$ is alkylene, preferably lower alkylene, $R^6$ is hydrogen, alkyl, preferably lower alkyl, alkoxyalkyl, alkylamino, phenyl, phenylamino, or a substituted derivative thereof; $R^7$ is lower alkyl, hydroxyl or hydrogen, $R^8$ is hydrogen, lower alkyl or phenyl; $X^1$ represents the atoms necessary to complete a five or a six-membered aliphatic ring or a benzene ring; and Y is a radical comprising a silver halide developing substituent, preferably a p-dihydroxyphenyl silver halide developing substituent. As used throughout the specification and claims, the term "lower alkyl" refers to alkyl substituents containing 1–6 carbon atoms, e.g., methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl, hexyl, etc.

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-dimethylhydroquinone; 2,5,6-trimethyl-hydroquinone, etc., all of which are per se 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. 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. 3,019,107; alkyl-thio 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 preferred azomethine dyes contemplated by the present invention are yellow dyes of the formula:

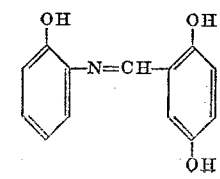
(H)



wherein the alkoxy moiety contains 1–5 carbon atoms, e.g., methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, and pentoxy; $n^1$ and $m$ are positive integers from 1–2. The nitro substituent (or substituents) is (are) preferably meta to the nitrogen linkage. Where $m$ is two, the alkoxy substituents are preferably the same and are substituted in the ortho and para positions, respectively. In the most preferred yellow azomethines, $n^1$ is 1 and $m$ is 2. The respective benzene groups may also contain other substituents contributing to the spectral, physical and/or chemical properties of the dye, as will be appreciated by those skilled in the art. They may, for example, contain hydroxyl, amino or carboxy substituents.

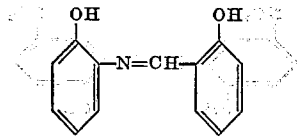
As examples of azomethine dyes useful in the preparation of the novel complexes of this invention, mention may be made of the following:

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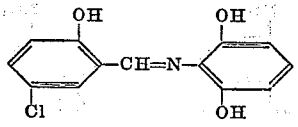


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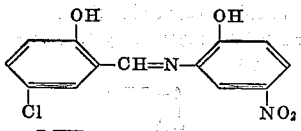
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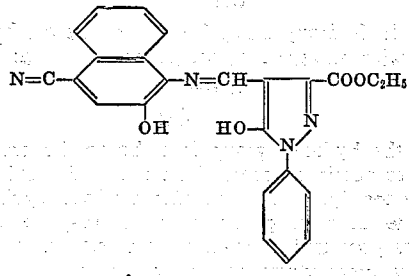
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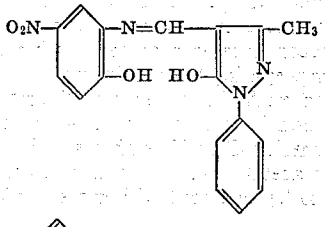
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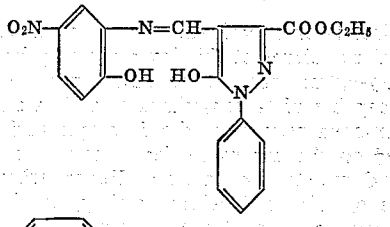
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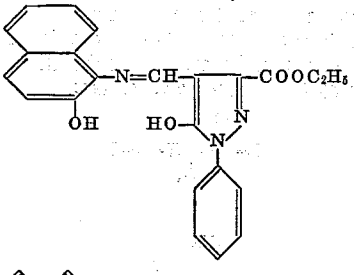
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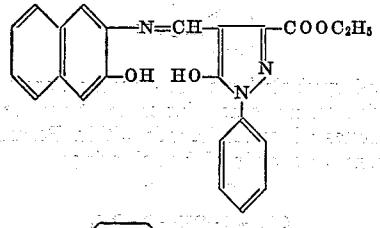
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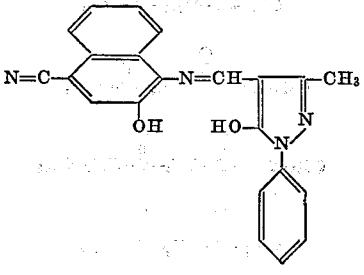
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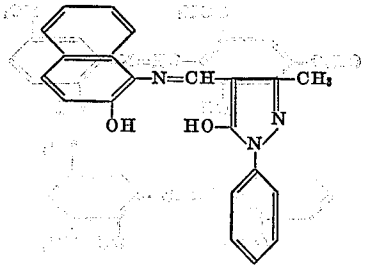


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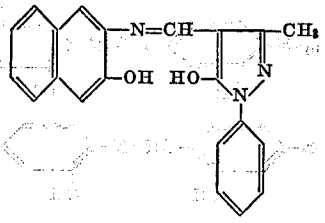


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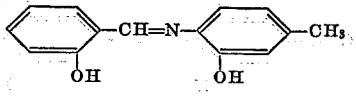
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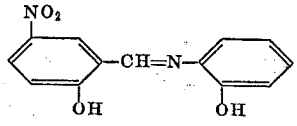
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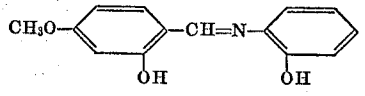
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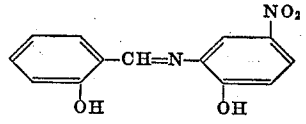
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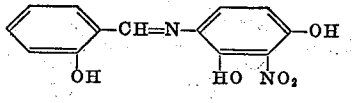
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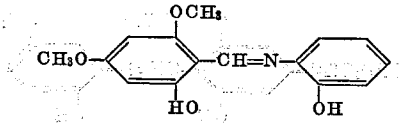
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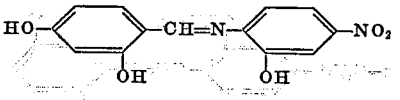
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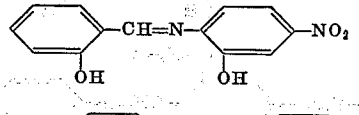
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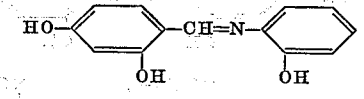
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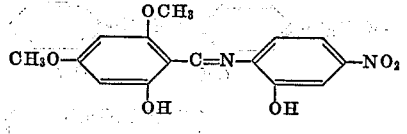
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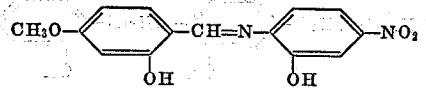
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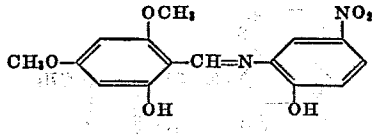


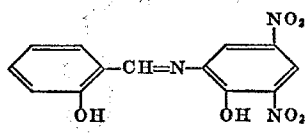
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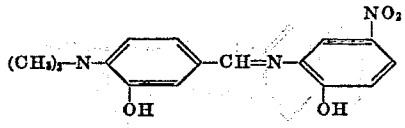


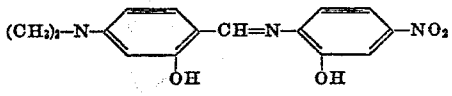
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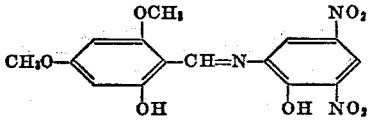


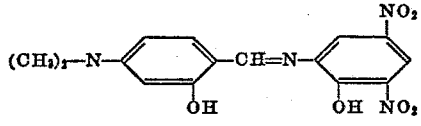
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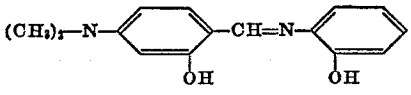
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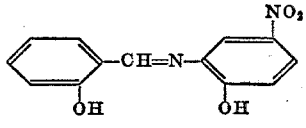
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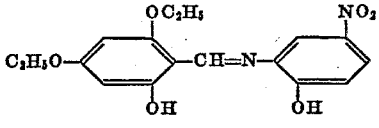
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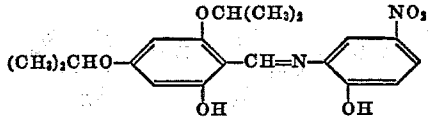
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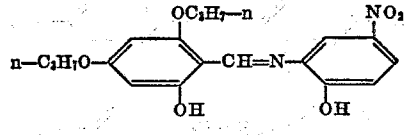
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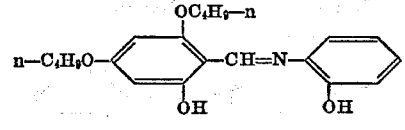
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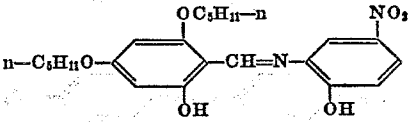
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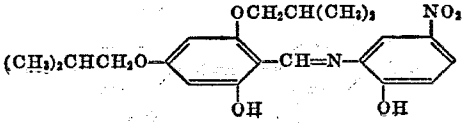
(32)


(33)


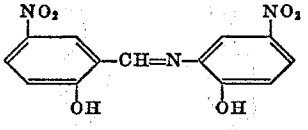
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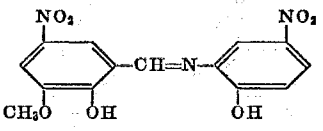
(35)


(36)


(37)




(38)


(39)


Where not readily available, the non-complexed azomethine dye may be obtained by reacting an aldehyde of the general formula:



wherein the hydroxy group is ortho to the aldehyde substituent, with an amine of the general formula:

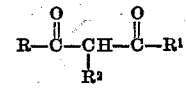


wherein the hydroxy group is ortho to the amine substituent, to obtain an azomethine dye of Formula C.

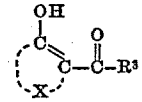
Where the dye moiety includes a dihydroxyphenyl silver halide developing substituent, it may be desirable to use its protected derivative form, e.g., diacyloxy, dibenzyloxy, dicathyloxy, etc., in which event, the desired dihydroxy substituents may be readily obtained by hydrolysis in accordance with procedures heretofore known in the art for preparing the developers.

A preferred method for preparing the novel complexes of this invention is to react the non-complexed dye, i.e., a dye of Formulae C or H, with a suitable chromic salt, e.g., chromic acetate, chromic chloride, etc. and the desired ligand to be described with more particularity hereinafter.

The ligands or coordination agents employed to form the metal complexes of this invention may be defined as $\beta$-hydroxy-$\alpha,\beta$-unsaturated carbonyl compounds, or compounds capable of tautomerizing to such a structure. As was mentioned previously, the developer moiety may be contained on the dye molecule; it may be contained on the ligand moiety; or on both. Hence, where the dye molecule contains a developer moiety, i.e., is a dye developer, the ligand need not contain a developer. Those ligands which need not contain a developer and which may be employed in the practice of this invention may be represented by the following formulae:

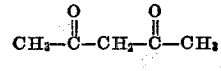
(I)


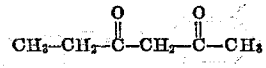
and

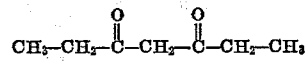
(J)


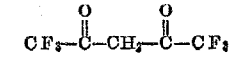
wherein: all symbols have the meaning heretofore given in connection with the description of Formulae A and B.

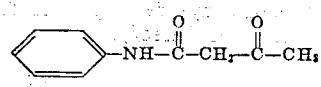
As examples of useful ligands within Formulae I and J, mention may be made of the following:

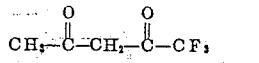


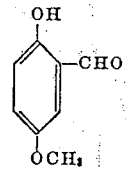


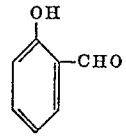


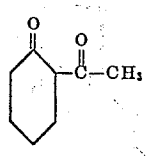


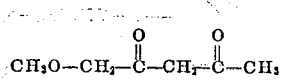


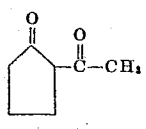


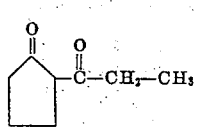






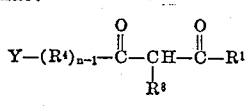




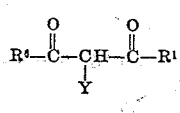


Those ligands containing a silver halide developing function ("developer-ligands") may be represented by the following formulae:

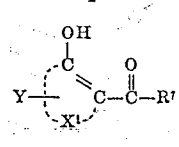
(K)



(L)

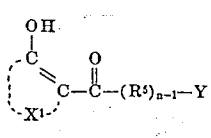


(M)



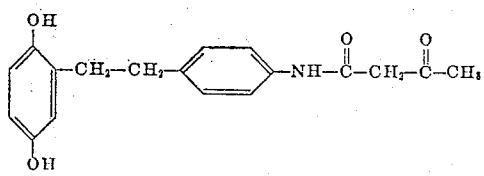
and

(N)

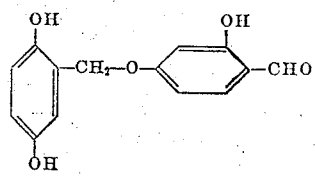


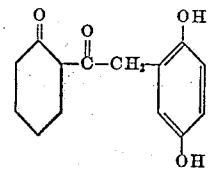
wherein: all symbols have the meanings described in connection with the discussion of Formulae D–G.

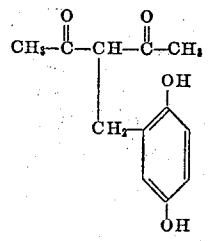
As examples of useful developer-ligands, mention may be made of the following:

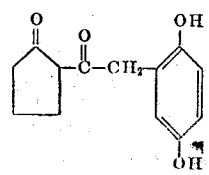


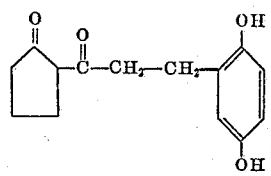


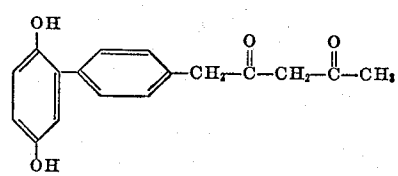


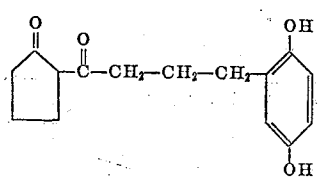












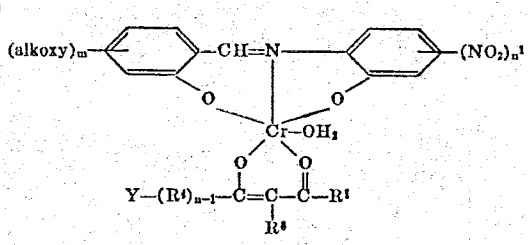
Developer-ligands of the foregoing desciption are described and claimed in the copending application of Elbert M. Idelson, Ser. No. 487,054, filed Sept. 13, 1965, now abandoned, and per se comprise no part of this invention.

In some instances it may be desirable to employ the protected form of the developer ligand, e.g., ligands wherein the hydroxy groups are replaced by acyloxy, benzyloxy, cathyloxy, alkoxy or acetoxy substituents, in which case the metal-complexed dye may be converted to the dihydroxyphenyl silver halide developing agent-containing ligand developer by hydrolysis, e.g., with a suitable mineral acid, at some stage after complexing.

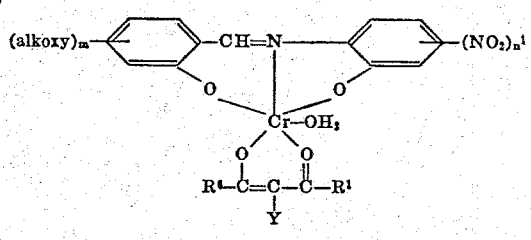
The preferred metal complexes of this invention are those formed by complexing an azomethine of Formula H with a developer-ligand of Formulae K, L, M or N.

These preferred complexes may be represented as being within one of the following formulae:

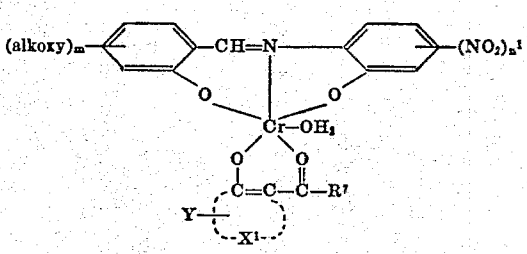
(O)



(P)

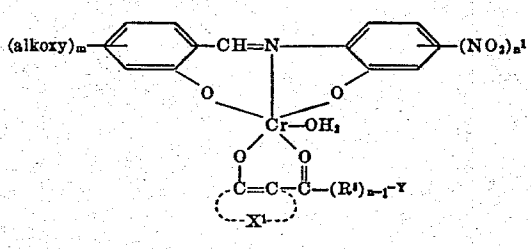


(Q)



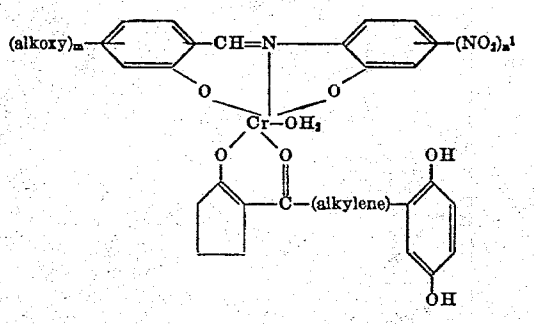
and

(R)



The most preferred metal complexes are those of the following formula:

(S)

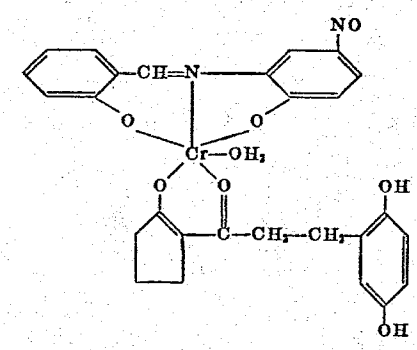


wherein the alkylene moiety contains 1–4 carbon atoms, i.e., methylene, ethylene, propylene, isopropylene, butylene or isobutylene.

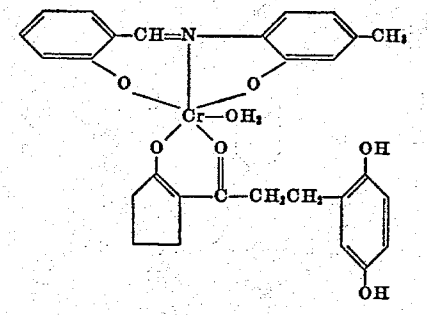
Metal complexes within the scope of Formulae O through S per se claimed in the copending application of Arthur B. Goulston and Paul S. Huyffer, Ser. No. 830,480 filed June 4, 1969.

The following are illustrative of the novel 1:1 chromecomplexed azomethine dye developers of this invention (or protected derivatives thereof):

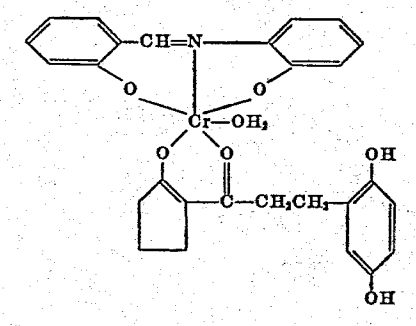
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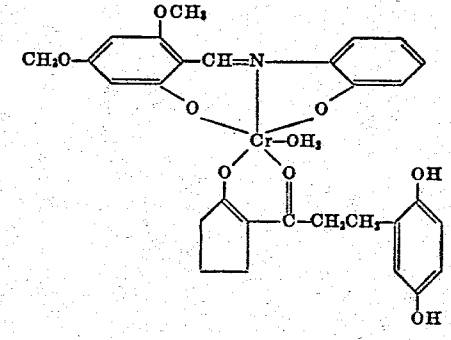
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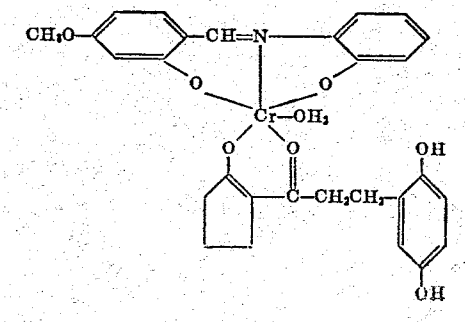
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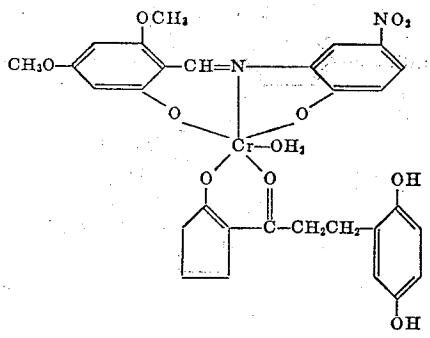
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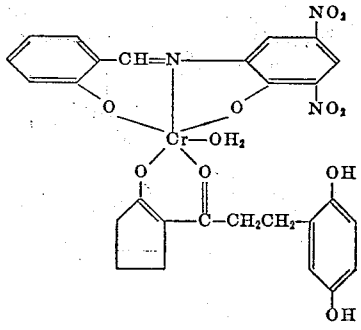
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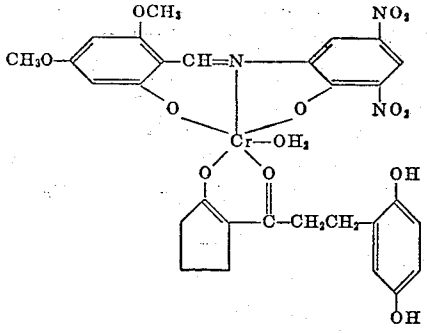
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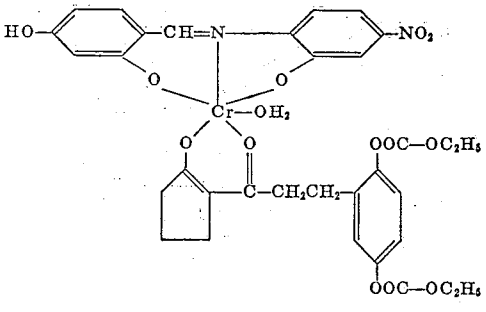
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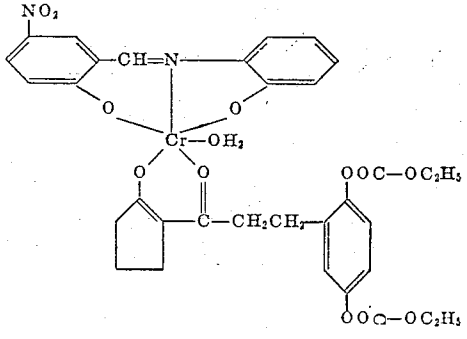
(47)



(48)

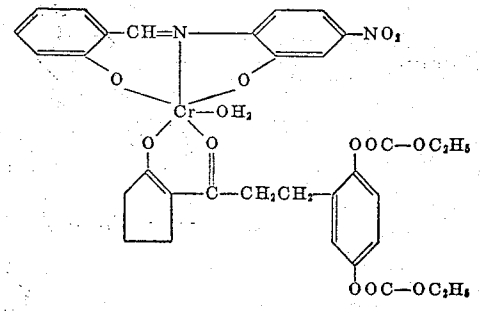


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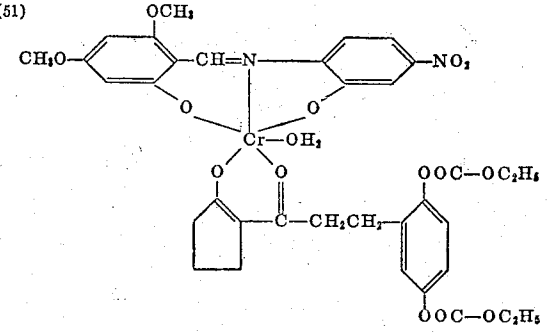




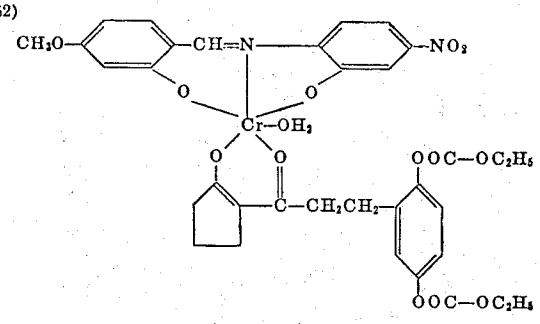
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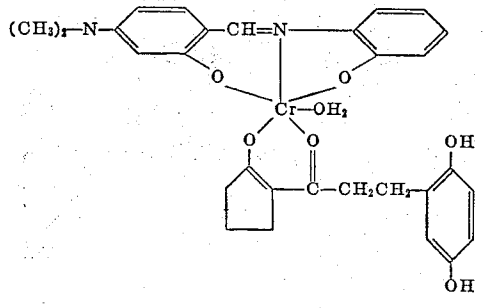
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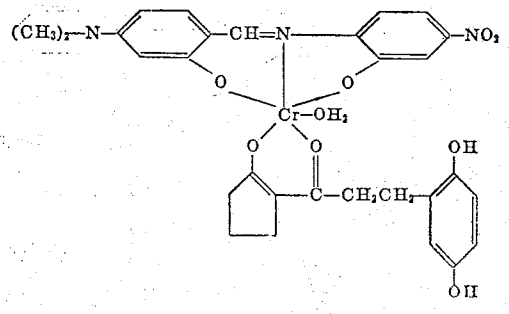
(52)



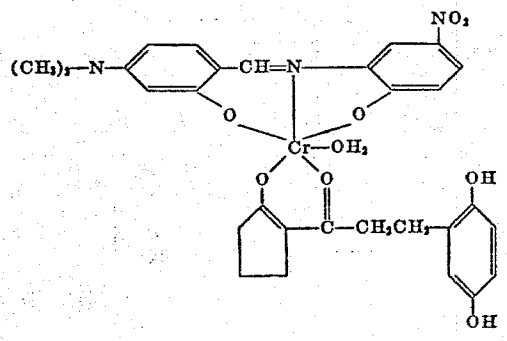
(53)



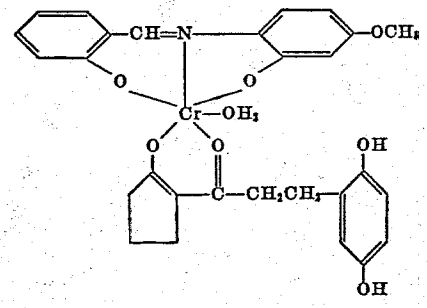
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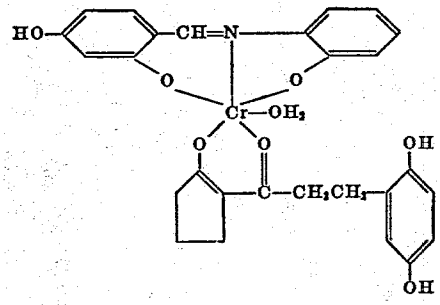
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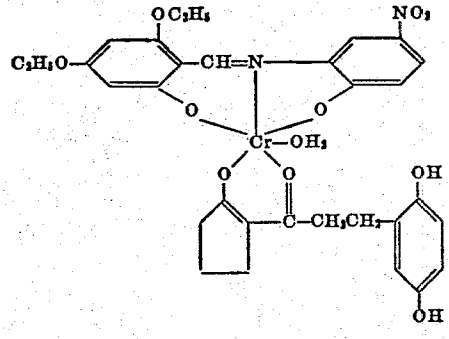
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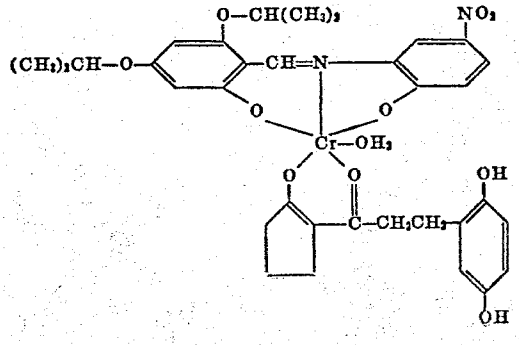
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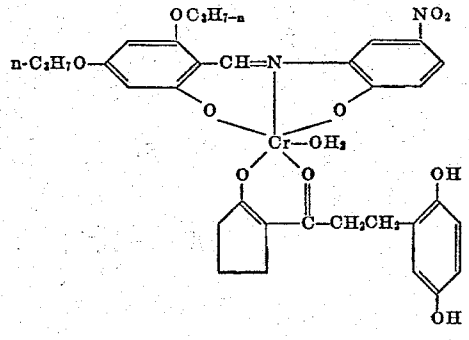


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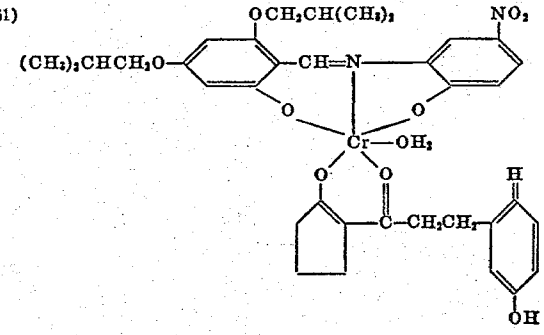




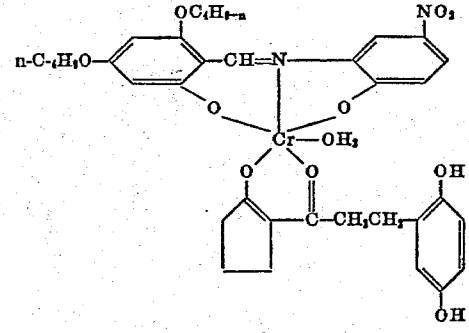
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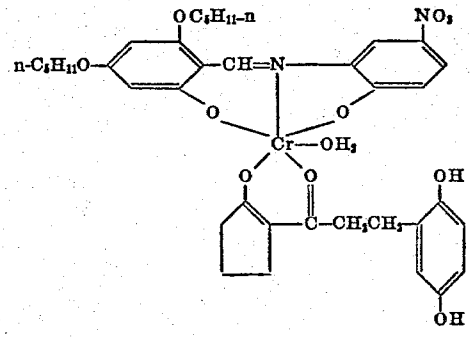
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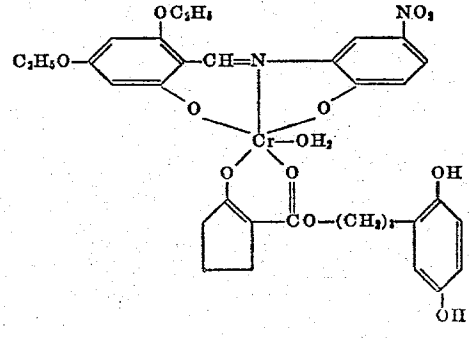
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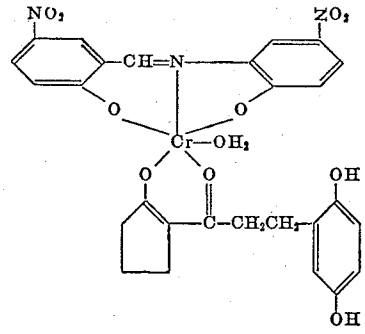
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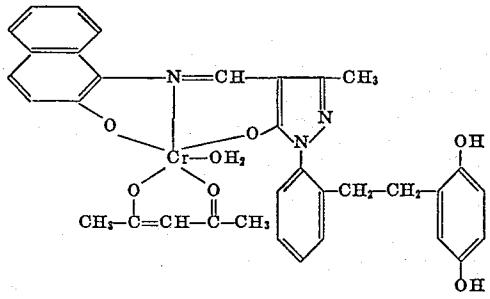
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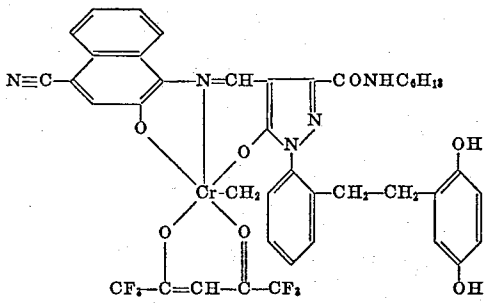
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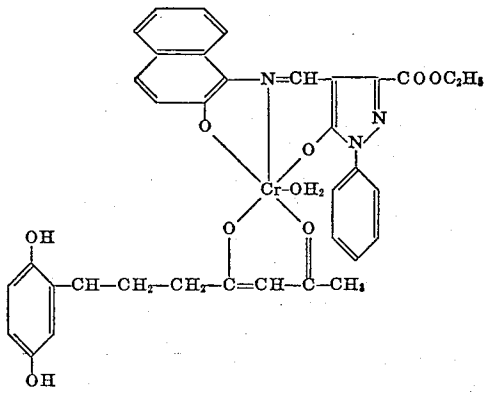
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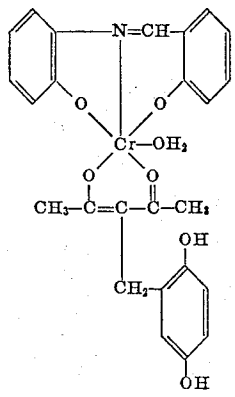
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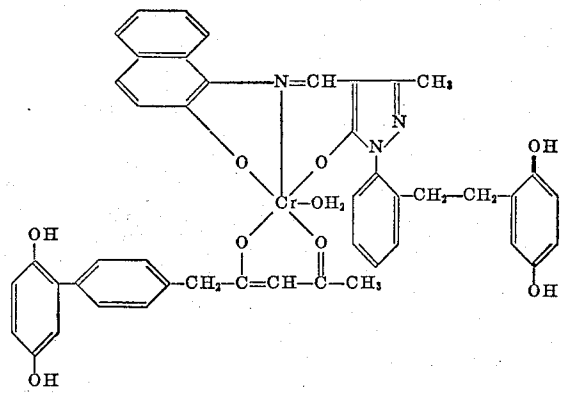


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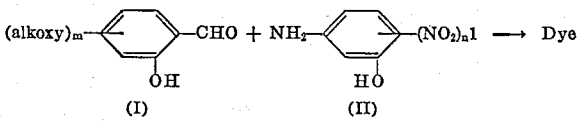




It will be noted that the complexes of Formulae 48–52 are protected derivatives, the desired dihydroxyphenyl analogue being readily obtainable by hydrolysis, as previously mentioned.

As was mentioned previously, azomethine dyes useful in the preparation of the metal complexes of this invention may be obtained by reacting the desired aldehyde with an amine.

Thus, for example, the preferred azomethines of Formula H may be obtained by the following reaction:



The following examples illustrate the preparation of azomethine dyes within the scope of Formula H.

Example 1

0.1 m. each of the aldehyde (I) and amine (II) were heated in 100 ml. of methyl Cellosolve for three hours on a steam bath. The resulting mixture was cooled to about 10° C. filtered. To the solid product so obtained 100 ml. of methyl Cellosolve were added and this mixture was heated on a steam bath for about thirty minutes and then cooled to about 10° C. The resulting product was separated by filtration, washed with cold methyl Cellosolve and methanol and then air-dried to obtain an 80–90% yield of an azomethine dye of Formula H.

Example 2

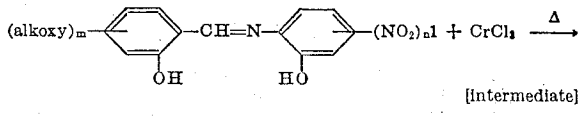
In the manner described in Example 1, 2-hydroxy-4,6-diisopropoxy-benzaldehyde and 2-hydroxy-5-nitro-aniline were reacted to yield the azomethine dye of Formula 33, M.P. 243° C.

In like manner were prepared the compounds of Formule 22, M.P. 276–276.5; Formula 23, M.P. 194–195; Formula 24, M.P. 303–4; Formula 28, M.P. 282–3; Formula 32, M.P. 247–8; Formula 34, M.P. 233–4; Formula 35, M.P. 228–9; Formula 36, M.P. 208–9; and Formula 37, M.P. 232–3, all melting points given in ° C.

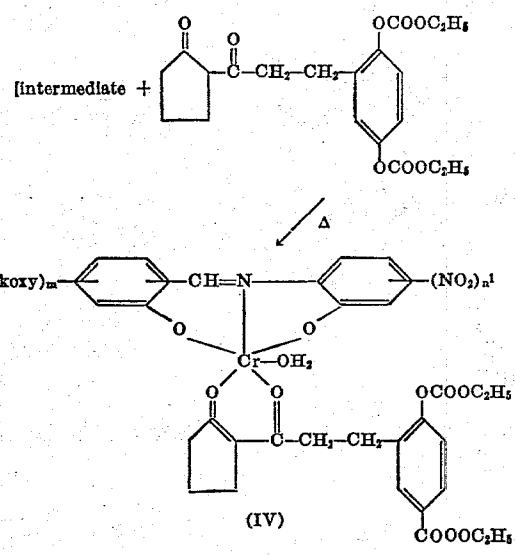
To prepare the metal complexes of this invention, the azomethine dye, e.g., a dye as prepared in the above examples, may be reacted with a chromic salt and the desired ligand. In instances wherein the developer is on the ligand, the protected derivative thereof, e.g., the dicathyloxy analogue, is preferably employed to yield the corresponding chrome complex wherein the dihydroxy substituents are protected. The desired dihydroxy analogue is then obtained by hydrolysis.

This series of reactions may be illustrated as follows:

(1)

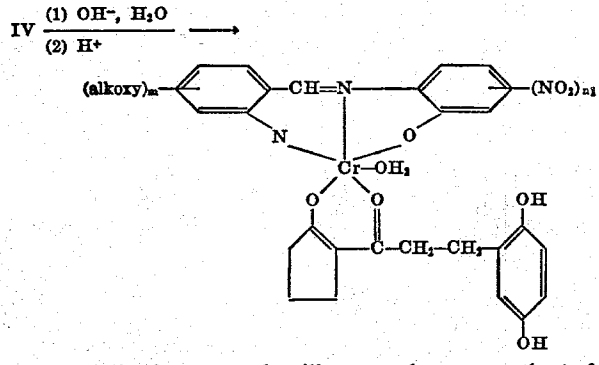


(2)




(IV)

(3)




The following examples illustrate the preparation of the chrome complexes of this invention in accordance with the foregoing sequence of reactions.

Example 3

0.06 m. of the azomethine of Formula H and 0.12 m. (32 g.) of $CrCl_3,6H_2O$ were refluxed in 1 liter of methanol for 72 hours. 0.09 m. (36 g.) of the protected ligand-developer (III) and 90 ml. of triethylamine were then added and the resulting slurry was refluxed for 1 hour and poured while still hot into a solution of 3 l. water/90 ml. conc. HCl. The resulting gummy product solidified on trituration and the cloudy supernatant liquid was decanted off. The product was washed several times with water by decantation, filtered off and air-dried to yield the protected chrome complex (IV). This complex was dissolved in 500 ml. of methyl Cellosolve by warming on a steam bath. The solution was cooled to room temperature and deaerated with nitrogen for 15–20 minutes. A deaerated solution of 36 ml. each of 50% W/W aqueous sodium hydroxide solution and water was added all at once, producing a slight exotherm, and a moderately rapid stream of nitrogen was passed in for about 30 minutes. A deaerated solution of 120 ml. conc. HCl/1 l. water was added, first slowly and then more rapidly as the initial foaming subsided. The resulting gummy product soon solidified and the cloudy supernatant liquid was decanted off. The resulting chrome complex (V) was washed a few times with hot water by decantation, filtered off, dissolved in 500 ml. of hot methyl Cellosolve, and again filtered. 1 liter of a hot filtered solution of 1% HCl was poured into the above filtrate. A gummy product soon solidified and the supernatant liquid was decanted off. This product was washed several times with hot water by decantation, finally sucked dry and dried in vacuo. It was then dissolved in 500 ml. of warm acetone, the solution was filtered, and 1.5 l. of hexane was poured into it while stirring. The resulting gummy product was triturated until it solidified, filtered off, washed several times with hexane and dried in vacuo to yield the pure chrome complex (V).

Example 4

In the manner described in Example 3, the chrome-complexed dye of Formula 59 was prepared, a yellow dye developer, $\lambda_{max}$=400, $\epsilon$=18,600; $\lambda_{max}$=440, $\epsilon$=17,400 in methyl Cellosolve.

Example 5

In like manner, the chorme-complexed dye of Formula 58 was prepared, $\lambda_{max}$=400, $\epsilon$=18,400; $\lambda_{max}$=440, $\epsilon$=17,200 in methyl Cellosolve.

Example 6

In like manner, the chrome-complexed dye of Formula 60 was prepared, $\lambda_{max}$=400–410, $\epsilon$=20,400; $\lambda_{max}$=440, $\epsilon$=19,400 in methyl Cellosolve.

The following examples illustrate the use of the novel complexed dyes of this invention in color photography.

Example 7

The dye complex of Example 6 was precipitated from methyl Cellosolve into distilled water at a pH of about 1. The resulting precipitate was washed ten times and collected each time by means of a centrifuge. To the resulting paste was added 10% by weight (based on dye solids) of "Lomar D" (trademark of Nopco Chemical Co. for a sodium salt of a condensed mononaphthalene sulfonic acid dispersant) and a high shear mechanical agitator was then applied to form a dispersion. 10 cc. of the resulting dye dispersion (containing about 1.0 g. of dye) were mixed with 7.7 g. of 15% gelatin, 26.2 cc. of water and 2.8 cc. of 1% "Aerosol O.T." (trademark of American Cyanamid Co. for dioctyl ester of sodium sulfosuccinic acid wetting agent) and this mixture was then coated upon a subcoated film base at a calculated dry coverage of about 103 mg. of complexed dye developer per square foot of surface area. After this coating dried, a blue-sensitive silver iodobromide emulsion was coated thereupon at a coverage of about 100 mg. of silver per square foot of surface area. The resulting photosensitive element was exposed and the thus exposed element was then processed by spreading between the exposed photosensitive element and a superposed image-receiving element at a gap of about .0026 inch an aqueous processing composition comprising the following proportion of ingredients:

| | | |
|---|---|---|
| Water | cc. | 100.0 |
| Potassium hydroxide | g. | 11.2 |
| Hydroxyethyl cellulose | g. | 3.8 |
| Benzotriazole | g. | 3.5 |
| Potassium thiosulfate | g. | 0.5 |
| N-benzyl-α-picolinium bromide | g. | 2.0 |
| Zinc nitrate | g. | 0.5 |
| Lithium nitrate | g. | 0.5 |
| 4'-methylphenyl hydroquinone | g. | 0.2 |

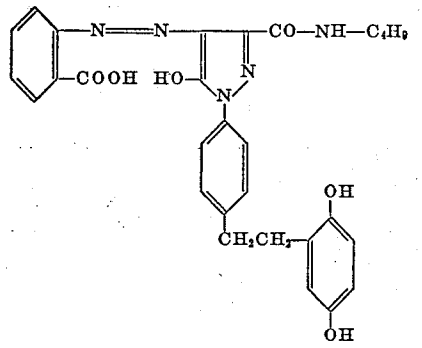
The image-receiving element comprised a baryta paper support carrying, in order, a layer of a partial butyl ester of poly-(ethylene/maleic anhydride); a layer of polyvinyl alcohol; and a layer of a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine. [Image-receiving elements of this type are disclosed in U.S. Pat. No. 3,362,819 issued to Edwin H. Land.] After an imbibition period of about 60 seconds, the two elements were separated to reveal a yellow transfer image having a $D_{max}$ of 1.90.

The novel chrome-complexed azomethines of this invention exhibit markedly greater stability against the color degradation effects of actinic radiation than do non-complexed dyes of similar color. This is consistent with the knowledge of those skilled in the art that dye complexes are more light stable, e.g., fade less or are less prone to color shift, than non-complexed dyes.

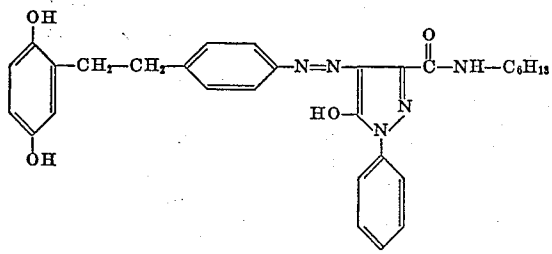
On the other hand, the present invention provides dyes possessing a color which makes them superior to prior dye complexes for multicolor photography. Thus the metal-complexed yellow dye developers of this invention give more faithful color recordation in multicolor photographic elements such as mentioned above including a yellow dye developer, a magenta dye developer and a cyan dye developer, than the heretofore known metal-complexed yellow dye developers. Stated another way, the metal-complexed yellow azomethines of this invention have superior spectral absorption curves giving less absorption in unwanted regions of the spectrum than do prior complexed yellow dye developers.

In summation, the yellow dye developers of this invention are more stable than prior non-complexed yellow dye developers and may be of superior color; while on the other hand, they possess a better color for multicolor photography than prior complexed yellow dye developers, although they are not necessarily more stable than these prior yellow complexes. It will thus be seen that the present invention combines desirable features of prior yellow dye developers not heretofore obtainable to provide dye developers which, considering the combined features of color and stability, are superior to those heretofore known.

The foregoing may be illustrated by comparing illustrative yellow dye developers of this invention with (I) a typical yellow complex of the prior art, the chromium complex of the yellow azo dye:




and (II) a standard test or control non-complexed yellow dye developer employed in evaluating the merits of yellow dye developers:




In order to do so, color images employing each of these dye developers were prepared under test conditions using standard controls so that the only essential difference in the three was the particular dye developer employed. In this instance, for each of the yellow dye developers to be compared, a photosensitive element comprising an emulsion layer and the dye developer layer was exposed and developed in the manner described in Example 7.

The resulting three dye images were subjected to a standard light stability test by placing under a Xenon arc weatherometer for predetermined periods of time and calculating the percent of fading (loss of density) after each period of time.

The results comparing two of the yellow dye developer complexes of this invention with the aforementioned azo yellow dye developer complex and control non-complexed dye developer are shown in the following table.

TABLE

| | Percent fading after— | | | |
|---|---|---|---|---|
| | 6 hrs. | 12 hrs. | 24 hrs. | 48 hrs. |
| Formula 60 | 0 | 0 | 0 | 0 |
| Formula 59 | 0 | 0 | 0 | 0 |
| Azo yellow complex | 2 | 6 | 3 | 5 |
| Non-complexed yellow | 13 | 35 | 63 | 88 |

As far as color is concerned, the dye developers of formulae 59 and 60 were both superior to the azo yellow complex and non-complexed yellow controls, particularly in that the dye developers of this invention both exhibited substantially greater of the desired absorption in the blue region of the spectrum.

The dye developers of this invention are also quite stable to pH change. Thus, for example, whereas the aforementioned non-complexed yellow is pH sensitive and at a pH of between 5–7 shifts bathochromically towards the orange, the present dye developers do not.

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, mention may be made of the photosensitive elements disclosed and claimed in U.S. Pat. No. 3,345,163 of Edwin H. Land and Howard G. Rogers, wherein at least two selectively sensitized 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.

They may also be employed, for instance, in photosensitive elements of the type disclosed in U.S. Pat. No. 3,414,644 issued to Edwin H. Land.

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," sold by Polaroid Corporation, Cambridge, Mass. 02139, 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. Pats. 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 toluhydroquinone, 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 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, now U.S. Pat. 3,502,468.

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 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 of 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.

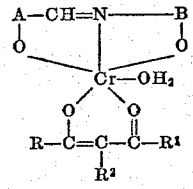
The novel complexes herein disclosed are also suitable for use as dyes for textile fibers, such as nylon.

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.

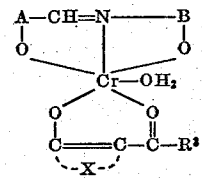
Since certain changes may be made in the above products, compositions and processes without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

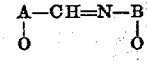
**1.** A 1:1 chrome complexed azomethine dye within the formulae:



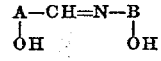
and



wherein A is a phenyl or naphthyl nucleus, B is a phenyl or a naphthyl radical, said



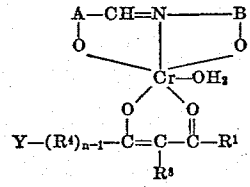
is the radical of an ortho, ortho'-dihydroxy-azomethine dye of the formula:

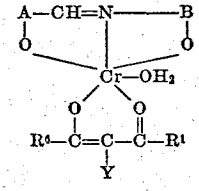


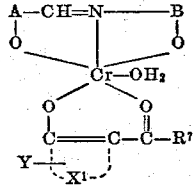
X represents the atoms necessary to complete an aliphatic or aromatic ring, R and $R^1$ are each selected from the group consisting of alkyl, fluoroalkyl, alkoxyalkyl, phenyl, and phenylamino radicals, $R^2$ is selected from the group consisting of hydrogen and alkyl and phenyl radicals and $R^3$ is selected from the group consisting of hydrogen, lower alkyl and hydroxyl, provided that when X represents the atoms necessary to complete an aromatic ring, $R^3$ is selected from the group consisting of hydrogen and lower alkyl radicals.

**2.** The compound as defined in claim **1** wherein each of said A and B moieties comprises a benzene nucleus.

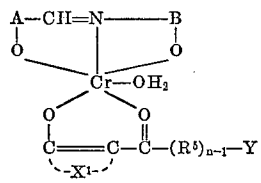
**3.** A 1:1 chrome-complexed azomethine dye as defined in claim **1**, said complex being within the formulae:







and



wherein $R^4$ is selected from the group consisting of alkylene, phenylene and phenylamino radicals, $R^5$ is an alkylene radical, $R^6$ is selected from the group consisting of hydrogen, alkyl, alkoxy alkyl, alkylamino, phenyl and phenylamino radicals, $R^7$ is lower alkyl, hydroxy or hydrogen, $R^8$ is hydrogen, alkyl or phenyl, $X^1$ represents the atoms necessary to complete a 5 or a 6-membered aliphatic ring or a benzene ring and Y is a radical comprising a p-dihydroxyphenyl silver halide developing substituent.




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HELEN M. S. SNEED, Primary Examiner

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