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PROCESS FOR THE PRODUCTION OF PHOTOGRAPHIC IMAGES

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U.S. Cl. 96—48 R 14 Claims

ABSTRACT OF THE DISCLOSURE

Photographic images are produced by imagewise production of nuclei for the decomposition of peroxy compounds in the presence of reaction components for a color-forming oxidizing reaction.

The image dye consists at least in part of the dye obtained by the oxidizing reaction.

The invention relates to a new process for the production of photographic images by catalytic decomposition of peroxy compounds of imagewise distributed noble metal nuclei.

A wide variety of processes is known for the production of photographic images. The conventional photographic processes in which silver halide emulsion layers are exposed and developed with conventional developer substances have for a long time been of greatest practical importance but they have their limitations regarding sensitivity and sharpness of the image so that there have been many attempts to develop new processes which make use of both physical and chemical principles.

It is among the objects of the invention to provide processes for the production or intensification of monochrome or multicolored photographic images in a simple and economical manner.

I now have found a process for the production of photographic images including the following steps:

(1) Imagewise exposure of light-sensitive layers to produce nuclei for the decomposition of peroxy compounds in imagewise distribution, the nuclei being of noble metals of the Groups *Ib* and VIII of the Periodic Table of Elements.

(2) Treatment with peroxy compounds which are catalytically decomposable at these nuclei in the presence of reagents for a color-forming oxidation reaction.

Photochemical decomposition of noble metal compounds to form the free metals has been known for a long time. Thus, gold compounds are photochemically decomposed to form gold nuclei. The same applies to noble metal compounds of the eighth group of the periodic system. The noble metal compounds are preferably salts of the noble metals with organic acids such as citric acid, tartaric acid, oxalic acid, salicylic acid, lactic acid, benzoic acid, mucic acid, etc., as well as halides, cyanides, thiocyanates and the like. See, for example, the relevant chapter in the work by J. Plotnikow "Allegemeine Photochemie," publishers W. de Gruyter & Co., Berlin-Leipzig, (1936), and the work by A. Hay "Handbuch der Wissenschaftlichen und Angewandten Photographie," publishers Springer-Verlag, Vienna (1929), volume 3. For the process according to the invention, compounds of this type may be incorporated in layers in concentrations of 10^{-3} to 10^{2} g./m.^{2}, preferably 10^{-1} to 10 g./m.^{2}. Upon the photochemical decomposition nuclei are formed on which the color-forming reactions described below can be carried out.

In the light-sensitive layers of the type described above the noble metal compounds are themselves sufficiently sensitive to light so that catalytically active noble metal nuclei are formed in sufficient quantities in the exposed areas. However, one can also use for the process according to the invention layers in which other substances undergo an imagewise change on exposure so that the noble metal compounds which are present at the same time in the layer or which are added subsequently are converted in the exposed areas into noble metal nuclei which are then capable of catalytically decomposing peroxides. Layers of this type are known per se. They are layers which contain photo-conductive compounds such as zinc oxide, titanium dioxide, bismuth oxide, tin dioxide, lead oxide, halides, sulfides or selenides of these metals and others. In this connection, I refer to the publication by A. Goetz et al. in Rev. Mod. Physics 20 (1948) 131 and the publication by G. M. Schwab et al. in Photographic Science, Focal Press London/New York (1963), page 343 or British Pat. No. 1,043,250.

Layers which are particularly suitable are those which contain zinc oxide or titanium dioxide embedded in any binders but in particular in hydrophilic binders, such as silica gel, polyvinyl acetate, partially hydrolysed polyvinyl acetate, polyvinyl alcohol, cellulose esters, carboxymethyl cellulose or natural binders such as gelatin.

The noble metal compounds are added to these layers before or after exposure. The noble metal compounds need not themselves to be light-sensitive. The noble metal compounds are reduced in the exposed areas of the layers so that noble metal nuclei which are capable of catalytically decomposing peroxy compounds are formed in imagewise distribution.

The process of the invention exhibits particular utility for intensifying conventional photographic silver images which have been produced with conventional silver halide emulsion layers and in particular images in layers of this type which have a low silver content. For this purpose the imagewise exposed silver salt emulsion layer is first developed in a conventional way. The silver image thus formed is capable of the catalytically decomposing the peroxy compound.

If desired, the catalytic activity of the surface of the developed silver image may be still further increased by taking suitable measures after development and before treatment with the peroxy compound. Such increases in the catalytic activity of the developed silver image may be achieved, for example, by depositing traces of catalytically more active noble metals (e.g. Au, Pt, Pd, Ru, Os) on the surface of the image silver or by brief oxidative pretreatment of the image silver, for example with peroxy compounds preferably inorganic peroxy compounds, e.g. with dissolved or gaseous H_2O_2, dissolved perborate, percarbonate or the like.

A certain increase in the catalytic activity of the developed image silver also occurs if additional silver ions are deposited on the surface of the silver image from the solution phase by brief physical after-development. The silver surface is then "purified" by displacement of adsorbed, inactivating substances (e.g. emulsion stabilizers), and its catalytic activity is increased.

Due to the high catalytic activity of silver, silver oxide or noble metal nuclei on the decomposition of peroxide, even invisible traces of the noble metal in particular of silver initiate the color-forming oxidation reaction. In other words, parts of the image become visible which would remain invisible if processed only according to conventional photographic processing of exposed silver halide emulsion layers. The relative gain in sensitivity lies between 5 and 10° DIN.

For instance a low sensitivity fine grained silver halide emulsion layer which upon conventional processing has a sensitivity of about 13° DIN can be exposed as an emulsion with a sensitivity of 20° DIN if processed according to the present invention, without any loss of details or density in the resulting image.

The gain in photographic sensitivity by the process of the invention is particularly high if silver salt emulsion layers with the conventional higher silver content are used.

But images of high density and contrast can be obtained also using light-sensitive silver salt emulsion layers especially silver halide gelatin emulsion layers which have a silver content of only about 0.05–0.3 gram silver per square meter in the form of light-sensitive silver salt. Apart from the considerable economic advantage this leads to images of exceptionally high sharpness because light scattering in layers having a low silver halide content is reduced as compared with conventional silver halide layers, which have a much higher silver halide content.

In general, the fixing or bleach fixing process can be omitted for layers which have an extremely low silver halide content since the photolytic coloration in daylight of layers which have an exceptionally low silver content is much less than that of conventional layers which have a much higher silver content.

The process of the invention can be performed with silver salt emulsion layers of common composition, for example silver halide, gelatin emulsion layers, which however may contain as already mentioned above for less silver salts. The silver salt emulsion layers used for the process of the present invention may contain the usual additives such as spectral or chemical sensitizers, accelerators, stabilizers, hardening agents, wetting agents, and so on.

The process according to the invention may be used both for intensifying black-white silver images and for intensifying color photographic images.

Peroxy compounds which are suitable for the process according to the invention are preferably inorganic peroxy compounds, e.g. hydrogen peroxide, perborates, percarbonates or persulfates, the last mentioned peroxy compounds preferably in the form of their alkali metal salts. Organic peroxy compounds, e.g. benzoyl peroxide, may also be used.

The treatment with the peroxy compounds is performed in the presence of reagents which yield very deeply colored oxidation products so that the image which was previously invisible or hardly visible becomes clearly visible.

These reagents may be organic compounds which yield an image dye on oxidation, preferably (1) amino and/or hydroxy substituted aryl compounds, in particular those of the benzene or naphthalene series or (2) amino and/or hydroxy substituted heterocyclic aromatic compounds, such as 5- or 6-membered heterocyclic rings, in particular rings with nitrogen as a ring member, for example rings of the pyrol, pyridine, pyrazole, imidazole, triazole, pyridazine, pyrimidine or pyrazine series, whereby these heterocyclic rings contain anellated benzene rings, such as indol, indazole, quinazoline, quinoxazaline, acridine or phenazine. The compounds are preferably water soluble.

The following are given as examples: Phenol, aniline, pyrocatechol, resorcinol, hydroquinone, o-, m- and p-phenylenediamines, N,N-dimethyl-phenylenediamine, N,N-diethyl-phenylenediamine, N,N-ethylmethyl-phenylenediamine, o-, m- and p-aminophenols, p-methylaminophenol, 2,4-diaminophenol-(1), 1,7-, 1,5- or 2,3-dihydroxy-naphthalene, 1,6,7-trihydroxynaphthalene, 1,2-diamino-naphthalene, 1,8-diaminonaphthalene, benzidine, 2,2'-dihydroxybenzidine, 2,4-diamino diphenylamine; 3,8-dihydroxy quinoline, 5-hydroxyquinoline, 2-hydroxycarbazol, 1-phenylpyrazolone-(3), etc.

The amino, hydroxy or aminohydroxy compounds may also be substituted, e.g. with halogen, sulfonic, alkyl, aryl, alkoxy or aroxy nitro, keto, aldehyde groups, carboxy

or carbamoyl. The following are given as examples: 2,5-dichloro-p-phenylenediamine, 1-hydroxy-2-aminobenzine-4-sulfonic acid, 1-amino-2-hydroxybenzene-4-sulfonic acid, 3-amino-5-sulfosalicyclic acid, 1,6,7-trihydroxynaphthalene-3-sulfonic acid, 1,8-dihydroxynaphthalene-disulfonic acid-(3,6)-benzidine-2,2'-disulfonic acid, benzidine-3,3'-disulfonic acid, 4-methylphenol, 2-phenylphenylenediamine-(1,4), 2-methoxyphenol, 2-amino-4-phenoxyphenyl-(1), 4-nitro-pyrocatechol, 2,4-diaminobenzaldehyde, 1-carboxy-pyrocatechol-(3,4). More substituted compounds are listed in Example 6.

In some cases, mixtures of several such compounds show a much stronger dye formation on oxidation than the individual components. Thus, for example, a mixture of o-phenylenediamine and pyrocatechol results in increased dye formation. A mixture of N,N-diethyl-phenylenediamine and pyrocatechol yields a deeper and more neutral black dye than the individual compounds. Even components which do not form a dye upon oxidation on their own, such as tetrabromohydroquinone or tetrabromopyrocatechol, may enhance dye formation when added to other hydroxy, amino or aminohydroxy compounds.

Oxidation of the aromatic amino, hydroxy and/or aminohydroxy compounds yields monomeric or polymeric dyes which are related to quinonimines and azines. Some examples of this oxidative dye formation are described in H. R. Schweizer's work "Künstliche Organische Farbstoffe und ihre Zwischenprodukte," publishers Springer-Verlag, Berlin, Göttingen, Heidelberg (1964), pages 222, 275, 281 and 293; N. I. Woroshow "Grundlagen der Synthese von Zwischenprodukten und Farbstoffen," publishers Akademie-Verlag, Berlin (1966), pages 703 to 789, A. Schaeffer "Chemie der Farbstoffe und deren Anwendung" (Technische Fortschrittsberichte, volume 60), publishers Theodor Steinkopff-Verlag, Dresden-Leipzig (1963), pages 59 et seq.

Apart from dye precursors, one may, of course, also use leuco dye compounds and vat dyes which can be oxidized to dyes. For examples, of these see H. R. Schweizer "Künstliche Organische Farbstoffe und Zwischenprodukte," Springer-Verlag, Berlin-Göttingen, Heidelberg (1964), pp. 250 and 320.

Oxidisable organic compounds of the type which yield the image dye only in a sequence of reactions with other compounds are also suitable for use in the process of the invention. In principle, any reaction system which yields dyes on oxidative coupling may be used. Special reference may be made here to the so-called color-forming photographic developers of the phenylenediamine or aminopyrazolone series (see, e.g. C. E. K. Mees and T. H. James, "The Theory of the Photographic Process," 3rd edition, MacMillan Co., New York (1966), page 382; H. R. Schweizer, "Künstliche Organische Farbstoffe und ihre Zwischenprodukte," Springer-Verlag, Berlin-Göttingen-Heidelberg (1964), page 295). Isocyclic and heterocyclic hydrazines can also be coupled oxidatively with suitable components to yield dyes (see e.g. H. Hünig et al., Angew. Chem. 70 (1958) 215; S. Hünig, Chimia 15 (1961) 133 and Angew. Chem. 74 (1962) 818). The color-forming photographic developed substances are catalytically oxidized on the imagewise distributed noble metal nuclei or noble metal particles by the peroxy compounds. Their oxidation products may then react with known photographic color couplers which are also present to form dyes. Any color couplers are suitable for this purpose, for example those of the phenol or naphthol series as cyan couplers, those of the pyrazolone indazol series as magenta couplers and those of the benzoyl-acetanilide series as yellow couplers.

EXAMPLE 1

A gelatin layer (thickness of layer 25 μm.) on a cellulose triacetate support is treated with a saturated aqueous solution of $Na_2[Pd(C_2O_4)_2]$.

After drying and imagewise exposure with ultraviolet light, the layer is treated for two minutes at 20° C. in the following developer bath:

Solution 1: 5 cc. of glacial acetic acid are added to 500 cc. of water. 3 g. of 3-aminobenzidene hydrochloride and 2 g. of pyrocatechol are then dissolved in this solution.
Solution 2: 10 g. of sodium acetate are dissolved in 500 cc. of water. 25 cc. of 30% aqueous H_2O_2 are then added.

The two solutions are mixed before use.

Nuclei of palladium metal are formed on the exposed areas of the layer during exposure. On development, these nuclei catalytically decompose the hydrogen peroxide present in solution 2 and the amine and phenol of solution 1 are imagewise oxidized to yield a brownish-black negative image of the original. The image dye is fast to diffusion.

After development, the layer is washed and dried.

EXAMPLE 2

A transparent support of cellulose triacetate is coated with a solution which contains 6 ml. of a 10% aqueous solution of polyvinyl alcohol and 2 g. of TiO_2 of particle size 0.3 to 0.4 μm. and 0.1 mg. of erythrosin as spectral sensitizer in 400 cc. of water. The layer is then dried.

Processing

The dry layer is exposed in a sensitometer customarily used in the art behind a grey step wedge and then treated for 10 minutes with a 5% aqueous solution of $NaAuCl_4$. It is then washed and treated for 2 minutes in a bath of the following solutions at 20° C.

Solution 1: 5 g. of 3-carbamoyl-4-aminopyrazolone-(5) and 20 g. of $Na\text{-}H_2PO_4 \cdot H_2O$ is dissolved in 500 cc. of water.
Solution 2: 10 g. of $Na_2HPO_4 \cdot 12H_2O$ and 0.5 g. of $Na_2P_2O_7$ are dissolved in 500 cc. of water, and 50 cc. of a 30% aqueous solution of hydrogen peroxide are aded thereto.
Solution 3: 10 g. of Na_2HPO_4 and 10 g. of 1-naphthol-2-sulfonic acid are dissolved in 500 cc. of water and adjusted to pH 8.5 by the addition of aqueous sodium hydroxide solution.

The three solutions are mixed before use.

The developed material is washed for half a minute and dried. A blue-violet negative image of the original is obtained.

Similarly satisfactory results are obtained by treating the exposed layer with a 5% aqueous solution of silver nitrate instead of a solution of $Na(AuCl_4)$.

EXAMPLE 3

A silver iodobromide gelatin emulsion layer (4.5 mols percent of AgJ) which must be as free as possible from fog, is applied onto a support of polyethylene terephthalate. Conventional silver content of about 10 g. silver per square meter. Layer thickness approximately 10μ.

After imagewise exposure (0.5 second with X-rays between fluorescent intensifying foils), the layer is treated for 5 minutes in the following developer at 20° C.:

	G.
p-Methylaminophenol	3.5
Hydroquinone	9.0
Na_2SO_3 anhydrous	60.0
Na_2CO_3	40.0
KBr	1.0

In 1 liter of H_2O.

After a brief washing, the layer is then fixed for 5 minutes in a bath of the following composition:

	G.
$Na_2S_2O_3 \cdot 5H_2O$	250.0
$NaHSO_3$	20.0

In 1 liter of H_2O.

After another brief washing, the layer is treated for 5 minutes in a solution which contains 25 g. of sodium percarbonate and 200 cc. of 30% aqueous H_2O_2 in 1 liter of H_2O. The catalytic activity of the surface of the developed silver is thus increased.

The layer is then treated for 2 minutes in the following bath:

Solution 1: 10 g. of pyrocatechol in 200 ml. water.
Solution 2. 10 g. of 1,7-dihydroxy naphthalene in 800 ml. water and added thereto 20 g. of sodium carbonate and 20 ml. of a 5-N-sodium-hydroxide solution.
Solultion 3: 14 g. sodium perborate in 1 liter of water.

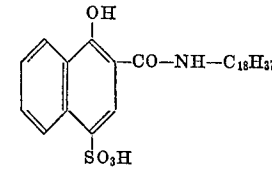
Solutions 1, 2 and 3 are mixed before use and the pH-value is adjusted to 12.

The layer is finally rinsed and dried. The treatment with the last-mentioned bath may be performed in daylight. The contrast of the original silver image is greatly enhanced by the after treatment. The sensitivity of the material is apparently also strongly increased since one either obtains much more image detail for the same exposure followed by conventional photographic processing or the exposure time required to obtain the same quality of final image is much less (factor 10 to 100) than would be required if exposure were followed by conventional photographic processing.

Instead of the intermediate treatment with sodium percarbonate which increases the catalytic activity of developed silver, the intermediate treatment may be carried out e.g. with a 2% aqueous sodium perborate solution, a 1% aqueous $PdCl_2$ solution, a 1% aqueous $PtCl_2$ solution or a 1% aqueous $AuCl_3$ solution. A brief treatment with gaseous H_2O_2 at a temperature of about 80° C. (especially in the form of a mixture with gaseous NH_3) also increases the catalytic activity of the image silver.

EXAMPLE 4

10 ml. of a silver bromide gelatin emulsion which is as free as possible from fog are added to 250 cc. of a 5% gelatin solution. 50 ml. of a 10% aqueous solution of the cyan color coupler:



are stirred into this solution. The mixture is applied to form a layer of about 20 μm. in thickness. Silver content unusually low, approximately 0.08 g./m.^{2}.

After drying, the layer is exposed in a sensitometer for 1 second behind a grey step wedge and then treated with a color-forming developer for 2 minutes in the conventional manner in the following bath:

	G.
N,N-diethyl-p-phenylenediamino sulfate	2.8
Na_2SO_3 anhydrous	2.0
Ethylenediamino tetraacetic acid sodium	2.0
KBr	2.0
Hydroxylamine sulfate	1.2
K_2CO_3	75.0

To 1 liter of H_2O.

A very weak, negative cyan dye image which contains image silver is obtained.

The layer is then treated for 5 minutes in a solution which contains 20 g. of sodium perborate and 100 cc. of 30% H_2O_2 to 1 liter of H_2O. The catalytic activity of the silver image surface is thereby increased.

The layer is then treated for 5 minutes in the following bath:

Solution 1: 15 g. of phenylhydrazine-2-sulfonic acid sodium are dissolved in 500 cc. of 0.1% aqueous acetic acid.

Solution 2: 7 g. of sodium perborate and 40 g. of sodium acetate are dissolved in 500 cc. of water. 50 cc. of 30% of H_2O_2 are then added.

The two solutions are mixed before use.

The cyan dye image is considerably increased in intensity by this after treatment. With phenylhydrazine-3-sulfonic acid sodium instead of the phenylhydrazine-2-sulfonic acid sodium a red image is obtained.

The dye image is considerably increased in intensity by this after treatment.

The layer is finally washed and dried. Since the layer has a very low silver halide content, no fixing is necessary.

EXAMPLE 5

A color photographic multi-layered material which comprises a red-sensitive silver halide emulsion layer containing a cyan color coupler, a green-sensitive silver halide emulsion layer containing a magenta coupler, a filter layer containing tartrazine as yellow filter dye, and a blue-sensitive silver halide emulsion layer containing a yellow coupler is exposed behind a grey step wedge, using a light intensity which is about one-tenth of the amount required for conventional processing. The material is then developed for 8 minutes in the conventional manner in the color-forming developer of Example 4.

The layer is treated three times in succession for 1 minute each alternately with a 2.5% sodium percarbonate solution and the color development solution indicated above. The original dye image is intensified by this alternating bath after treatment.

After brief intermediate washing and bleach fixing in the following bath:

Solution 1: 50 g. $Na_2S_2O_3$ in 500 cc. H_2O.
Solution 2: 25 g. $K_3[Fe(CN)_6]$ in 500 cc. H_2O. (The two solutions mixed before use), the layer is washed and dried.

EXAMPLE 6

A high speed silver bromo iodide gelatin emulsion containing 10% by weight of silver halide, silver iodide content 1 mol percent is applied onto a cellulose triacetate support and dried. The emulsion layer contains per square meter 0.1 g. of silver in the form of silver halide.

The above layer is arranged between two intensifying foils of calcium tungstate and exposed to X-rays behind a stepwedge of aluminum. Thereafter the exposed layer is developed for one minute at a temperature of 20° C. with the following developing bath:

	G.
p-Methylaminophenol	5
Sodium sulfite	40
Hydroquinone	6
Potassium carbonate	40
Potassium bromide	1

Water up to 1 liter.

Fixation is not necessary since the coloration by photolytic formation of silver in the low silver halide content layer upon exposure to daylight is negligible.

After development the layer is treated for 2 minutes in a solution of the following composition:

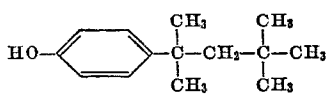
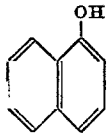
50 ml. of 30% aqueous H_2O_2
20 g. of sodium perborate (or 25 g. sodium percarbonate), sodium carbonate to adjust a pH-value of 10, water up to 1 liter

Thereafter, the layer is contacted with a solution having also a pH-value of 10 and which contains a compound listed in the following table alone or in combination with pyrocatechol. The concentration of each of the reaction components in the treating solution is 10 g. per liter.

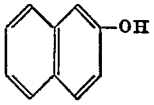
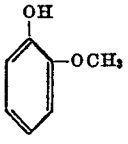
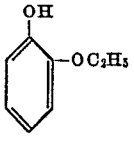
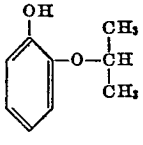
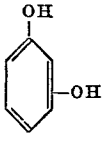
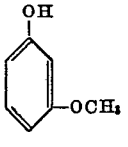
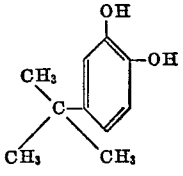
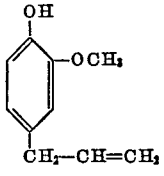
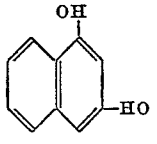
Upon treatment with the last mentioned bath negative images of the color shown in the following table are formed:

The conventional black-and-white development of the imagewise exposed silver halide emulsion layer and the dye formation by the catalytic oxidation of the color-forming compounds can be accelerated by increasing the temperature of the baths. The development and the color-forming treatment can be performed for example at temperatures between 40 and 60° C.

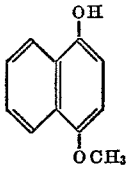
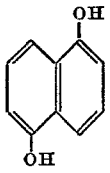
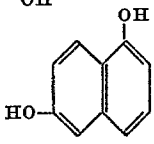
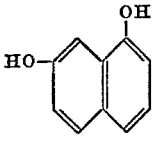
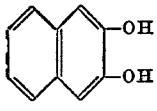
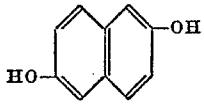
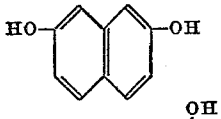
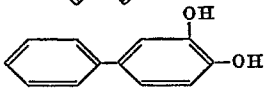
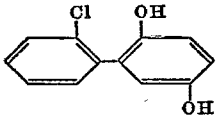
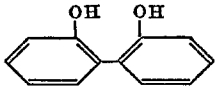
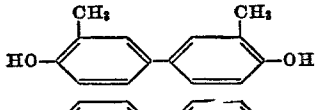
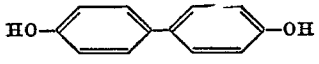
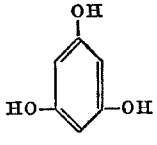
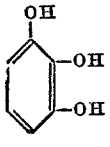
The dye forming oxidation process can be stopped and the image can be stabilized for storage by aftertreatment with an aqueous solution of Na_2SO_3, $NaHSO_3$ or formaldehydebisulfite.

Colorformer	Color	In combination with pyrocatechol color
	----------	Blackish brown.
	Black----------	Black.
	-----do----------	Do.
	Brown----------	Blackish brown.

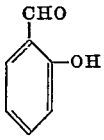
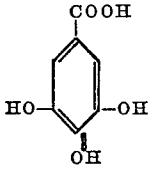
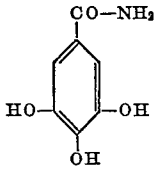
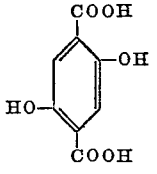
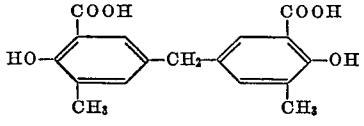
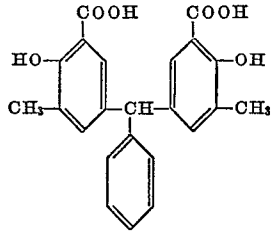
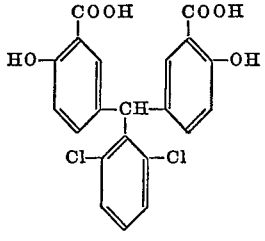
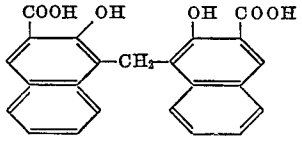
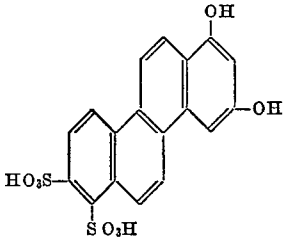
TABLE—Continued

Colorformer	Color	In combination with pyrocatechol color
	Brown	Blackish brown.
	Blackish brown	
	Brown	Do.
	do	Do.
	Black	Do.
		Brown.
	Brown	Do.
	do	Blackish brown.
	Black	Black.
	Blackish brown	Blackish brown.
	Black	Black.

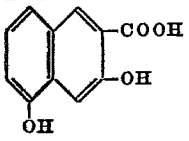
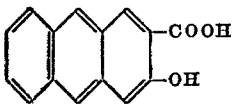
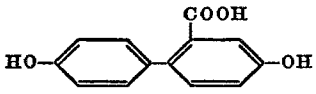
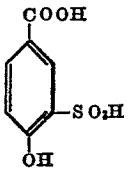
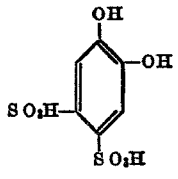
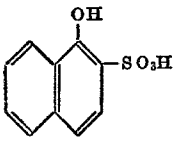
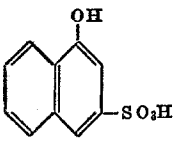
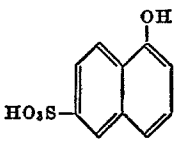
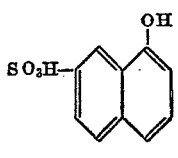
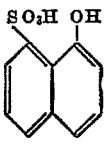
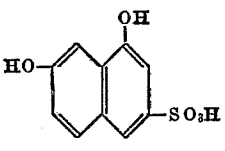
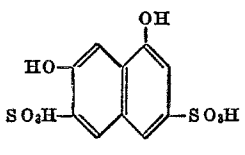
TABLE—Continued

Colorformer	Color	In combination with pyrocatechol color
	Blue	Bluish black.
	Greenish black	Black.
	Black	Do.
	do	Violet black.
	Brown	Brownish yellow.
	Blackish brown	Blackish brown.
	Brown	Brown.
	do	Blackish brown.
	do	Do.
	do	Brown.
	do	Do.
	do	Do.
	Black	Black.
	do	Do.

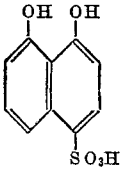
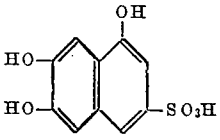
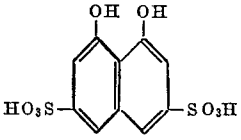
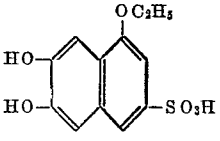
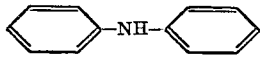
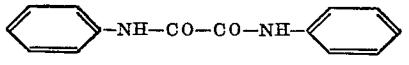
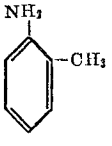
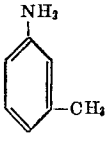
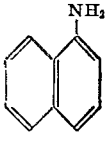
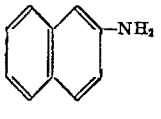
TABLE—Continued

Colorformer	Color	In combination with pyrocatechol color
	Brownish black	Brownish black.
	----do----	Do.
	----do----	Do.
	----do----	Do.
	Brown	Brown.
	----do----	Do.
	Brownish red	Do.
	Brown	Do.
	Black	Black.

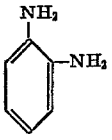
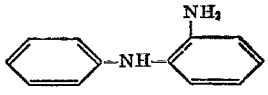
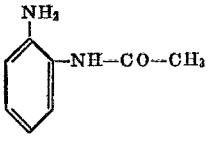
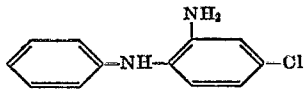
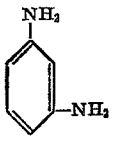
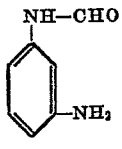
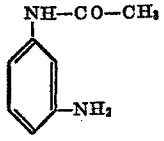
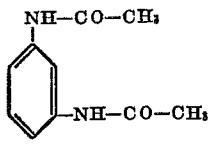
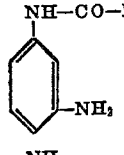
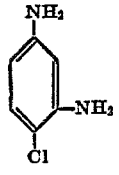
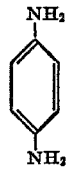
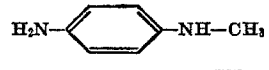
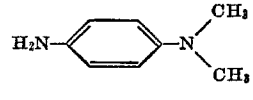
TABLE—Continued

Colorformer	Color	In combination with pyrocatechol color
	Greenish black	Black.
	Yellow	Yellowish green.
	Brown	Brown.
		Blackish brown.
	Brown	Do.
	do	Brown.
	do	Do.
	Blue black	Do.
	Violet black	Brownish black.
	do	Do.
	do	Violet black.
	Brownish black	Brownish black.

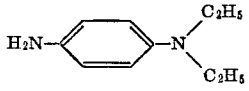
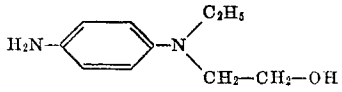
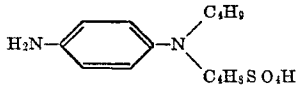
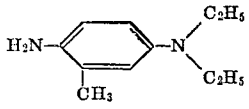
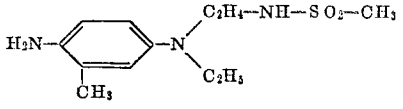
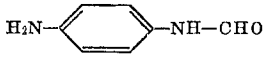
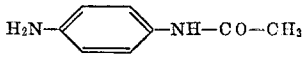
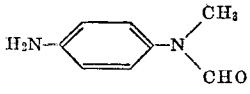
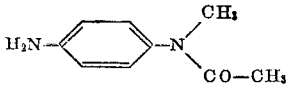
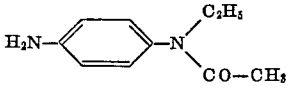
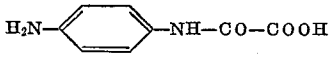
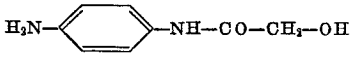
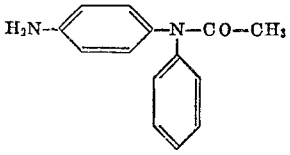
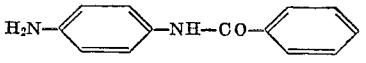
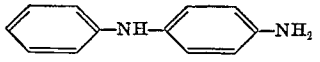
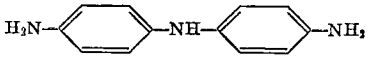
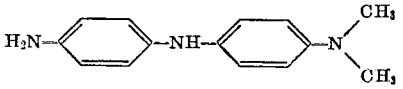
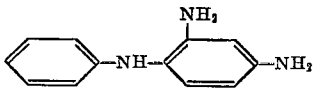
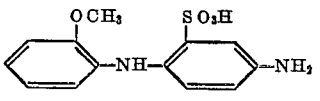
TABLE—Continued

Colorformer	Color	In combination with pyrocatechol color
	Black	Black.
	do	Do.
	Blackish brown	Do.
	do	Do.
		Brownish black.
		Yellow brown.
		Brown.
	Brown	Brownish black.
	do	Do.
	do	Do
	Reddish brown	Blackish brown
	Blackish brown	Do.

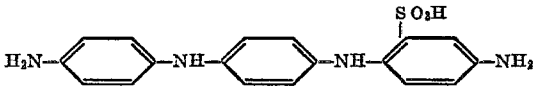
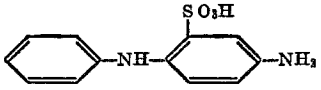
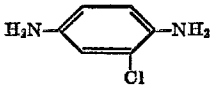
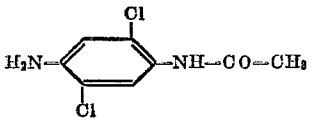
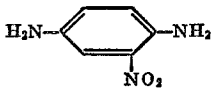
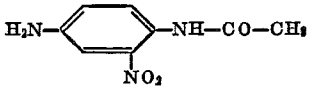
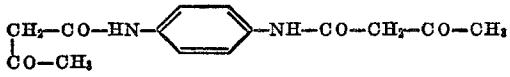
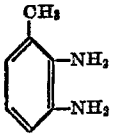
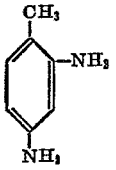
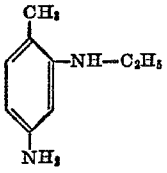
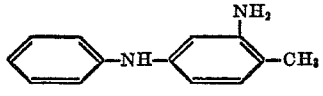
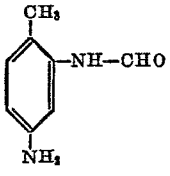
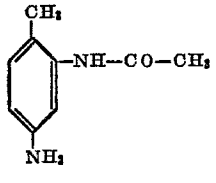
TABLE—Continued

Colorformer	Color	In combination with pyrocatechol color
	Blackish brown	Reddish brown.
	Brownish red	Brown:
	Brown	Do:
	do	Blackish brown:
	do	Do:
	do	Brown:
	do	Do:
	do	Do:
	do	Brownish black:
	do	Brown:
	Black	Black:
	Blackish brown	Do:
	Black	Do:

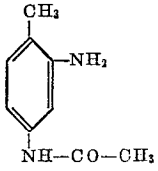
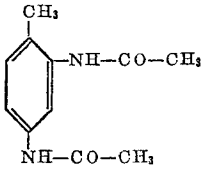
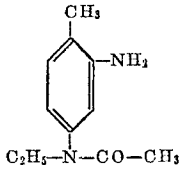
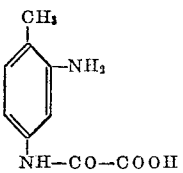
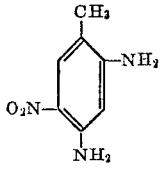
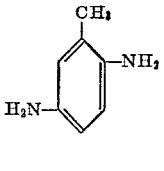
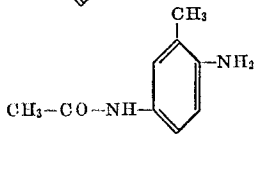
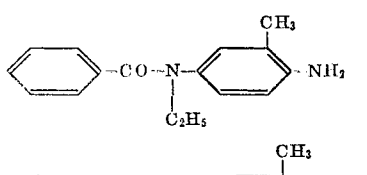
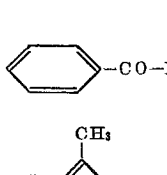
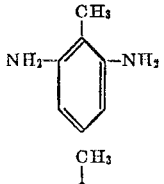
TABLE—Continued

Colorformer	Color	In combination with pyrocatechol color
	Black	Black.
	do	Do.
	do	Do.
	do	Do.
	do	Do.
	Brown	Do.
	Orange	Brown.
	Brown	Blackish brown.
	do	Do.
	do	Black.
	do	Greenish brown.
	do	Black.
	Yellow brown	Yellow brown.
	Orange	Brown.
	Black	Blackish brown.
	do	Black.
	Brownish black	Do.
	do	Do.
	Blackish blue	Blackish blue.

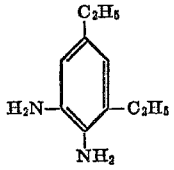
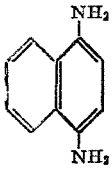
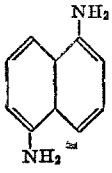
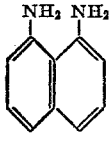
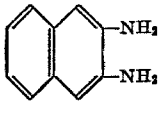
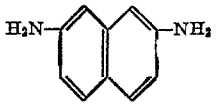
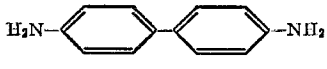
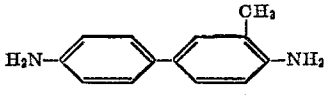
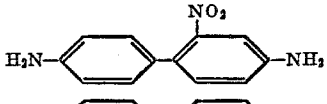
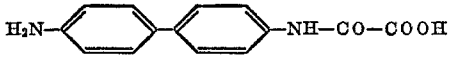
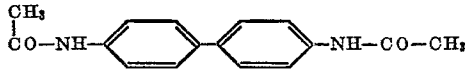
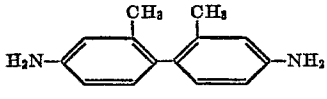
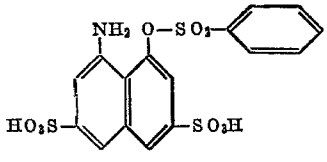
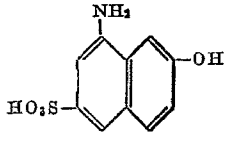
TABLE—Continued

Colorformer	Color	In combination with pyrocatechol color
	Brownish black	Brownish black.
	do	Do.
	do	Black.
	Blackish brown	Do.
	Orange	Brown.
	Reddish brown	Do.
	Brown	Do.
	Light red	Black.
	Brown	Blackish brown.
	Yellow brown	Do.
	Brown	Brown.
	do	Blackish brown.
	do	Do.

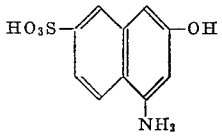
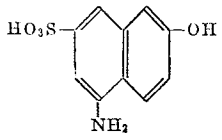
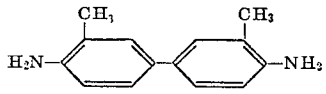
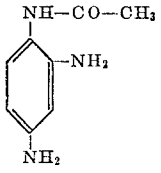
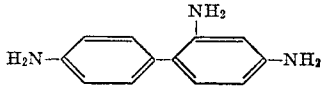
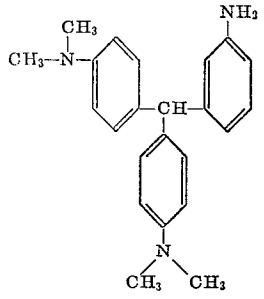
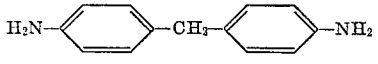
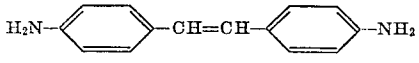
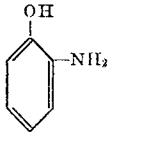
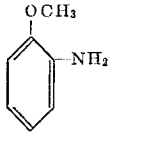
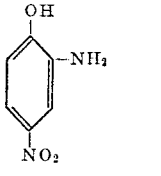
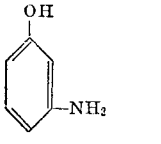
TABLE—Continued

Colorformer	Color	In combination with pyrocatechol color
	Brown	Brown.
	------	Do.
	------	Do.
	Brown	Do.
	Black	Black.
	---do---	Do.
	Brown	Brownish black.
	---do---	Brown.
	Yellow brown	Do.
	Green grey	Do.
	Brown	Yellow brown.

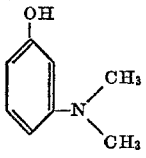
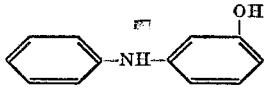
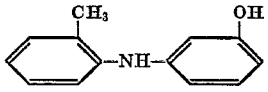
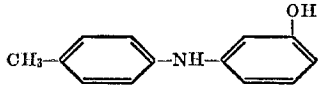
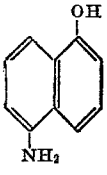
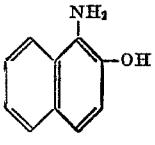
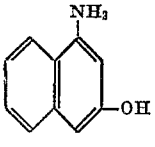
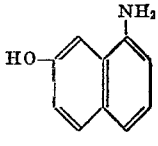
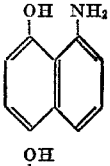
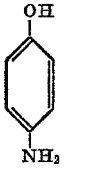
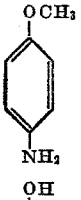
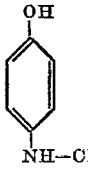
TABLE—Continued

Colorformer	Color	In combination with pyrocatechol color
	Brown	Brown.
	Black	Black.
	do	Do.
	do	Do.
	do	Do.
	do	Do.
	Blackish brown	Blackish brown.
	Brown	Blackish brown.
	do	Brown.
	do	Do.
		Do.
	do	Black.
	do	Brown.
	Black	Black.

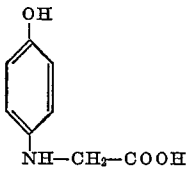
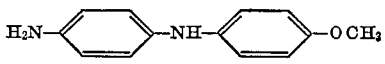
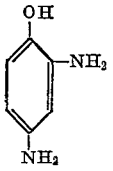
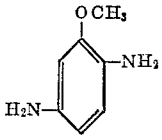
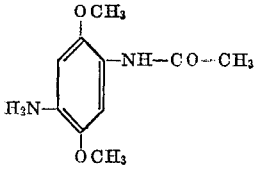
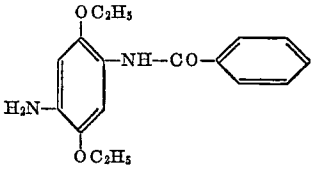
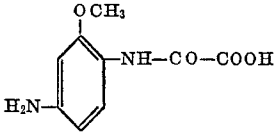
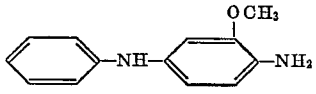
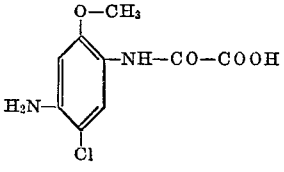
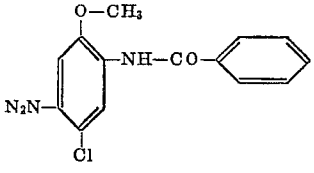
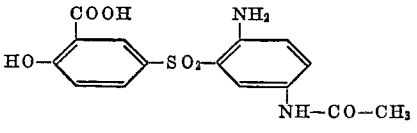
TABLE—Continued

Colorformer	Color	In combination with pyrocatechol color
	Brown	Black.
	do	Do.
	do	Do.
	do	Brown.
	Brownish black	Brownish black.
	Greenish black	Greenish black.
	Brown	Black.
	do	Do.
	do	Reddish brown.
	do	Brown.
	Yellow brown	Yellow brown.
	Brown	Brown.

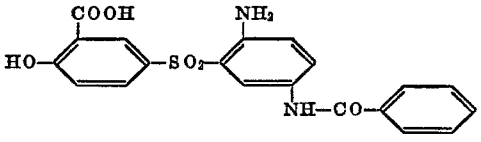
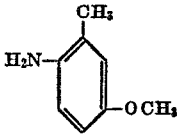
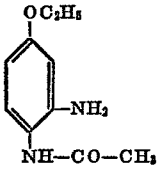
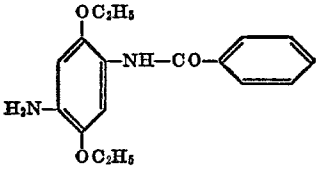
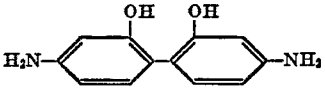
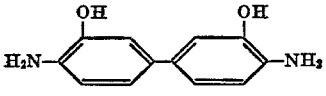
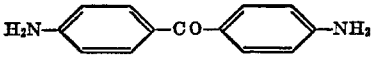
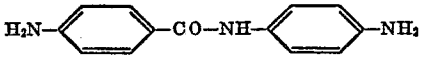
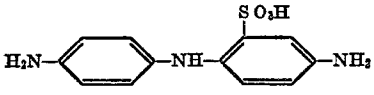
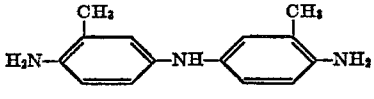
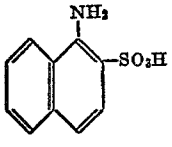
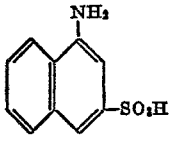
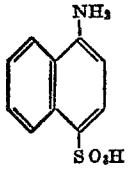
TABLE—Continued

Colorformer	Color	In combination with pyrocatechol color
	Brown	Brown.
	do	Black.
	do	Do.
	do	Brownish black.
	Violet black	Violet black.
	Brownish black	Brownish black.
	do	Do.
	do	Do.
	do	Do.
	Blackish brown	Black.
	do	Do.
	do	Do.

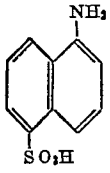
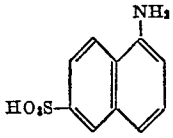
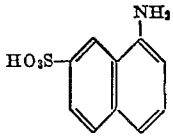
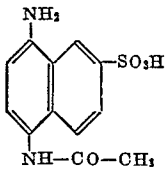
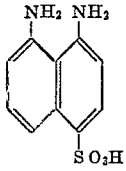
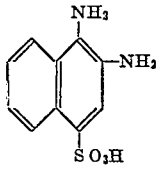
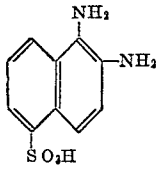
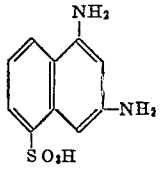
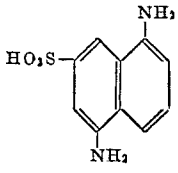
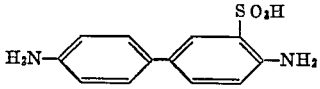
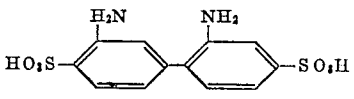
TABLE—Continued

Colorformer	Color	In combination with pyrocatechol color
	Blackish brown	Blackish brown.
	do	Do.
	do	Do.
	do	Do.
	Bluish violet	Brownish black.
	do	Do.
	Black	Black.
	do	Do.
	do	Do.
	do	Do.
	do	Do.

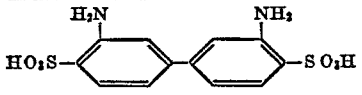
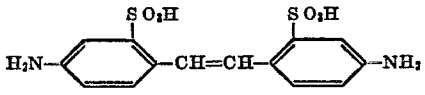
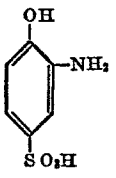
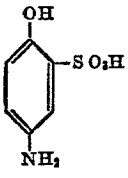
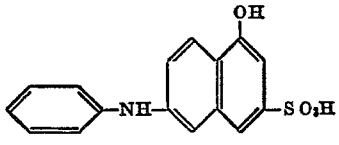
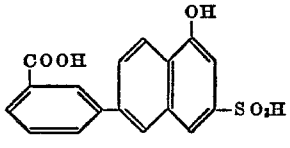
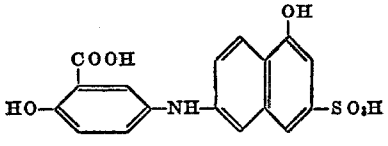
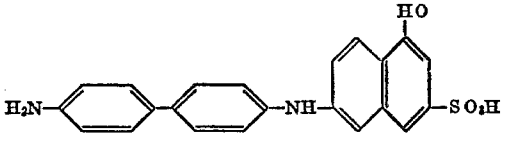
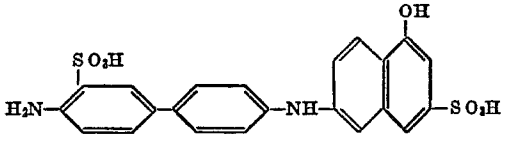
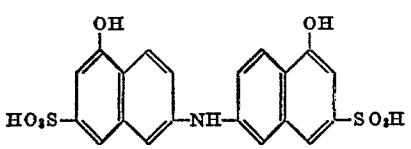
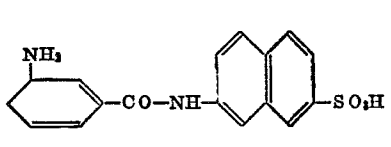
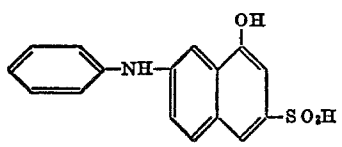
TABLE—Continued

Colorformer	Color	In combination with pyrocatechol color
	Black	Black.
	do	Do.
	Brown	Brown.
	Yellow brown	Yellow brown.
	do	Do.
	Brown	Brown.
	do	Do.
	Black	Black.
	do	Do.
	do	Do.
	Brownish black	Brownish black.
	do	Do.
	do	Do.

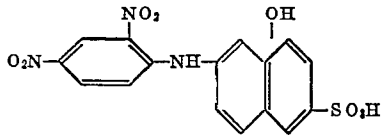
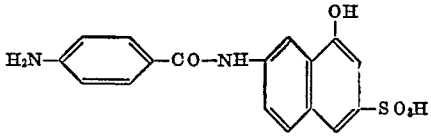
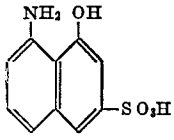
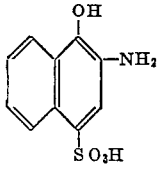
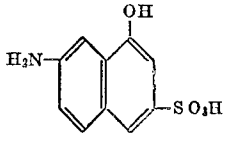
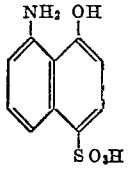
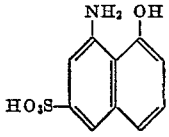
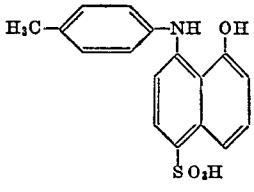
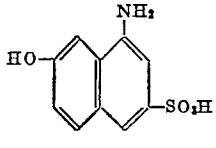
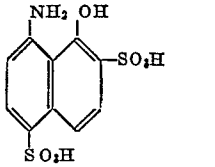
TABLE—Continued

Colorformer	Color	In combination with pyrocatechol color
	Brownish black	Brownish black.
	do	Do.
	do	Do.
	do	Do.
	do	Do.
	Black	Black.
	Brownish black	Do.
	do	Do.
	do	Do.
	Black	Do.
	Brown	Blackish brown.

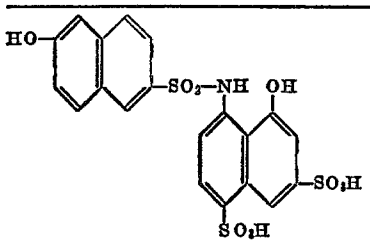
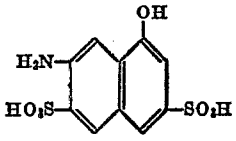
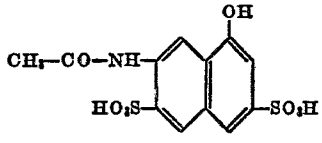
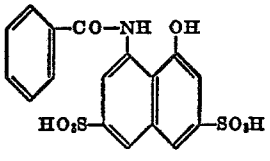
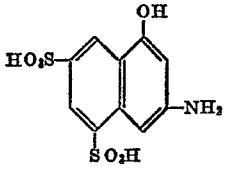
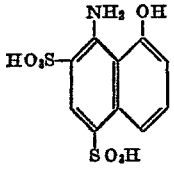
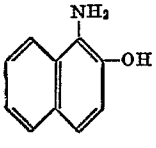
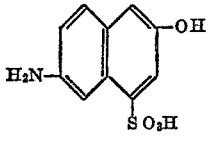
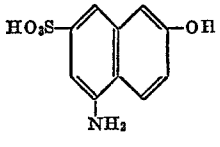
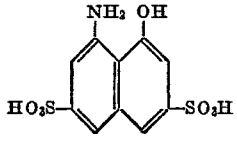
TABLE—Continued

Colorformer	Color	In combination with pyrocatechol color
	Brown	Black.
	Black	Do.
	Brown	Brown.
	Yellow brown	Do.
	Brown	Do.
	Yellow	Do.
	do	Do.
	Blackish brown	Blackish brown.
	Brown	Brown.
	Yellow	Do.
	Brown	Do.
	Yellow	Greenish yellow.

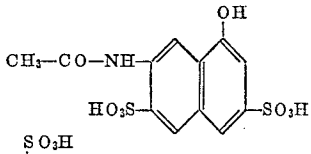
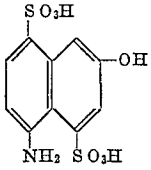
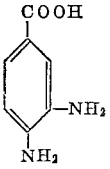
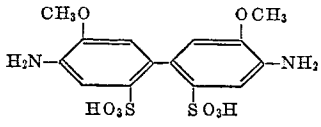
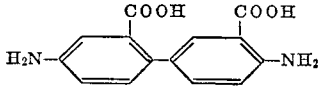
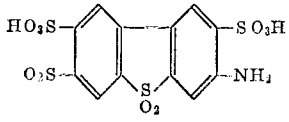
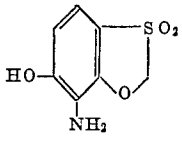
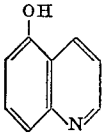
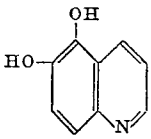
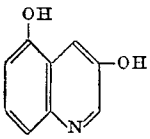
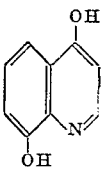
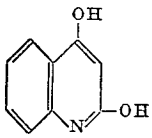
TABLE—Continued

Colorformer	Color	In combination with pyrocatechol color
	Brown	Brown.
	Orange	Do.
	Brownish black	Black.
	do	Do.
	Violet black	Do.
	Black	Do.
	do	Do.
	do	Do.
	do	Do.
	do	Do.
	do	Do.

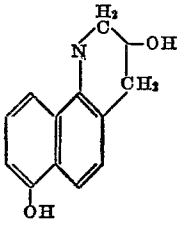
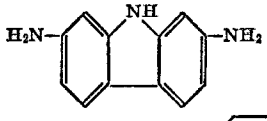
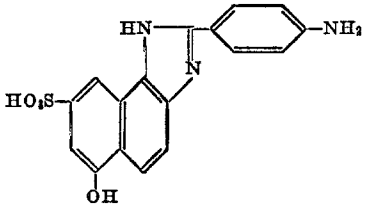
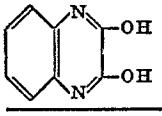
TABLE—Continued

Colorformer	Color	In combination with pyrocatechol color
	Black	Black.
	do	Do.
	do	Do.
	do	Do.
	do	Do.
	do	Do.
	do	Do.
	do	Do.
	do	Do.
	do	Do.

TABLE—Continued

Colorformer	Color	In combination with pyrocatechol color
	Black	Black.
	do	Do.
	Brown	Brownish black.
	do	Black.
	do	Do.
	Black	Do.
	Brown	Brown.
	Yellow	Yellow brown.
	do	Brown.
	Brown	Black.
	Black	Do.
	Blackish brown	Do.

TABLE—Continued

Colorformer	Color	In combination with pyrocatechol color
	Brown	Brown.
	Black	Black.
	Brown	Brown.
	----do----	Do.

I claim:

1. A process for the production of photographic images, including the steps of
   (a) imagewise exposing a light-sensitive layer wherein noble metal nuclei are producible,
   (b) producing therein in imagewise distribution nuclei of noble metals of the group consisting of copper, silver, gold, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum, and
   (c) treating the layer which contains the imagewise distribution of noble metal nuclei in the presence of a color-forming compound which on oxidation yields a dye with a solution containing a peroxy compound thereby catalytically decomposing said peroxy compound on the noble metal nuclei and oxidizing said color-forming compound to yield a dye image.

2. A process as defined in claim 1, wherein the light-sensitive layers contain light-sensitive compounds of silver, gold or a metal selected from the group consisting of the light and heavy platinum metals or light-sensitive substances of the type which are capable of decomposing these noble metal compounds in the exposed areas to form noble metal nuclei.

3. The process of claim 1, wherein the light-sensitive layer contains a light-sensitive silver salt emulsion which is exposed, developed and thereafter treated with peroxy compounds in the presence of color-forming compounds which on oxidation yield a dye.

4. The process of claim 3, wherein the exposed and developed silver salt emulsion layer is treated with a peroxy compound before the color-forming oxidizing reaction step.

5. The process of claim 1, wherein the exposed layer is treated with an aqueous solution of inorganic peroxy compounds.

6. The process of claim 1, wherein the color-forming compounds are
   (1) amino and/or hydroxy substituted aryl compounds or
   (2) amino and/or hydroxy substituted heterocyclic aromatic compounds.

7. The process of claim 6, wherein the treatment with peroxy compounds is carried out in the presence of color-forming photographic developers of the p-phenylenediamine series.

8. The process of claim 6, wherein the color-forming compounds are amino and/or hydroxy substituted compounds of the benzene or naphthalene series.

9. The process of claim 8, wherein the color-forming compounds are a hydroxy and/or amino substituted naphthalene and in addition a hydroxy substituted benzene.

10. The process of claim 8, wherein the color-forming compounds are a diamine from the benzene series and in addition a hydroxy substituted benzene or naphthalene.

11. The process of claim 8, wherein the color-forming compounds are a hydroxy substituted benzene or naphthalene, and in addition an aromatic hydrazine.

12. The process of claim 11, wherein the aromatic hydrazine is a sulfo substituted phenyl hydrazine.

13. The process of claim 7, wherein the treatment with peroxy compounds is carried out in the presence of photographic color couplers.

14. The process of claim 2, wherein the light-sensitive layers contain a light-sensitive photoconductive compound having the property after exposure to light of catalytically decomposing noble metal compounds to form noble metal nuclei in the exposed areas.

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R. E. FICHTER, Assistant Examiner

U.S. Cl. X.R.

96—3, 9, 77, 88, 48 PD