United States Patent [19]

Hayakawa et al.

[11] **3,874,947**

[45] **Apr. 1, 1975**

[54] **PROCESS FOR THE PRODUCTION OF POLYMER IMAGES**

[75] Inventors: **Yoshihide Hayakawa; Masato Satomura,** both of Asaka, Japan

[73] Assignee: **Fuji Photo Film Co., Ltd.,** Kanagawa, Japan

[22] Filed: **Oct. 4, 1972**

[21] Appl. No.: **295,079**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 848,085, Aug. 6, 1969, abandoned.

[30] **Foreign Application Priority Data**

Aug. 20, 1968 Japan 43-59401

[52] **U.S. Cl.** ..... **96/51,** 96/35.1, 96/48 R, 96/50 R, 96/115 P

[51] **Int. Cl.** **G03c 1/70,** G03c 1/68

[58] **Field of Search** ..... 96/35.1, 27, 48 R, 50 R, 96/51, 115 P

[56] **References Cited**

UNITED STATES PATENTS

2,887,376	5/1959	Tupis	96/35.1
3,019,104	1/1962	Oster	96/29
3,585,030	6/1971	Pelz et al.	96/29

OTHER PUBLICATIONS

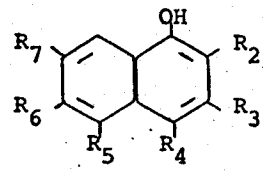
Mees, C. E. K., "The Theory of the Photographic Process," 1942, pages 343 & 356.

Primary Examiner—Ronald H. Smith
Attorney, Agent, or Firm—Sughrue, Rothwell, Mion, Zinn and Macpeak

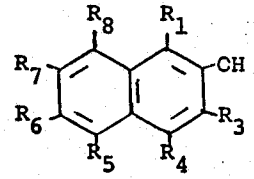
[57] **ABSTRACT**

A process for the formation of a polymer image which comprises adding at least one monomer of the group consisting of a vinylidene monomer and a vinyl monomer to a photographic silver halide emulsion layer having a latent image in the presence of radiation and in the presence of at least one compound selected from those represented by the following formulas:

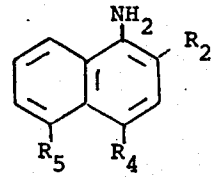
i. α-naphthol or a derivative thereof



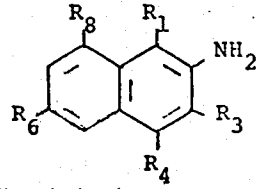
ii. β-naphthol or a derivative thereof



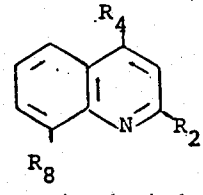
iii. α-naphthylamine or a derivative thereof



iv. β-naphthylamine or a derivative thereof



v. oxyquinoline derivative



whereby said monomer is selectively polymerized at the areas having said latent image. The individual moieties are further defined in the specification and claims.

33 Claims, No Drawings

PROCESS FOR THE PRODUCTION OF POLYMER IMAGES

CROSS-REFERENCE TO RELATED APPLICATIONS

The present application is a Continuation-In-Part Application of our earlier co-pending Application Ser. No. 848,085 filed Aug. 6, 1969, now abandoned, and claims priority from Aug. 20, 1968, based on Japanese Patent Application Ser. No. 59401/68.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a process for the formation of polymer images and more particularly to a process for selectively forming polymer images at the areas corresponding to photographic latent image-bearing areas by the action of a photographic silver halide emulsion and a reducing agent.

2. Description of the Prior Art

There have been proposed various processes of forming images by the formation of highly polymerized compounds by the photopolymerization of vinyl compounds. It has also been proposed to directly cause photopolymerizations using silver halides as catalysts (British Pat. No. 866,631; and S. Levinos et al., "Photographic Science and Engineering," Vol. 6, pages 222–226 (1962). It is believed, in this reaction, that the photo-induced decomposition product of the silver halide serves as a polymerization catalyst, and the sensitivity to light of this reaction does not reach the level which is easily attained by ordinary development of silver halide particles. Also, it has been proposed to form, imagewise, highly polymerized compounds by polymerizing vinyl compounds using as a catalyst a silver image or unreacted silver halide after the development of an exposed silver halide emulsion with an ordinary developing solution (Belgian Pat. No. 642,477). This procedure has the disadvantage that the development and polymerization should be conducted separately. It is theoretically of great interest to effect the polymerization of vinyl compounds by the oxidation product, or intermediate thereof, formed in the course of development of a photographic silver halide emulsion by a reducing agent in the presence of the vinyl compounds, since it can be expected that, in this procedure, the polymerization is effected by both of amplifying effect of development and that of chain polymerization. It has already been proposed to effect such a reaction using as a reducing agent a benzenoid compound having at least two hydroxyl, amino or alkyl- or aryl-substituted amino groups in ortho- or para-positions to each other on a benzene ring (U.S. Pat. No. 3,019,104 and G. Oster; "Nature"; Vol. 180, page 1275 (1957)).

Moreover, other investigators have reported that they could not perform the experiments of these procedures with success (S. Levinos and F. W. H. Mueller; "Photographic Science and Engineering", Vol. 6, page 222 (1962).

SUMMARY OF THE INVENTION

An object of the present invention is to convert a latent image on a photographic silver halide emulsion layer, given by electromagnetic waves or particle rays, into an image of a highly polymerized substance by a simple procedure.

Another object of this invention is to obtain a polymer image having the desired properties by employing this procedure in recording or printing.

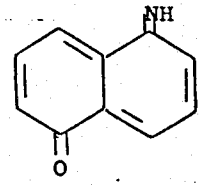
The inventors have discovered that the polymerization of a vinyl compound is effected by reducing a silver halide, in the presence of the vinyl compound, with a naphthol, a naphthylamine, an oxyquinoline or derivatives thereof as disclosed hereinafter. In cases where the silver halide is in the form of a silver halide photographic emulsion, the reaction proceeds at a higher rate when the silver halide grains control development centers that when the grains have no development centers, so that the polymerization can be selectively performed, with proper selection of reaction conditions and reaction time, in the areas of the emulsion where the silver halide particles containing centers of development exist; that is, in the case where the photographic emulsion layer has a latent image.

DETAILED DESCRIPTION OF THE INVENTION

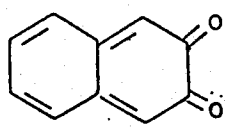
The objects of the present invention are attained by employing the fact mentioned above; that is, by subjecting a silver halide photographic emulsion layer having a photographic latent image to the action of a naphthol, a naphthylamine, or an oxyquinoline as described below in the presence of a polymerizable vinyl compound to thereby selectively polymerize the vinyl compound in the areas of the emulsion layer bearing the latent image.

The feature of the naphthol, naphthylamine, and oxyquinoline (or their derivatives) used in the present invention is that when the compound has more than 2 amino groups of hydroxyl groups, the oxidized type thereof can be shown by the following conjugate type as Kekule's structure:

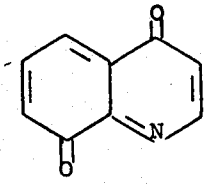
Example 1.



Example 2.



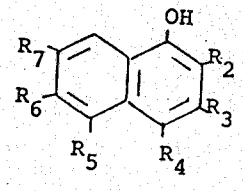
Example 3.



In particular, when the aforesaid compound has two amino groups and/or hydroxy groups in one ring thereof, the compound is a 1,2- or 2,3-substituted one, which is also a feature of the compound.

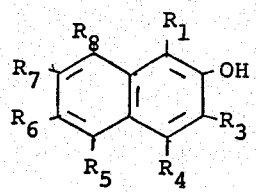
Typical examples of the naphthols, naphthylamines, oxyquinolines, and derivatives thereof used in the present invention are as follows:

i. α -naphthol or derivative thereof:



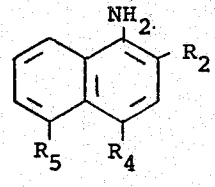
wherein R_2 represents a hydrogen atom, a sulfone group, a substituted aryl group or a chlorine atom; R_3 represents a hydrogen atom or a sulfamoyl group; R_4 represents a hydrogen atom, a sulfone group, or a chlorine atom; R_5 represents a hydrogen atom, a sulfone group, a hydroxyl group, an amino group or an acylamino group; R_6 represents a hydrogen atom, a carboxyl group or a sulfone group; and R_7 represents a hydrogen atom, a hydroxyl group or an amino group.

ii. β -naphthol or derivative thereof:



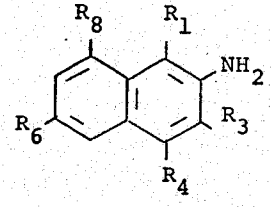
wherein R_1 represents a hydrogen atom, a formyl group, a sulfone group, a carboxyl group, a nitroso group, an arylazo group, or an amino group; R_3 represents a hydrogen atom, a hydroxyl group or —CONHR′ (R′ is an aryl group or an alkyl group); R_4 represents a hydrogen atom, a sulfone group, a chlorine atom, or a sulfone group; R_2 represents a hydrogen atom or a nitro group; and R_6 to R_8 each represents a hydrogen atom or a sulfone group.

iii. α -naphthylamine or derivative thereof:



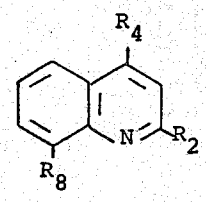
wherein R_2 represents a hydrogen atom, a substituted alkyl group, an amino group, or a hydroxyl group; R_4 represents a hydrogen atom or a sulfone group; and R_5 represents a hydrogen atom, an amino group or a hydroxyl group.

iv. β -naphthylamine or derivative thereof:



wherein R_1 represents a hydrogen atom or an amino group; R_3 represents a hydrogen atom, a sulfone group or an amino group; R_4 represents a hydrogen atom or a sulfone group; R_6 represents a hydrogen atom or a sulfone group; and R_8 represents a hydrogen atom, a sulfone group or a hydroxyl group.

v. Oxyquinoline derivative:



wherein when R_8 is a hydroxyl group, R_2 represents a hydrogen atom or a carboxyl group and R_4 represents a hydrogen atom or a hydroxyl group and when R_4 is a hydroxyl group, R_2 represents a carboxyl group and R_8 represents a hydrogen atom.

A photographic latent image is an invisible image formed in a silver halide photographic emulsion by the action of electromagnetic waves or particle rays and can be converted into a visible image by development. In the photographic emulsion layer utilized for forming a negative image, the latent image is formed by the formation of development centers in silver halide grains irradiated by electromagnetic waves or particle rays, while in a photographic emulsion layer utilized for forming a direct positive image, the latent image is formed by providing development centers in the whole silver halide grains present in the layer and then removing the development centers by the irradiation of electromagnetic waves or particle rays (see, for example, James and H. Huggins, "Fundamentals of Photographic Theory", Chapters 3 and 4, 2nd edition, Morgam & Morgam Co.).

In the process of the present invention, the aforesaid photographic silver halide emulsion utilized for forming negative images as well as the photographic silver halide emulsion utilized for forming positive images can be employed.

In the present invention, as a silver halide photographic emulsion that gives a negative image, an emulsion which is suitable for ordinary developing out processes may conveniently be used. Thus, silver chloride, silver bromide, silver chlorobromide, silver iodobromide, and silver chloro-iodobromide photographic emulsions can be used. Chemical sensitization and optical sensitization which are applicable to ordinary photographic emulsions can be applied to the silver halide emulsions for the present invention. Thus, sulfur sensitization and noble metal sensitization are applicable for chemical sensitization (see, for example, P. Glafkides, "Chimie Photographic", 2nd edition, Photocinema Paul Montel, Paris 1957 pp. 247–301). As for optical sensitization, optical sensitizers for ordinary photographic emulsions, such as Cyanine dyes and mercocyanine dyes, can be used conveniently (see, for example, Kikuchi et al., "Kagaku Shashin Benran (Handbook of Scientific Photography)", Vol. II, pp. 15–24, Maruzen Co., 1959). The emulsion to be used in the present invention may also contain stabilizers as employed in conventional photographic techniques.

The direct positive silver halide emulsion which can be employed in the present invention may be prepared by applying solarization, the Herschel effect, the Clayden effect or the Sabatier effect. Full explanations of these effects are given in Chapter 6 and 7, C.E.K.

Mees, "The Theory of the Photographic Process"; 2nd edition, published by MacMillan Co., 1954. To prepare direct positive silver halide emulsions by solarization, a silver halide emulsion susceptible to solarization is prepared, and then subjected to uniform exposure of light or to the action of a chemical to render it developable without image exposure. Methods of preparation of such emulsions are disclosed in, e.g., British Pat. Nos. 443,245 and 462,730.

The Herschel effect is produced by exposing a photographic emulsion which has been rendered developable by a uniform exposure to light of shorter wave length or a uniform action of a chemical reagent to a light of longer wave length. In this case, it is preferable to use a silver halide emulsion containing for the most part silver chloride and a desensitizer, such as pynakryptol yellow or phenosafranine, to enhance the effect. A method of preparing the direct positive emulsions applying the Herschel effect is disclosed in, e.g., British Pat. No. 667,206 and U.S. Pat. No. 2,857,273.

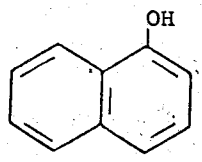
In order to directly obtain a positive image by using the Clayden effect, it is necessary to subject an emulsion overall exposure to light of a relatively low intensity after imagewise exposure to light of a high intensity for a short period of time. The areas of the emulsion which have not been exposed to the irradiation of the high intensity light become developable after this overall exposure.

The Sabatier effect is produced by exposing to a uniform action of light or a chemical reagent, in a state of immersion in a developing solution, a silver halide photographic emulsion layer that has received an imagewise exposure to light to thereby give to a developability in the area that has not been exposed to the imagewise exposure. The Clayden effect and the Sabatier effect are easily and practically obtained in silver halide emulsions that have a tendency of yielding centers of development, by the first exposure, in the inner portion, rather than in the surface portion of the silver halide grains.

Methods of preparing emulsions having a tendency to yield internal centers of development are disclosed in e.g., U.S. Pat. Nos. 2,592,250 and 2,497,876, British Pat. No. 1,011,062 and German Pat. No. 1,207,791.

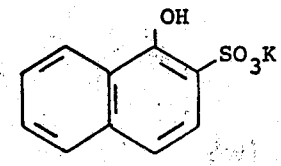
The photographic emulsions as mentioned above consist of dispersion systems in which particles of silver halide are dispersed in a solution of a high molecular weight polymer. Gelatin is widely employed as the high molecular weight polymer, while polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylamide, carboxymethyl cellulose, oxyethyl ether and dextran may also be employed, alone or in mixtures with gelatin (see, e.g., F. Evva; "Zeitschrift für Wissenschafliche Photographie", Photophysik und Photochemie, Vol. 52, pp. 1–24, 1957).

Practical examples of the naphthols, naphthylamines, oxyquinolines, and derivatives thereof which may be employed in the present invention are as follows:

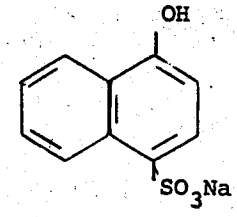


(1) α-naphthol

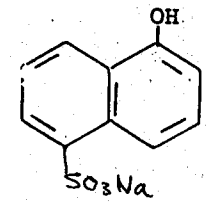
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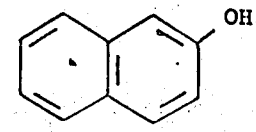
(2) Potassium 1-naphthol-2-sulfonate



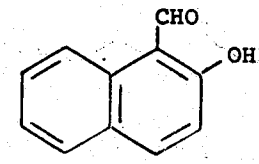
(3) Sodium 1-naphthol-4-sulfonate



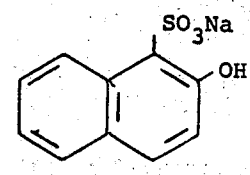
(4) Sodium 1-naphthol-5-sulfonate



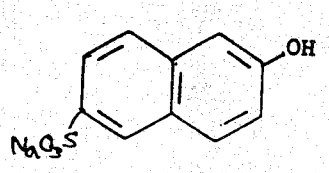
(5) β-naphthol



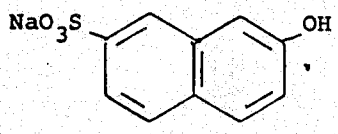
(6) 2-hydroxy-1-naphthoaldhyde



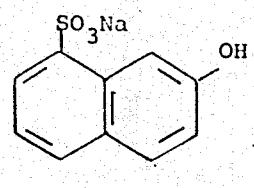
(7) 2-naphthol-1-sodium sulfonic acid



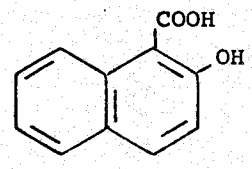
(8) 2-naphthol-6-sodium sulfonate



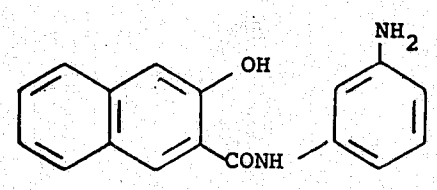
(9) 2-naphthol-7-sodium sulfonate



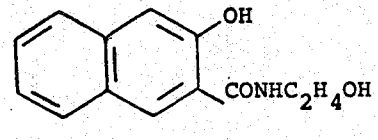
(10) 2-naphthol-8-sodium sulfonate



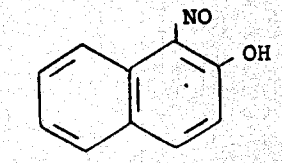
(11) 2-hydroxy-1-naphthoic acid



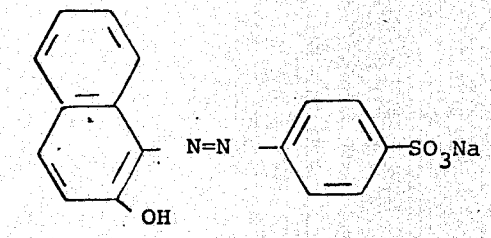
(12) m-N-(2-hydroxy-3-naphthoyl)-phenylenediamine



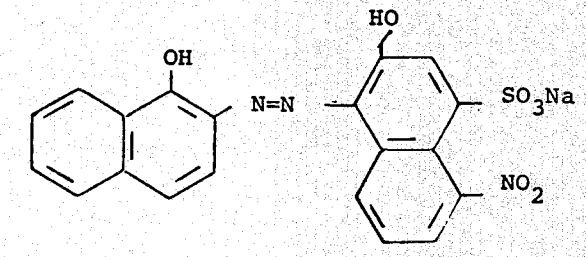
(13) β-(2-hydroxy-3-naphthoyl) aminoethanol



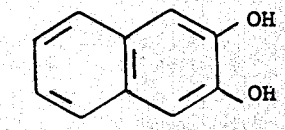
(14) α-nitroso-β-naphthol



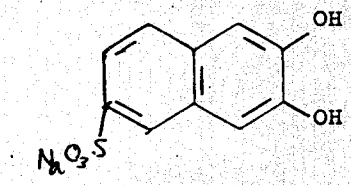
(15) naphthol orange



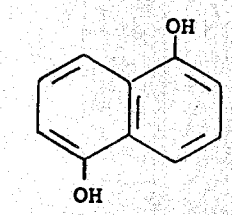
(16) 1-(α-hydroxy-2'-naphthylazo)-5-nitro-2-naphthol-4-sodium sulfonate



(17) 2,3-naphthalenediol

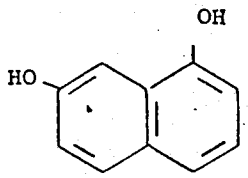


(18) 2,3-dihydroxynaphthalene-6-sodium sulfonate

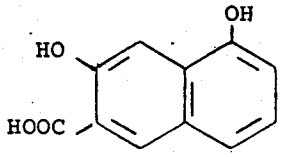


(19) 1,5-dihydroxynaphthalene

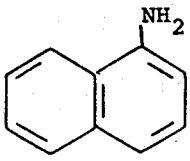
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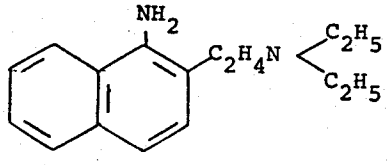
(20) 1,7-dihydroxy-naphthalene



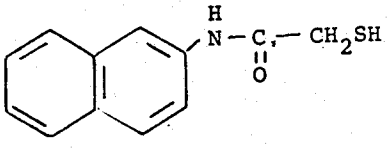
(21) 1,7-dihydroxy-6-naphthoic acid



(22) α-naphthylamine

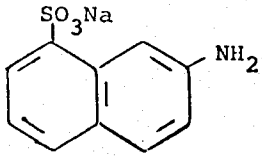


(23) β-diethylaminoethyl-α-naphthylamine

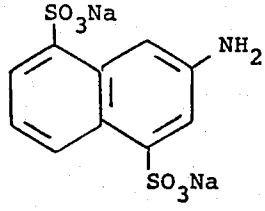


(24) thioanalide

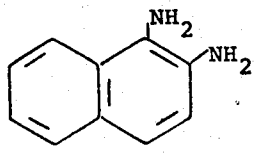
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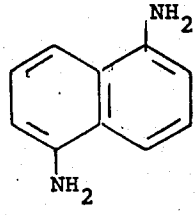
(25) 2-naphthylamine-8-sodium sulfonate



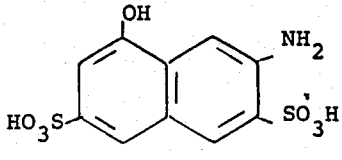
(26) 2-naphthylamine-4,8-disodium sulfonate



(27) 1,2-naphthalenediamine

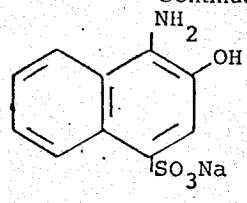


(28) 1,5-naphthalenediamine

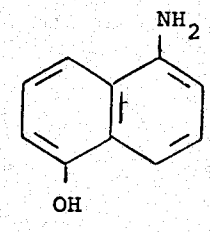


(29) 2-amino-8-naphthol-3,6-disulfonic acid

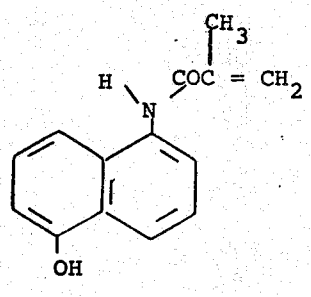
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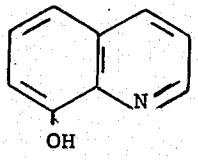
(30) 1-amino-2-naphthol-4-sodium sulfonate



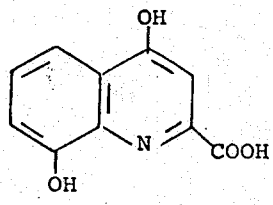
(31) 1-amino-5-naphthol



(32) 5-methacryloylamino-1-naphthol

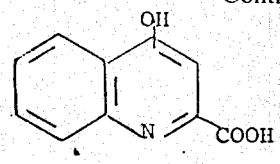


(33) 8-oxyquinoline

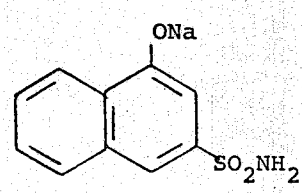


(34) 4-8-dihydroxyquinoline-2-carboxylic acid

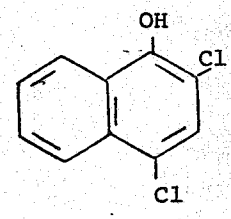
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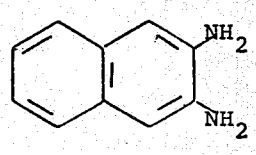
(35) 4-hydroxyquinoline-2-carboxylic acid



(36) 1-naphthol-3-sulfoneamide sodium



(37) 2,4-dichloro-1-naphthol



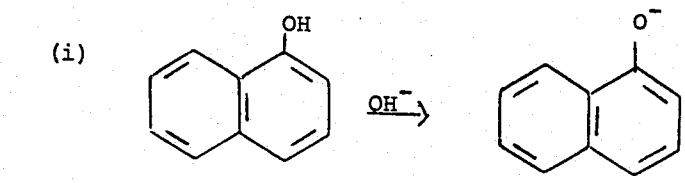
(38) 2,3-naphthalene-diamine

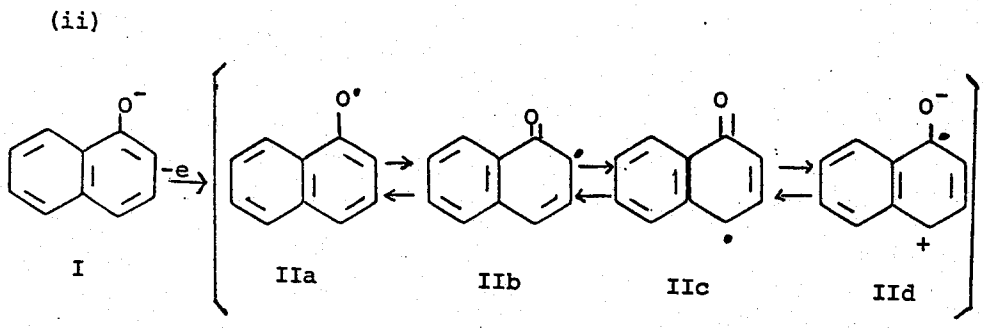
Processes for preparing the aforesaid compounds are well known in the art and the above compounds are also commercially available.

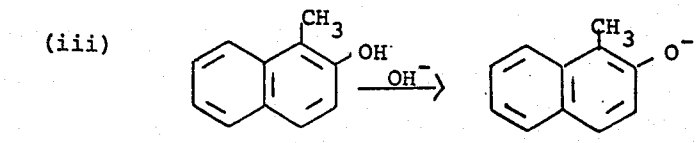
In the present invention, silver halide is used as a form of the silver halide photographic emulsion layer for increasing the difference in reactivity, that is, the selectivity in reaction between the areas irradiated by electromagnetic waves or particle rays and the areas not subjected to such irradiation.

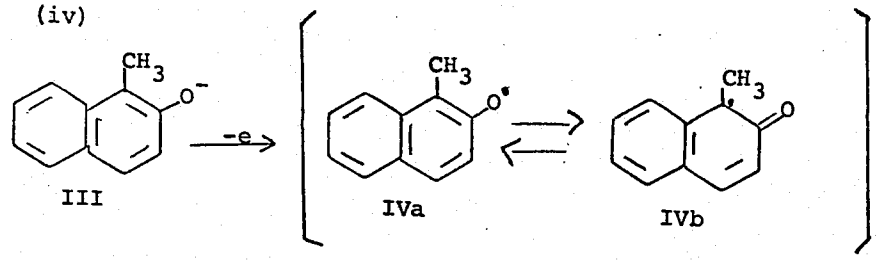
It has not yet been confirmed that the polymerization of this invention is initiated by a certain kind of intermediate products formed by the co-action of the silver halide and the naphthol, naphthylamine or derivatives thereof as shown above but there are many reports about the oxidation of naphthols and these reports also refer to these intermediate products. For example, they are reported in T. J. Stone & W. A. Waters; "Chem. & Ind.", 213 (1964), M. Adams, M. S. Blois Jr., and R.

H. Sands; "Chem. Phys.", 28, 774 (1958), and R. Pummer and I. Veit; "Chem. Ber.", 86, 412 (1953). According to these reports, the formation of the following intermediate products are provided.

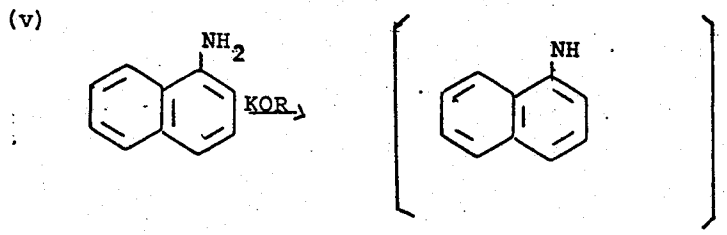


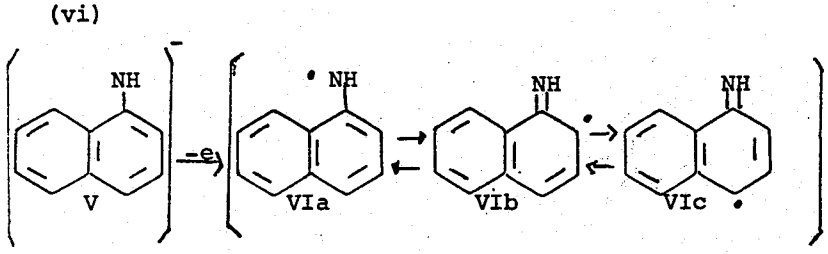






The oxidation of naphthylamines is reported in, e.g., L. Horner and J. Dehnert; "Chem. Ber.", 96, 786 (1963). According to the teachings of the report, the formation of the intermediate product is assumed to be as follows:



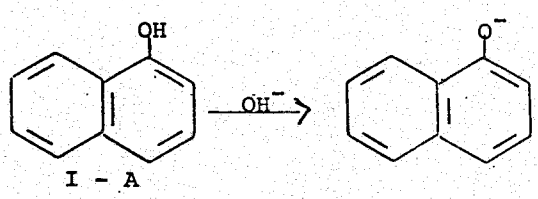


In the report mentioned above, the polymerization of a vinyl or vinylidene monomer using the intermediate product formed by the oxidation was not attempted. Also, it is known that 1,2-dihydroxynaphthalene or 1,5-dihydroxynaphthalene is effective as a developing agent (C. E. K. Mees; "The Theory of the Photographic Process", Chapter 14, 2nd edition, published by McMillan Co., 1954, New York).

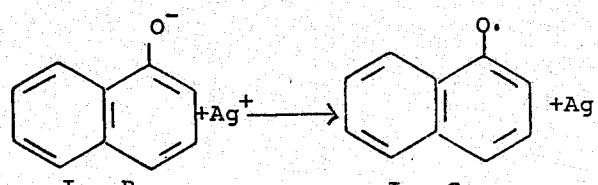
When each of the two rings of naphthalene has a hy-

droxyl or an amino group as in the present invention, it is considered that the polymerization of the vinyl or vinylidene compound is caused while the radical formed at development is not so stable. Furthermore, when one ring of the naphthalene ring has two hydroxyl groups or amino groups at the 1,4-positions, the radical formed at development is too stable to initiate the polymerization, but when the groups are present at the 1,2-positions or 2,3-positions, the radical formed at development is not so stable and hence the polymerization of the vinyl or vinlidene compound is caused. It is considered that the above phenomenon relates to the fact that in a so-called aromatic photographic developing agent having a hydroxyl group or an amino group, the activity of the developing agent of the *p*-substituent is generally higher than that of the *o*-substituted developing agent, in other words, there are differences in stabilities of radicals between the two cases.

The reaction mechanism of the polymerization of a vinyl compound of a vinylidene compound as the result of the reduction of silver halide by the naphthol, naphthylamine, oxyquinoline or derivatives thereof, according to the present invention has not yet been determined. However, it is generally considered that, since a compound susceptible to radical polymerization is being used, and since it is being reacted in an aqueous media and also because a radical polymerization inhibitor retards the reaction, the polymerization proceeds through a radical polymerization mechanism. It has not yet been determined whether the radical is directly formed by the reaction of the reducing agent of the present invention with the silver halide, or whether the radical is formed by the co-action of the water, oxygen, etc. present in the system. However, although the influence of oxygen is not clear from the above-mentioned report, it is considered, when a naphthol for example is employed as the reducing agent, that the following reaction will occur:

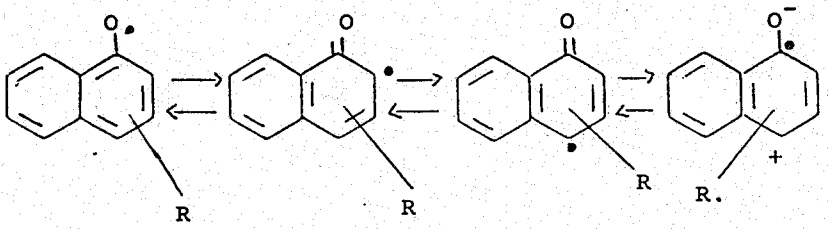


I - A



I - B I - C

Furthermore, in the radicals thus formed according to the above reaction, the following resonance structures are thought to exist, one or more of which are considered to contribute to the initiation of polymerization.



Also, it is clear that the polymerization of the vinyl compound or vinylidene compound occurs at the same time that the silver halide is reduced, since when the vinyl compound or the vinlidene compound is added to the reaction system after the reduction with the reducing agent, no polymerization is observed. Therefore, it is considered that the intermediate product of the silver halide and the reducing agent used in the present invention contributes to the initiation of the reaction. Also, when the reaction is stopped after a proper period of time, the irradiated portions are selectively accompanied with the formation of a highly polymerized material, but when the reaction is further continued, the highly polymerized material is formed on the portions which have not been subjected to the irradiation. This fact is thought to occur by the difference in the rate of the formation of (I-C) caused by the difference between the reactivity of the irradiated silver halide and the non-irradiated silver halide. However, the fact that the density of the unexposed portions reaches that of the exposed portions when the reaction is continued for a longer period of time is the same as the phenomenon that occurs when the development is continued for a longer period of time in a conventional photographic process; that is, the entire portion, including the exposed portions and non-exposed portions, are blackened. Thus, the fact that the aforesaid phenomenon occurs in the process of this invention will not injure the practicability of the present invention.

As a method for forming an image of a high molecular weight material by utilizing the light sensitivity of silver halide, there is known a so-called tanning development product wherein gelatin is cross-linked by the oxidation product of the developing agent. However, in the process of this invention, images of highly polymerized compounds having various properties can be obtained in accordance with vinyl compounds or vinylidene compounds to be used and, therefore, images having quite excellent properties (such as dyeing property and chemical resistance — which have never been attained in the case of employing the cross-linked product of gelatin) can be obtained.

Furthermore, the present inventors have discovered that if sulfite ions are present in the reaction system of this invention, the polymerization of the vinyl compounds or vinylidene compounds can be accelerated.

Sulfite ions may be added to the reaction system, either in the form of a compound which has sulfite ions originally present in the molecule, such as alkali metal sulfites or ammonium sulfite; or in the form of a compound which will give sulfite ions as the result of hydrolysis in an aqueous solution, such as pyrosulfites of alkali metals or ammonium or the adducts of bisulfites with aldehyde such as formaldehyde or glyoxal. Although the appropriate amount of sulfite ions to be added to the system depends on the kind and amount of the reducing agent and the vinyl compound, the pH of the system, and the like, more than 0.04, particularly more than 0.2, mole per liter of the reaction system is effective.

It is commonly known in the art to add a sulfite to photographic developing solutions. But, in such cases, it is believed that the sulfite prevents both the auto-oxidation of the developing agent and the uneven occurrence of development by reacting with the oxidation products of the developing agents such as hydroquinone or *p*-aminophenol (cf., for example, C. E. K. Mees; "Theory of the Photographic Process", 2nd edition, page 652 published by McMillan Co., 1954). It should be noted that since the intermediate product of the oxidation of the naphthol, the naphthylamine, the oxyquinoline, or their derivatives initiates the polymerization of the vinyl or vinylidene compound in the process of this invention, the polymerization-promoting effect of the sulfite ions is essentially different from the action of removing the oxidation products, as in the orinary developing solutions mentioned above.

If the sulfite simply removes the oxidation products as in conventional developing processes, the polymerization would be inhibited rather than promoted.

While the mechanism of the action of sulfite ions in the process of the present invention is not yet clear, it is considered to be appropriate that the sulfite ions prevent the polymerization inhibiting action of oxygen. Also, the development and polymerization of the present invention can be promoted by using, together with the reducing agent, a conventional photographic developing agent or a quaternary salt. This is the same phenomenon as in the case when a resorcinol, a phenol or a 5-pyrazolone is used as the reducing agent, and a small amount of a conventional developing agent is added thereto, thus promoting the development and polymerization.

As conventional developing agents, there are the compounds represented by the formula A $\rightarrow$ C=C $\rightarrow$ B, wherein A and B each represents —OH, —NH_2, or —NHR, a so-called phenidone, i.e., 1-aryl-3-oxopyrazolidine or a derivative thereof, and 1-aryl-3-iminopyrazolidine. As mentioned before, the aforesaid developing agent by itself does not promote the polymerization by development, but it is considered that it promotes the developing action of a reducing agent having a polymerization initiating power, and then promotes the polymerization of the monomers. As the quaternary salt, there may be used a quaternary salt of pyridine such as laurylpyridinium chloride. The fact that the use of the quaternary salt promotes the development and polymerization is based on the fact that an ordinary photographic silver halide emulsion contains halogen in an excessive state, and that the surface of the silver halide particles in the emulsion is negatively charged but the quaternary salt acts to neutralize the charges, thereby facilitating the approach of reducing agent and promoting the reaction.

As the vinyl compound in this invention, there is used an addition polymerizable vinyl compound which is liquid or solid at normal temperature, or a mixture of such vinyl monomers. Examples of such vinyl compounds are acrylamide, acrylonitrile, N-hydroxymethyl acrylamide, N-*t*-butylacrylamide, methacrylic acid, acrylic acid, calcium acrylate, sodium acrylate, methyl methacrylate, ethyl acrylate, vinylpyrrolidone, dicyclopentadiene methacrylate, vinyl butyrate, 2-vinylpyridine, 4-vinylpyridine, 2-methyl-N-vinylimidazole, potassium vinylbenzene sulfonate, and vinylcarbazole. In the process of this invention, a vinyl compound having more than 2 vinyl groups is particularly preferable and such a compound may be used alone or together with the aforesaid vinyl compound having only one vinyl group. Examples of such a vinyl compound having more than two vinyl groups are N,N′-methylenebis-acrylamide, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, polyethylene glycol dimethyacrylate, divinylbenzene, bisphenol A dimethacrylate, butylene dimethacrylate, trimethylolpropane trimethacrylate, pentaerythritol tetraacrylate, and the like.

In the present invention, a water-soluble vinyl compound is conveniently used but a water-insoluble vinyl compound may also be employed by adding it to the reaction system as an emulsion thereof. The emulsification may be conducted by means of a suitable stirrer in the presence of a surface-active agent and/or a high molecular weight compound according to conventional methods.

Any electromagnetic wave or particle rays to which ordinary photographic light-sensitive emulsions are sensitive can be utilized in the process of this invention. For example, the following may be utilized: visible rays, ultraviolet rays, infrared rays having wave lengths shorter than 1.3 microns, X-rays, gamma rays, alpha rays and electron rays.

For carrying out the process of this invention, it is necessary to conduct the two steps of irradiation by electromagnetic waves or particle rays and of reduction and polymerization. Particularly, in the recording of images, it is necessary that the silver halide particles in the emulsion change their locations little during the period between the irradiation by electromagnetic waves or particle rays and the polymerization in the reaction system and, thus, it is preferable that the reaction system be maintained in a highly viscous liquid state or in a gel state. While photographic emulsions have some viscosity or can be gelled since they contain natural or synthetic high molecular weight materials, a high molecular weight material may further be added to the emulsion if this property is insufficient.

During the irradiation by electromagnetic rays or particle rays, the silver halide particles may be dispersed in an aqueous solution or held in a dry gel. Thus, a highly viscous or gelled photographic emulsion may be subjected to the irradiation on a support in an undried state or the emulsion may be subjected to the irradiation on a support in a dried state. As the reduction and polymerization take place at the same time, the reduction must be conducted in the presence of a vinyl compound. While the compound of the present invention and the vinyl compound may be incorporated in the photographic emulsion before exposure, one of them may be first incorporated in the emulsion before exposure, and the other added to the emulsion after exposure. Furthermore, both components may be added to the system after irradiation.

As the reduction and polymerization of this invention must be conducted in the presence of water, it is necessary to conduct the reaction in an aqueous solution or in a wet gel state.

The reaction of this invention proceeds smoothly in an alkaline state and the most suitable pH of the reaction system depends on the kinds and concentrations of silver halide, the reducing agent, and the highly polymerized compound used as the medium and also on the reaction temperature. The reaction can be performed at a pH greater than 6 but a pH greater than 7 is particularly preferable.

When the photographic silver halide emulsion is used

as a coated emulsion layer on a support, the reaction may be performed by immersing the photographic emulsion layer formed on a support in an alkaline aqueous solution, after the emulsion layer has been exposed to the electromagnetic waves or particle rays. In this case, it is convenient to incorporate in the alkaline aqueous solution the reducing agent or the vinyl compound.

Although the reactions can be readily stopped by reducing the pH of the reaction system to, e.g., less than 5, it may be stopped by cooling, removing the reactants by washing, dissolving the silver halide by a photographic fixing solution, or adding a polymerization inhibitor to the system.

When the high molecular weight compound (i.e., the vehicle for the silver halide) and the vinyl monomer are formed into a layer, it is preferable to add a small amount of a thermal polymerization inhibitor in order to prevent the spontaneous overall thermal polymerization of the vinyl monomer. As such a thermal polymerization inhibitor, any of the known thermal polymerization inhibitors utilized for radical polymerization may be utilized, such as: *p*-methoxyphenol, hydroquinone, an alkylhydroquinone, 2,6-di-*t*-butyl-*p*-cresol, and the like.

When the vinyl monomer is incorporated in the system from the first, the weight thereof is usually from 1.30 to 30 times, preferably one fourth to 4 times, the weight of the high molecular weight compound which is originally present in the system. The silver halide is conveniently used in an amount by weight of from 1.20 to 2 times, preferably one tenth to one half times, the amount of the high molecular weight compound originally present in the system. Also, when the reducing agent is incorporated in the system from the first, the amount of the reducing agent is preferably from one one-thousandth to 20 moles per mole of the silver halide. Furthermore, when the aforesaid thermal polymerization inhibitor is added to the system, the amount is conveniently from one one-hundred thousandths to two one-hundredths of the weight of the vinyl monomer. When the vinyl monomer is incorporated in the processing solution, it is preferable to dissolve it in as high a concentration as possible, and hence the amount of the vinyl monomer is determined mainly by its solubility in the processing solution. In the case where the naphthol, the naphthylamine or the oxyquinoline, used as a reducing agent, is incorporated in the processing solution, the concentration thereof is from one two-thousandths to 5 moles, preferably from one one-hundreth to 1 mole per liter.

As in ordinary silver halide photographic processes, there can be any interval of time between the exposure to electromagnetic waves or particle rays and the polymerization step. Depending on the properties of the photographic emulsion, the state where the system is allowed to stand, the length of the interval of time, the irradiation effect may be diminished to some extent and in such a case, the desired effect can be obtained by increasing the amount of exposure.

When the process of this invention is utilized for the recording of images, it is possible to utilize the various differences in solubility, light scattering, tackiness, dye-receptivity, and other physical and chemical properties between the vinyl monomer and the polymer thereof. By utilizing the difference in solubility, a relief image of a high molecular weight material can be formed by dissolving off the unpolymerized portions after irradiation and polymerization to leave the high molecular weight material only at the irradiated portions.

In this case, it is convenient that the high molecular weight compound originally present in the reaction system be dissolved off together with the unreacted monomer. Therefore, it is preferable that the high molecular weight compound originally present in the system be a so-called two-dimensional, linear and substantially uncrosslinked one, or a crosslinked one in which the main chain or the cross linkage may be readily broken and that the high molecular weight compound be formed by the polymerization of the monomer by the reaction be a so-called three-dimensional crosslinked one. For these purposes, it is convenient to employ a compound having a plurality of vinyl groups as mentioned above, either alone or in combination with a compound having only one vinyl group. However, it is not essential to employ the compound having a plurality of vinyl groups since, even if the high molecular weight compound thus formed is a two-dimensional water-soluble one, there frequently occurs a remarkable difference in solubility between the areas where the high molecular weight compound is formed by the reaction and the areas where such a compound is not formed as the result of the co-action with the high molecular weight compound originally present in the system (for example, the case of polyacrylic acid and gelatin).

The images of the high molecular weight compound formed by the process of this invention can be utilized in various printing processes.

Furthermore, the process of this invention can be utilized for the formation of color images. In such a case, useful as the vinyl compound is a vinyl monomer having a group capable of having charges by electrolytic dissociation or by the addition of a hydrogen cation, to thereby form a polymer capable of having charges by electrolytic dissociation or by the addition of a hydrogen cation. The polymer images are then selectively dyed by a dye having the opposite charge to that of the polymer. Also, the dye images thus formed may be transferred to other supports by various methods.

Examples of such addition polymerizable vinyl compounds, capable of having charges by electrolytic dissociation or by the addition of a hydrogen cation used in the present invention are as follows: as a vinyl compound capable of providing negative charges to the high molecular weight compound formed, the following may be used: a vinyl compound having a carboxyl group, such as acrylic acid, methacrylic acid, itaconic acid, and maleic acid; a vinyl compound having a metal salt or an ammonium salt of a carboxylic acid, such as ammonium acrylate, sodium acrylate, potassium acrylate, calcium acrylate, magnesium acrylate, zinc acrylate, cadmium acrylate, sodium methacrylate, calcium methacrylate, magnesium methacrylate, zinc methacrylate, cadmium methacrylate, sodium itaconate, and sodium maleate; a vinyl compound having a sulfonic acid group, such as vinyl sulfonic acid and *p*-vinylbenzene sulfonic acid; and a vinyl compound having a metal salt or an ammonium salt of sulfonic acid, such as ammonium vinyl sulfonate, sodium vinylsulfonate, pottasium vinylsulfonate, and potassium p-vinylbenzene sulfonate; and, as a vinyl compound capable of providing positive charges to the high molecular weight compound formed therefrom, the following may be utilized: a vinyl compound having a basic nitrogen atom, such as 2-vinylpyridine, 4-vinylpyridine, 5-vinyl-2-methylpyridine, N,N-dimethylaminoethyl acrylate,

N,N-dimethylaminoethyl methacrylate, N,N-diethylaminoethyl acrylate, and N,N-diethylaminoethyl methacrylate; and a vinyl compound having a quaternary nitrogen salt prepared from a base of the aforesaid vinyl compound having a basic nitrogen atom and methyl chloride, ethyl bromide, dimethyl sulfate, diethyl sulfate, methyl *p*-toluenesulfonate, or the like. These compounds may be prepared by well known methods or may be commercially available. These compounds may be used alone or in combination. Also, they may be used together with a water-soluble addition polymerizable vinyl compound having no charge. As the latter type of vinyl compound, there may be illustrated: acrylamide, N-hydroxymethyl acrylamide, methacrylamide, methyl methacrylate, vinylpyrrolidone, N,N-methylene-bis-acrylamide, triethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, and the like. In the case of using the vinyl compound having no charge, the reactivity and the proportion of the vinyl compound must be so selected that a high molecular weight compound having substantially no electrolytically dissociating group is formed as the result of the polymerization of only the vinyl compound having no charge.

As a dye capable of having charges by electrolytic dissociation used in the present invention, any conventional acid or basic dye may be employed. Thus, when a vinyl compound capable of providing a high molecular weight compound having negative charges is used, a basic dye is used; whereas when a vinyl compound capable of providing a high molecular weight compound having positive charges is employed, an acid dye is used. In other words, since a basic dye has positive charges, it selectively dyes a high molecular weight compound having negative charges, whereas since an acid dye has negative charges, it selectively dyes a high molecular weight compound having positive charges. Thus, a dye image or a color image can be obtained in conformity with the high molecular weight compound formed imagewise.

When gelatin is employed as the binder for the photographic emulsions, the isoelectric point of the gelatin must be considered for dyeing purposes, since gelatin is an amphoteric electrolyte. That is, if the pH of the system is higher than the isoelectric point of gelatin, the gelatin has negative charges, while if the pH is lower, the gelatin has positive charges. Accordingly, when a high molecular weight compound having negative charges is formed, only the image of the high molecular weight compound can be dyed without dyeing the gelatin by dyeing the imagebearing emulsion layer with a basic dye. Also, when an emulsion layer having the polymer image is first uniformly dyed at a pH higher than the isoelectric point of gelatin, and, thereafter, the thus-dyed layer is washed with a washing solution at a pH lower than the isoelectric point, only the dye on the areas of the emulsion layer having no polymer image is washed away, and hence only the areas having the polymer image can be kept in the dyed state.

When it is desired to dye the image of a high molecular weight compound having positive charges with an acid dye, the image may be dyed at a pH higher than the isoelectric point of the gelatin. Of course, if the pH of the reaction system is too high or too low, the solubility of the dye is lowered and the electrolytic dissociation of the high molecular weight compound to be charged is hindered. Thus, although the optimum pH range of the system depends on the kinds of vinyl compound and dye employed, as well as the kind of binder, such as gelatin, when normal gelatin is subjected to a lime processing and has an isoelectric point of about 4.9, the pH is suitably 2.5–4.5 when a high molecular weight compound having negative charges is dyed by a basic dye, and 5.0–8.0 when a high molecular weight compound having positive charges is dyed with an acid dye.

Typical examples of the acid dyes used in the process of this invention are C.I. Acid Yellow 7 (C.I. 56,205), C.I. Acid Yellow 23 (C.I. 19,140), C.I. Acid Red 1 (C.I. 18,050), C.I. Acid Red 52 (45,100), C.I. Acid Blue 9 (C.I. 42,090), C.I. Acid Blue 45, C.I. Acid Blue 62 (C.I. 62,045), C.I. Acid Violet 7 (C.I. 18,055), and the like. Also, typical examples of the basic dyes used in the present invention are C.I. Basic Yellow 1 (C.I. 49,005), C.I. Basic Yellow 2 (C.I. 41,000), C.I. Basic Red 1 (C.I. 45,160), C.I. Basic Red 2 (C.I. 50,240), C.I. Basic Blue 25 (C.I. 52,025), C.I. Basic Violet 3 (C.I. 42,555), C.I. Basic Violet 10 (C.I. 45,170), and the like.

The numbers of the dyes given above are taken from Color Index (2nd edition).

For carrying out the process of this invention, it is necessary to first conduct the reduction and polymerization after conducting the irradiation of the electromagnetic waves or particle rays, and then conduct the dyeing.

By washing away only the unreacted vinyl monomer after the irradiation and the reduction and polymerization, polymer images can be obtained. A polymer is generally less soluble in water than a monomer and hence when a high molecular weight compound originally present in a photographic silver halide emulsion and used as a binder is left therein without being dissolved in water as gelatin, only the polymerized portion is left to form an image since the polymer can scarcely diffuse into the gelatin phase. When a monomer having more than two vinyl groups is used together with the aforesaid vinyl monomer, the insolubility and the non-diffusion properties of the polymer can be further increased.

By dyeing the polymer images with the dye as mentioned above, the dye images or color images corresponding to the polymer images can be obtained. The dye images thus produced can be utilized as clear color images by removing the silver halide by a fixing procedure and further dissolving away the silver images by the action of an oxidizing agent and a solvent for the silver salt. When a reducing agent having a quite high polymerization initiating effect is employed, the polymerization reaction occurs sufficiently even when only a very slight amount of reduced silver is formed; and hence, in such a case, it is scarcely or not at all necessary to remove the silver images by oxidation.

Furthermore, the dye images formed may be transferred to another support. For carrying out the transfer, the emulsion layer having the dye images thereon is wetted with a solvent for the dye, such as methanol, water, an aqueous solution of an acid, a base or a salt and then the layer is brought into intimate contact with the surface of the support receiving the dye image. As such supports, there may be used ordinary paper, a paper having coated thereon a hydrophilic polymer layer or a gelatin layer, and a film having coated thereon a hydrophilic polymer layer or a gelatin layer.

When the dye images are transferred to a support having coated thereon a gelatin layer, it is convenient

to use a support treated with a mordant such as an aluminum salt, as is used in a conventional dye-transfer process. When an image of a high molecular weight compound capable of having charges is once formed, it is possible to make a number of copies therefrom by dyeing and transferring as mentioned above. Also, since several copies of transferred images can be obtained from only one dye image, and since one polymer image can be repeatedly dyed, many copies can be easily obtained in accordance with the present invention.

The present invention will be further illustrated by the following non-limiting examples.

EXAMPLE 1

A photographic fine grain silver chlorobromide emulsion containing about 60 g./liter of gelatin and about 42 g./liter (as silver) of silver chlorobromide, and having a chlorine to bromine mole ratio of 7:3, a pH of 5.8 and a pAg of 7.6 was divided into two parts, one of which was exposed to a fluorescent lamp. For carrying out the exposure, about 200 ml. of the emulsion, melted at about 35°C., was spread over a vat of 20 cm. × 25 cm. and then the liquid layer thus spread was exposed, with stirring, to a fluorescent lamp of about 300 luxes for about 5 minutes. Into a test tube of 1.6 cm. in diameter was charged 2 ml. each of the exposed and the unexposed emulsion and, after adding 6 ml. of water to each tube, 4.0 g. of acrylamide was dissolved in each solution and then 10^{-3} mole of sodium 1-naphthol-4-sulfonate (compound 3) was added thereto. After stirring sufficiently, the temperature of the system was adjusted to 60°C. and the test tubes were placed in a heat insulating material. The insulating material was covered by foamed polystyrene of about 2 cm. in thickness and the whole system was immersed in a water bath kept at 60°C. Thereafter, 4.0 ml. of a 1 N aqueous sodium hydroxide solution was immediately added to each system and the change of temperature was recorded by using a thermister-type temperature recorder. The temperature of the exposed emulsion was increased by the heat of polymerization caused by the polymerization of the acrylamide and, after about 118 minutes from the start of the reaction, the temperature reached 91.5°C. Further, the contents of the test tube increased in viscosity because of the polyacrylamide thus formed and were not dissolved even by a large amount of methanol.

On the other hand, the temperature of the unexposed emulsion system reached only 75°C.

Thus, it was clear from the generation of heat of polymerization and the change in fluidity of the whole system that the polymerization occured in the exposed emulsion system. In fact, the reduction of the silver halide might possibly generate heat in addition to that generated by the polymerization reaction, but the amount of heat generated by the reduction of the silver halide would be too slight to be detected as a temperature change in this system. For example, when hydroquinone was used in the aforesaid procedure instead of sodium 1-naphthol-4-sulfonate, the silver halide was reduced into black silver but no generation of heat was observed. Also, when sodium 2-naphthol-1-sulfonate (compound 7) was used instead of sodium 1-naphthol-4-sulfonate, the temperature of the exposed emulsion reached 94°C. after 123 minutes, whereas the temperature of the unexposed emulsion system reached only 80°C.

From the aforesaid facts, that in the exposed emulsion system, the polymerization preferentially occurred under the same conditions as compared with the system using the unexposed emulsion, it was confirmed that the exposed emulsion took part in the reaction and, in fact, caused the reaction.

EXAMPLE 2

A photographic light-sensitive film having coated thereon a photographic gelatino silver chloriodobromide emulsion layer was exposed and processed to conduct imagewise polymerization in a solution containing 1,7-dihydroxy-6-naphthoic acid (compound 21), acrylamide, and methylene-bis-acrylamide. The photographic film was prepared as follows: Both surfaces of a polyethylene terephthalate film were undercoated, onto one of the surfaces was then coated an anti-halation layer and onto the other was coated a gelatino fine particle silver halide emulsion containing 100 g. of gelatin and about 0.7 mole of chlorine, about 0.3 mole of bromine and about 0.001 mole of iodine per 1 mole of silver, and having incorporated therein a merocyanine dye having the maximum sensitivity at 550 m. as a sensitizing dye, about 1.5 g. of mucochloric acid per 100 g. of gelatin as a hardening agent, and a proper stabilizer and surface active agent so that the layer thus coated contained 50 mg. of silver per 100 $cm.^3$ of the layer. Then, a protective layer of gelatin having a thickness of about 0.8 micron was applied to the emulsion layer. Such a photographic film is usually used for preparing net images or line images by a photoengraving process.

A negave having line images was placed on the photographic light-sensitive film, the system was exposed for 2 seconds to light of about 100 luxes, and then the emulsion layer was immersed, under a stable red light, in a solution having the following composition:

Acrylamide	90 g.
Methylene-bis-acrylamide	10 g.
1,7-dihydroxy-6-naphthoic acid (compound 21)	0.3 g.
Potassium metabisulfite	3.0 g.
Water	100 ml.
2N NaOH solution	the amount necessary to adjust the pH to 11.5.

When the film was allowed to stand for 30 minutes at 30°C., a slight image was observed at the exposed areas. When the reaction was stopped by a 1 percent aqueous solution of acetic acid and, after washing the layer with water, the gelatin of the emulsion layer was decomposed by using an aqueous solution of 1 percent gelatin-decomposing enzyme (trade name Bioprase PN 4); the gelatin at the unexposed areas was completely washed away and undecomposed film was left at the unexposed areas, which showed that the polymerization selectively occurred at the exposed areas. The same results were obtained when the same procedure was conducted using 0.07 g. of 5-amino-1-naphthol (compound 32) instead of 1,7-dihydroxy-6-naphthoic acid.

EXAMPLE 3

The photographic light-sensitive film as in Example 2 was exposed as in that example and processed, in a solution having the following composition, to conduct the development and polymerization:

1-vinyl-2,3-dimethylimidazolium-p-toluene sulfonate	75 g.
1,2-diaminonaphthalene (compound 27)	10 mg.
Potassium metabisulfite	2 g.
2N solution of sodium hydroxide	amount necessary to adjust the pH to 11.6
Water	75 ml.

The 1-vinyl-2,3-dimethylimidazolium-*p*-toluene sulfonate had been prepared by reaction 1-vinyl-2-methylimidazole and methyl *p*-toluene sulfonate at a normal temperature and recyrstallizing the product from ethanol and ether. The melting point of the crystal was 1,425°C.

When the layer was processed for 10 minutes at 30°C. in the above solution, a faint brown silver image and, at the same time, an image of a quaternary salt polymer were formed, which was confirmed by the following procedure.

That is, the layer was washed for 30 seconds with a 1.5 percent aqueous solution of acetic acid and fixed by a fixing solution having the following composition:

Anhydrous sodium thiosulfate	150 g.
Potassium metabisulfite	15 g.
Water to make	1 liter.

After sufficiently fixing and washing, the image thus formed was dyed by a 0.1 percent aqueous solution of a blue acid dye, Suminol Leveling Sky Blue R-extra conc., C.I. Acid Blue 62 and then washed for 5 minutes with a 1 percent aqueous solution of sodium bicarbonate to provide a blue image.

As the brown image was a silver image, it could be readily dissolved away by a Farmer's reducer. When dissolving away the silver image, a clear blue image could be obtained. Moreover, when the dyeing procedure was conducted after the removal of the silver image, that is, when the silver image was first removed to provide a colorless and transparent image and then the image was dyed as above, a similar blue image could be obtained.

The color image thus formed could be transferred onto a paper. That is, when an ordinary writing paper was slightly wetted with methanol, and the color image thus obtained was closely brought into contact with the paper wetted, after 30 seconds the former was separated from the latter, and the color image was transferred onto the paper.

Also, when a gelatin layer of about 10 microns was applied on the surface of a baryta-coated paper and the paper was immersed in an aqueous solution of an alum followed by drying to provide a transfer paper, and then the paper was after being wetted with water, brought into close contact with the color image mentioned above, and after 1 minute, the transfer paper was separated from the latter, a clear blue image having a high density was obtained on the transfer paper.

Furthermore, when the polymer image was immersed for 5 minutes in an aqueous solution of 0.1 percent of a red acid dye, Solar Rhodamine B extra C.I. Acid Red 52 instead of immersing the aforesaid aqueous solution of Suminol Leveling Sky Blue R extra conc. and then washed with water, a sample was obtained where only the image portions were dyed in red.

The red image could also be transferred onto a writing paper wetted by ethanol. Moreover, the color image could be transferred onto the aforesaid gelatin layer-containing transfer paper wetted by water.

Also, when the polymer image was dyed by a yellow dye, Solar Blue Yellow 8 G.C.I. Acid Yellow 7 or Tartrazine C.I. Acid Yellow 23 and washed with a buffer solution having a pH of 5.0, a yellow image was obtained and the image could be transferred onto a writing paper wetted by methanol or the aforesaid gelatin layer-containing paper wetted by water.

Also, the same reaction was conducted at a pH of 11.5 using 2,3-dioxynaphthalene (compound 17) instead of 1,2-diaminonaphthalene, for 30 minutes, and almost the same results were obtained.

EXAMPLE 4

The photographic light-sensitive film as in Example 2 was exposed as in Example 2 and was processed in a solution having the following composition and containing the reducing agent as shown in Table I:

Methacrylic acid	58.9 ml.
Sodium carbonate (monohydrate)	43.0 g.
Reducing agent shown in Table I.	amt. shown in Table I
Potassium metabisulfite	3.0 g.
Water	87.5 ml.
2N-Sodium hydroxide	the amount necessary to adjust the pH to the value shown in Table I.

After processing for the period of time shown in Table I at 30°C., the film was fixed and washed with water as in Example 2 to provide an image of polymethacrylic acid, which was dyed by a 1 percent solution of a basic dye, Rhodamine 6 GCP. The transmission densities to green light were measured about the exposed and the unexposed portions of the photographic film before and after dyeing. The kind of reducing agent, the pH of the system at processing, the processing time, and the optical densities before and after dyeing are shown in Table I.

No.	Reducing Agent	Amount of reducing agent (g)	Processing time (min)	Density of unexposed area before	Density of unexposed area after	Density of exposed area before	Density of exposed area after	pH
1	α-Naphthol	2.05	15	0.22	0.64	0.72	2.41	11.53
2	1-Naphthol-2-potassium sulfonate	1.18	20	0.10	1.07	0.11	2.88	11.55
3	1-Naphthol-4-sodium sulfonate	1.07	50	0.09	1.16	0.09	1.41	11.55
4	1-Naphthol-5-sodium sulfonate	1.11	30	0.12	1.30	0.13	2.25	11.50
5	β-Naphthol	6.48	30	0.08	0.71	0.09	2.54	11.50
6	2-hydroxy-1-naphthoaldehyde	7.74	50	0.14	0.54	0.16	1.90	11.50
7	2-Naphthol-sodium sulfonate	11.07	50	0.07	0.35	0.09	0.48	11.60
8	2-Sodium-6-sodium sulfonate	11.07	70	0.10	1.46	0.14	1.68	11.50
9	2-Naphthol-7-sodium sulfonate	11.07	40	0.25	1.12	0.20	1.78	11.33
10	2-Naphthol-8-sodium sulfonate	11.07	40	0.13	1.60	0.14	2.09	11.50
11	2-Hydroxy-1-naphthoic acid	8.46	40	0.17	1.00	0.18	2.23	11.50
12	m-N-(2-hydroxy-3-naphthoyl)phenylenediamine	5.00	70	0.22	3.10	0.32	3.62	11.50
13	β-(2-hydroxy-3-naphthoyl)aminoethanol	10.40	70	0.10	0.61	0.13	2.51	9.00
14	α-Nitroso-β-naphthol	0.08	70	0.07	0.46	0.08	1.07	9.10
15	Naphtholorange	1.00	70	0.10	0.37	0.12	1.64	11.55

—Continued

No.	Reducing Agent	Amount of reducing agent (g)	Processing time (min)	Density of unexposed area before	Density of unexposed area after	Density of exposed area before	Density of exposed area after	pH
16	1-(1-hydroxy-2-naphthylazo)-5-nitro-2-naphthol-4-sodium sulfonate	0.50	30	0.40	1.37	0.44	2.73	11.45
17	2,3-Naphthalenediol	7.20	15	0.17	0.92	0.68	3.70	11.50
18	2,3-dihydroxynaphthalene-6-sodium sulfonate	11.79	40	0.08	0.28	0.06	1.32	11.50
19	1,5-dihydroxynaphthalene	7.20	20	0.08	0.55	0.28	1.63	9.00
20	1,7-dihydroxynaphthalene	0.16	30	0.08	0.35	0.14	1.84	9.15
21	1,7-dihydroxy-6-naphthoic acid	0.756	60	0.10	1.34	0.10	2.10	9.05
22	α-naphthylamine	0.44	50	0.08	0.42	0.05	0.57	9.05
23	β-diethylaminoethyl-α-naphthylamine	8.32	70	0.12	0.52	0.12	0.66	10.50
24	thionalide	3.52	70	0.15	0.69	0.16	1.77	10.50
25	2-naphthylamine-8-sodium sulfonate	10.04	70	0.09	0.43	0.07	1.12	11.50
26	2-naphthylamine-4,8-disodium sulfonate	15.61	70	0.10	0.41	0.15	0.91	11.50
27	1,2-naphthalenediamine	0.71	10	0.09	0.25	0.48	2.93	9.00
28	1,5-naphthalenediamine	7.11	30	0.11	0.30	0.16	1.90	11.50
29	2-amino-8-naphthol-3,6-disulfonic acid	14.35	20	0.12	0.85	0.12	2.54	11.50
30	1-amino-2-naphthol-4-sodium sulfonate	0.01	40	0.12	0.51	0.22	1.41	9.03
31	1-amino-5-naphthol	7.16	7	0.22	0.84	1.21	3.10	11.50
32	5-methaacryloylamino-1-naphthol	10.22	25	0.18	0.25	0.26	1.80	11.50
33	8-oxyquinolin	6.53	70	0.08	0.22	0.08	0.56	11.50
34	4,8-dihydroxyquinolin-2-carboxylic acid	6.00	30	0.09	0.29	0.12	2.24	11.50
35	4-hydroxyquinolin-2-carboxylic acid	8.50	70	0.11	0.36	0.12	0.63	11.50
36	1-naphthol-3-sulfonamide sodium salt	1.00	30	0.18	2.51	0.19	3.34	11.50
37	2,4-dichlor-1-naphthol	0.96	30	0.99	3.70	1.05	above 4	11.50
38	2,3-diaminonaphthalene	3.50	15	0.07	0.62	0.07	2.44	11.50

From the above results, it was confirmed that the density of the color image was higher in the exposed portions than in the unexposed portions and hence the exposed portions were selectively dyed. This was also confirmed by the fact that when the silver image of each sample was removed by a Farmer's reducer, a clear red image was obtained.

When the reducing agent of compound 13 or 14 was used, the increase in density was large and a clear red image was obtained without bleaching the silver by a Farmer's reducer. Also, the color image obtained above could be transferred onto a writing paper using methanol as in Example 3.

EXAMPLE 5

By using the following films, A and B shown below, the polymerization of a system of sodium methacrylate and 2,3-naphthalene diol (compound 17) was conducted.

Film A: After subbing both surfaces of a cellulose triacetate support, one of them was coated with an antihalation layer. The other surface was coated with a gelatino middle grain size silver halide emulsion containing about 225 g. of gelatin, about 0.015 mole of iodine and about 0.985 mole of bromine per one mole of silver, and having incorporated therein 0.5 g. of mucochloric acid per 100 g. of gelatin as a hardening agent, a proper stabilizer, and a surface active agent so that the layer contained 60 mg. of silver per 100 $cm.^3$ Thereafter, a protective layer consisting of gelatin having a thickness of about 1 micron was applied to the emulsion layer. The film thus prepared was of the type used for preparing positives by photogravure.

Film B: A film support having subbing layers and an antihalation layer as in Film A was coated with a gelatino fine grain silver halide emulsion containing about 204 g. of gelatin, about 0.012 mole of iodine and about 0.988 mole of iodine per one mole of silver, sensitized by a rhodan complex of mono-valent gold, and having incorporated therein 0.3 g. of 6-methyl-4-hydroxy-1,3,3*a*,7-tetraazaindene per one mole of silver as a stabilizer, about 0.7 g. of mucochloric acid per 100 g. of gelatin as a hardening agent, and a proper surface active agent, so that the layer contained 60 mg. of silver per 100 $cm.^3$ Further, a protective layer of gelatin having a thickness of about 0.8 micron was applied to the emulsion layer. The photographic light-sensitive film thus prepared was of the type used for preparing line images or hard continuous tone positives by photogravure.

The two sample films were exposed as in Example 2 and processed in a solution having the following composition:

Sodium methacrylate	75 g.
2,3-naphthalene diol (compound 17)	0.72 g.
Potassium metabisulfite	3.0 g.
Water	75 ml.
2N-sodium hydroxide	amount necessary to adjust the pH to 11.5.

When the films were processed for 20 minutes at 30°C., faint brown images were obtained. Each of the samples was fixed and washed as in Example 3 and divided into two parts, one of which was dyed using rhodamine 6 GCP as in Example 4. After drying, the densities of the dyed sample and the unprocessed sample were measured as in Example 4, the results of which are shown in Table II.

Table II

Film	Density of unexposed area		Density of exposed area	
	Before dyeing	After dyeing	Before dyeing	After dyeing
A	0.06	0.50	0.07	2.73
B	0.06	0.43	0.07	2.82

In the exposed areas, a color image was formed although the formation of the silver image was scarcely observed, which showed that the polymerization could be initiated by the reduction of a very small amount of silver.

Also, each sample thus dyed was wetted with water, placed under pressure on the surface of a transfer paper as used in Example 3 and wetted by an aqueous solution of 1 percent sodium bicarbonate, and, after allowing it to stand for 3 minutes, the transfer paper was separated from the sample to provide a color image on the transfer paper.

EXAMPLE 6

Six films as in Example 2 were exposed to light of 50 luxes for 1 second through an optical step-wedge having a step difference of 0.15 and processed in solutions having the following compositions, respectively. In this example, the effect of adding a conventional developing agent is demonstrated.

Sample No.	1	2	3	4	5	6
Component						
Sodium methacrylate (g.)	100	100	100	180	100	100
α-naphthol (g.)	1.73	1.73	1.73			
2,3-naphthalenediol (g.)		0.		0.96	0.96	0.96
Catechol (mg.)		0.17	1.7			
p-methylaminophenol sulfate (mg.)					0.01	0.1
Potassium metabisulfite(g)	4	4	4	4	4	4
Water (ml.)	100	100	100	100	100	100
2N-sodium hydroxide	the amount necessary to adjust the pH of the system to 11.5.					

After processing for 10 minutes at 30°C., each sample was processed further as in Example 4. After being sufficiently fixed and washed, each sample was cut into two parts, one of which was processed in a Farmer's reducer to completely bleach the silver. Furthermore, about samples 1, 2, and 3, the optical density at the 5th step was measured and about samples 4, 5, and 6, the optical density of the 6th step was measured using a green filter, the results of which are shown in Table III.

Table III

Sample No.	Density of unexposed area	Density of exposed area	Number of final step susceptible to dyeing
1	0.26	0.44	8
2	0.28	0.72	10
3	0.25	0.93	11
4	0.27	1.10	10
5	0.61	1.51	11
6	0.44	1.59	11

The density shown above was that of the dye dyed to the selectively formed polymer in proportion to the amount of exposure and hence corresponds to the amount of polymer formed. Also, the number of final steps susceptible to dyeing shown in the above table was the step number through which the increase of color density could be observed as compared with the fogged portions when the sample thus dyed and bleached was observed by naked eye. That is, the number corresponds to the minimum amount of exposure capable of selectively forming the polymer; thus, the larger the number of the final step, the higher the sensitivity of the film.

Since the step difference of the optical wedge used was 0.15, the fact that sample 2 was 2 steps higher than sample 1 in the number of final steps as shown in Table III, shows that sample 2 gave the same extent of polymerization as sample 1 with one-half of the exposure amount for sample 1. In other words, the processing solution used for processing sample 2 gave the same effect as the case where the sample was exposed twice as much, as compared with processing the sample in the processing solution used for processing sample 1. Also, when sample 4 was compared with sample 6, the density corresponding to a so-called fog increased, but when the optical densities at the same 6th stage were compared, the increase in density by dyeing was larger in sample 4, and hence it was confirmed that the amount of the polymer formed by polymerization corresponding to the same amount of exposure was larger in sample 4. Thus, it was confirmed that by the use of a conventional developing agent together with the reducing agent of the present invention, the polymerization of the system was effectively promoted.

EXAMPLE 7

Five film samples as in Example 6 were prepared and, after exposure, were processed in a solution having the following composition. In this example, the effect of using a quaternary salt with the reducing agent of this invention was shown. As the quaternary salt, laurylpyridinium chloride was used.

Sample No.	1	2	3	4	5
Component					
Sodium methacrylate (g.)	100	100	100	100	100
2,3-naphthalene diol (g.)	0.96	0.96	0.96	0.96	0.96
1% laurylpyridinium chloride (ml.)		2.5	9	22.5	40
Potassium metabisulfite (g.)	4	4	4	4	4
Water (ml.)	100	100	100	100	100
2N-Sodium hydroxide	the amount necessary to adjust the pH of the system to 11.5.				

After processing for 10 minutes at 30°C., the samples were processed further as in Example 6, and the results are shown in Table V.

Table V

Control No.	Density of unexposed area	Density for 6th step	Number of final step susceptible to dyeing
1	0.27	1.10	10
2	0.51	1.91	11
3	0.46	1.97	12
4	0.46	2.15	12
5	0.53	1.77	12

The analysis of the data can be done as in Example 6. Thus, the results showed that in the case of using the quaternary salt together with the reducing agent of this invention, almost the same amount of polymer was obtained either when the exposure amount was less or when the processing period of time was less.

EXAMPLE 8

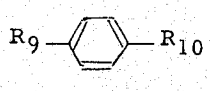
The film as in Example 2 was exposed to X-rays. Thereafter, the film was processed in solution 17 of Example 4.

The X-ray exposure was conducted by using a cobalt X-ray tube made by Philips Co. at 30 kv. and 10 ma. The sample was exposed to the X-ray tube at 1 cm. apart from the window of the X-ray tube while covering a part of the sample by a razor blade of 0.2 mm. in thickness.

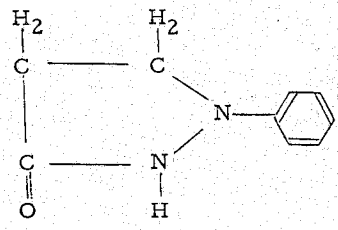
The samples were each exposed for 1 second, 3 seconds or 10 seconds, respectively, and were processed for 20 minutes at 30°C. By this procedure, only the portions exposed to X-rays gave a silver image, and by subjecting the image to the post-processing steps as in Example 7, the image portions were dyed, which showed that polymethacrylic acid was formed.

Thus, the process of this invention can be applied to a silver halide emulsion layer exposed to high energy rays, such as X-rays.

Further supplementing our discussion of the conventional developing agents and quaternary salts useful in the present invention, as described at Pages 25 and 26 of this application, of particular interest is a developing agent having the formula:



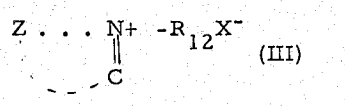
(I)



(II)

wherein R_9 and R_{10} represent a member selected from the group consisting of a hydroxyl group, an amino group and a $-NHR_{11}$ group, wherein R_{11} represents a member selected from the group consisting of an alkyl group having from 1 to 5 carbon atoms and a substituted alkyl group.

With respect to the quarternary salt compounds useful in the present invention, most excellent results have been achieved with a quaternary salt having a heteroaromatic ring including at least one nitrogen atom having an aliphatic amine, said quaternary salt having the following formula:



(III)

$(R_{12})_3N^+ \cdot R_{14}X^-$ (IV)

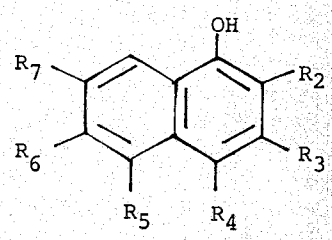
wherein X^- represents a member selected from the group consisting of a halogen atom and a $R_{13}SO_3^-$, R_{13} representing a member selected from the group consisting of an aliphatic group and an aromatic group; R_{12} represents a member selected from the group consisting of an alkyl group having from 1 to 18 carbon atoms and a substituted alkyl group; R_{14} represents a member selected from the group consisting of, an alkyl group having from 1 to 5 carbon atoms, and a substituted alkyl group; and Z represents a member selected from the group consisting of a carbon atom and a nitrogen atom necessary to complete a 5-membered or 6-membered heterocyclic ring.

Although the present invention has been adequately described in the foregoing specification and Examples included therein, it is readily apparent that various modifications and changes can occur, without departing from the spirit and scope thereof.

What is claimed is:

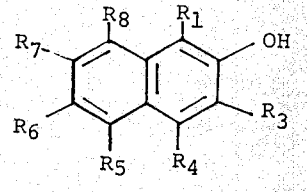
1. A process for the formation of a polymer image which comprises exposing a photographic silver halide emulsion so as to provide a latent image and subsequently, developing said latent image in the presence of one monomer of the group consisting of a vinylidene monomer and a vinyl monomer, and in the presence of at least one reducing agent compound selected from those represented by the following formulas:

i. α-naphthol or a derivative thereof



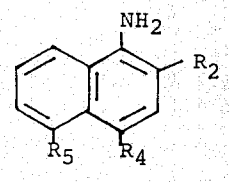
wherein R_2 represents a hydrogen atom, a sulfone group, a substituted arylazo group or a chlorine atom; R_3 represents a hydrogen atom, or a sulfamoyl group; R_4 represents a hydrogen group, a sulfone group or a chlorine atom; R_5 represents a hydrogen atom, a sulfone group, a hydroxyl group, an amino group, or an acylamino group; R_6 represents a hydrogen atom, a carboxyl group or a sulfone group; and R_7 represents a hydrogen atom, a hydroxyl group or an amino group;

ii. β-naphthol or a derivative thereof



wherein R_1 represents a hydrogen atom, a formyl group, a sulfone group, a carboxyl group, a nitroso group, an arylazo group or an amino group; R_3 represents a hydrogen atom, —CONHR′ (R′ represents an aryl group or an alkyl group), or a hydroxyl group; R_4 represents a hydrogen atom, a chlorine atom or a sulfone group; R_5 represents a hydrogen atom or a nitro group; and R_6, R_7 and R_8 each represents a hydrogen atom or a sulfone group;

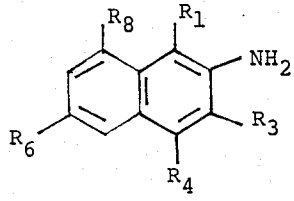
iii. α-naphthylamine or a derivative thereof



wherein R_2 represents a hydrogen atom, a substituted alkyl group, an amino group, or a hydroxy group; R_4

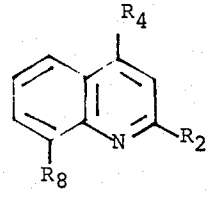
represents a hydrogen atom or a sulfone group, and R_5 represents a hyrogen atom, an amino group or a hydroxyl group;

iv. β-naphthylamine or a derivative thereof



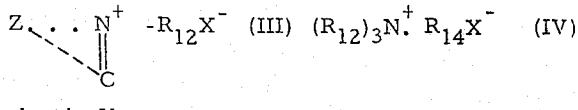
wherein R_1 represents a hydrogen atom or an amino group; R_3 represents a hydrogen atom, a sulfone group or an amino group; R_4 represents a hydrogen atom or a sulfone group; R_6 represents a hydrogen atom or a sulfone group, and R_8 represents a hydrogen atom, a sulfone group or a hydroxyl group; and

v. oxyquinoline derivative



wherein when R_8 is a hydroxyl group, R_2 represents a hydrogen atom or a carboxyl group and R_4 represents a hydrogen atom or a hyroxyl group; and when R_4 is a hydroxyl group, R_2 represents a carboxyl group and R_8 represents a hydrogen atom; whereby said monomer is selectively polymerized at the areas having said latent image in the presence of a sulfite ion and a developing agent, said sulfite ion being present in at least 0.04 mol per liter.

2. The process of claim **1,** wherein said polymerization reaction is conducted in the presence of a small amount of a quaternary salt having a heteroaromatic ring including at least 1 nitrogen atom or having an aliphatic amine, said quaternary salt having the following formulae (III) or (IV):

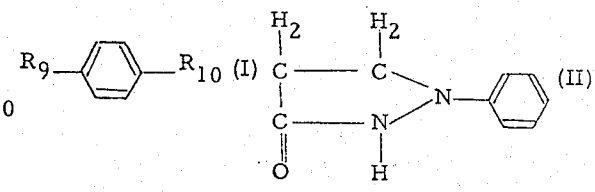


wherein X^- represents a member selected from the group consisting of a halogen atom and a $R_{13}SO^-_3$, R_{13} representing a member selected from the group consisting of an aliphatic group and an aromatic group; R_{12} represents a member selected from the group consisting of an alkyl group having from 1 to 18 carbon atoms and a substituted alkyl group; R_{14} represents a member selected from the group consisting of an alkyl group having from 1 to 5 carbon atoms, and a substituted alkyl group; and Z represents a member selected from the group consisting of a carbon atom and a nitrogen atom necessary to complete a 5-membered or 6-membered heterocyclic ring.

3. The process of claim **2,** wherein the formed polymer image is dyed by a dye.

4. A process for the formation of a polymer image as in claim **2,** wherein

said developing agent having the following general formula (I) or (II):



wherein R_9 and R_{10} represent a member selected from the group consisting of a hydroxyl group, an amino group and a $—NHR_{11}$ group, wherein R_{11} represents a member selected from the group consisting of an alkyl group having from 1 to 5 carbon atoms and a substituted alkyl group.

5. The process of claim **4,** wherein said quaternary salt is a quaternary salt of pyridine.

6. The process of claim **5,** wherein said quaternary salt is pyridinium chloride.

7. The process of claim **1,** wherein the formed polymer image is dyed by a dye.

8. The process of claim **7** wherein dying is accomplished by the affinity of the dye for the formed polymer.

9. The process of claim **7,** wherein the dye has a charge opposite to the charge of said formed polymer.

10. A process for the formation of a polymer image as in claim **9** wherein said thus-formed polymer image is further dyed by a dye having a charge opposite to the charge of said polymer when said polymer image is electrolytically dissociated or combined with a hydrogen cation.

11.. The process of claim **10,** wherein said polymer stems from a vinyl compound capable of providing a negative charge to said polymer, said compound being a member selected from the group consisting of a vinyl compound having a carboxyl group, a vinyl compound having a metal salt or an ammonium salt of a carboxylic acid, a vinyl compound having a sulfonic acid group, and a vinyl compound having a metal salt or an ammonium salt of sulfonic acid.

12. The process of claim **10,** wherein said polymer stems from a vinyl compound capable of providing positive charges to said polymer, said compound being selected from the group consisting of a vinyl compound having a basic nitrogen atom and a vinyl compound having a quaternary nitrogen salt.

13. The process of claim **12,** wherein said vinyl compound may be joined with a water-soluble addition polymerizable vinyl compound having no charge.

14. The process of claim **10.** wherein said dye is an acid dye selected from the group consisting of Acid Yellow No. 7, Acid Yellow No. 23, Acid Red No. 1, Acid Red No. 52, Acid Blue No. 9, Acid Blue No. 45, Acid Blue No. 62, and Acid Violet No. 7.

15. The process of claim **10,** wherein said dye is a basic dye selected from the group consisting of Basic Yellow No. 1, Basic Yellow No. 2, Basic Red No. 1, Basic Red No. 2, Basic Blue No. 25, Basic Violet No. 3, and Basic Violet No. 10.

16. A process for the formation of a polymer image as in claim **1,** wherein said compound is selected from

the group consisting of α-naphthol, 1-naphthol-2-potassium sulfonate, 1-naphthol-4-sodium sulfonate, 1-naphthol-5-sodium sulfonate, β-naphthol, 2-hydroxy-1-naphthoaldehyde, 2-naphthol-1-sodium sulfonate, 2-naphthol-6-sodium sulfonate, 2-naphthol-7-sodium sulfonate, 2-naphthol-8-sodium sulfonate, 2-hydroxy-1-naphthoic acid, m-N-(2-hyroxy-3-naphthoyl)phenylenediamine, β-(2-hydroxy-3-naphthoyl)aminoethanol, α-nitroso β-naphthol, naphtholorange, 1-(α-hydroxy-2-naphthylazo)-5-nitro-2-naphthol-4-sodium sulfonate 2,3-naphthalenediol, 2,3-dihydroxynaphthalene-6-sodium sulfonate, 1,5-dihydroxynaphthalene, 1,7-dihydroxynaphthalene, 1,7-dihydroxy-6-naphthoic acid, α-naphthylamine, β-diethylaminoethyl-α-naphthylamine, thionalide, 2-naphthylamine-8-sodium sulfonate, 2-naphthylamine-4,8-disodium sulfonate, 1,2-naphthalenediamine, 1,5-naphthalenediamine, 2-amino-8-naphthol-3,6-disulfonic acid, 1-amino-2-naphthol-4-sodium sulfonate, 1-amino-5-naphthol 5-methaacryloylamino-1-naphthol, 8-oxyquinolin, 4,8-dihydroxy-quinolin-2-carboxylic acid, 4-hydroxyquinolin-2-carboxylic acid, 1 -naphthol-3-sulfonamide sodium, 2,4-dichloro-1-naphthol, and 2,3-diaminonaphthalene.

17. A process for the formation of a polymer image as in claim **1,** wherein said monomer is selected from the group consisting of acrylamide, acrylonitrile, N-hydroxymethyl acrylamide, N-*t*-butylacrylamide, methacrylic acid, acrylic acid, calcium acrylate, sodium acrylate, methyl methacrylate, ethyl acrylate, vinyl pyrrolidone, dicyclopentadiene methacrylate vinyl butyrate, 2-vinylpyridine, 4-vinylpyridine, 2-methyl-N-vinylimidazole, potassium vinylbenzene sulfonate, vinyl carbazole, N,N'-methylene-bis-acrylamide, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, divinylbenzene, bisphenol A dimethacrylate, butylene dimethacrylate, trimethylolpropane trimethacrylate, pentaerythrito tetraacrylate, and the like.

18. The process of claim **1,** wherein said silver halide emulsion consists of a dispersion system in which particles of silver halide are dispersed in a solution of high molecular weight polymer selected from the group consisting of gelatin, polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylamide, carboxymethyl cellulose, oxyethyl ether, and dextrane, or mixtures of the aforementioned compounds.

19. The process of claim **1,** wherein said sulfite ions stem from a precursor which is a member selected from the group consisting of alkaline metal sulfites, ammonium sulfite, pyrosulfites, of alkaline metals, ammonium pyrosulfites, and aldehyde bisulfites.

20. The process of claim **19,** wherein said aldehyde bisulfite is a member selected from the group consisting formaldehyde bisulfite and glyoxal bisulfite.

21. The process of claim **1,** wherein the amount of sulfite ions present is greater than 0.2 mol per liter of reaction system.

22. The process of claim **1,** wherein said process is carried out at a pH greater than 6.

23. The process of claim **1,** wherein said process is carried out at a pH greater than 7.

24. The process of claim **1,** which further comprises the addition of an effective amount of a thermal polymerization inhibitor to prevent the spontaneous overall thermal polymerization of the vinyl monomer.

25. The process of claim **24,** wherein said inhibitor is a member selected from the group consisting of *p*-methoxyphenol, hydroquinone, an alkyl hydroquinone, and 2,6-di-*t*-butyl-*p*-cresol.

26. The process of claim **24,** wherein said amount of polymerization inhibitor ranges from 1/100,000 to 2/100 of the weight of the vinyl monomer.

27. The process of claim **1,** wherein said vinyl monomer is present in an amount of from 1.30 to 30 times the weight of the high molecular weight compound which is originally present in the emulsion.

28. The process of claim **27,** wherein said vinyl monomer is present in an amount of from one-fourth to 4 times the weight of the high molecular weight compound originally present in the emulsion.

29. The process of claim **1,** wherein the silver halide is present in an amount of from 1.20 to 2 times the amount of the high molecular weight compound originally present in the system.

30. The process of claim **1,** wherein said silver halide is present in an amount of from 1/10 to one-half times the amount of the high molecular weight compound originally present in the system.

31. The process of claim **1,** further comprising the presence of a reducing agent in an amount of from one one-thousandths to 20 mols per mol of silver halide.

32. The process of claim **1,** wherein said naphthol, naphthylamine, or oxyquinoline is present in an amount of from one two-thousandths to 5 mols per liter of processing solution.

33. The process of claim **1,** wherein said naphthol, naphthylamine or oxyquinoline is present in an amount of from one one-hundredth to 1 mol per liter of processing solution.

* * * * *