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(54) Heat-developable multilayered color photo-sensitive material.

(57) Heat-developable multilayered color photo-sensitive materials comprising a support having thereon layers sensitive to blue, green and red-light, each containing one or more of (a) a photo-sensitive silver halide, (b) an organic silver salt, (c) a developer and (d) a dye-providing compound exhibit improved properties with respect to color turbidity, fogging, contrast and staining, when a layer containing a diffusion-proof blue-lightabsorbing organic substance is interposed between the blueand the green-sensitive layers or between the blue- and the redsensitive layers.

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HEAT-DEVELOPABLE MULTILAYERED COLOR PHOTO-SENSITIVE MATERIAL

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a heat-developable multilayered color photo-sensitive material and more particularly to a heat-developable multilayered color photo-sensitive material in which a color contamination is improved.

Description of the Prior Art

With respect to the color photo-sensitive materials using silver halide, there are well-known processes such as a process using a dye formed by coupling the oxidant of a color developing agent to a coupler, another process (a silver dye bleach process) in which a dye is bleached by silver to obtain an image, or a further process being used in the so-called instant photography, in which a dye released through an oxidation-reduction reaction is diffused to transfer with an alkali-treating liquid.

To these photo-sensitive materials have been applied with a wet process in which an image is formed by making use of an alkali- or acid- treating liquid.

In recent years, in contrast with the wet processes, there have been developed simple and rapid processes using such a dry-treatment as a heat-treatment.

Heat-developable photo-sensitive materials and the processes thereof are described in U.S. Patent Nos. 3,152,904, 3,301,678, 3,392,020 and 3,457,075; Research Disclosure, No. 17029, June, 1978, pp. 9 - 15; and the like.

Among the processes of obtaining a color image through a heat-development process, the processes of forming a color image through a coupling of the oxidant of a developing agent to a coupler are described in U.S. Patent Nos. 3,531,286, 3,761,270 and 4,021,240; Belgian Patent No. 802,519; and the like. In these processes, however, there is such a defect that a sharp and clear color-image cannot be obtained because a silver-image and a color-image are produced at the same time.

There has been introduced a process in which silver is bleached in a liquid process or with the use of an activator-sheet so as to overcome the above-mentioned defect. However, this process is not also preferable.

On the other hand, there is known a process in which dyes are freed by a heat-development with the use of a dye silver salt. In this process, a sharp and clear image cannot also be

obtained because an exposed area and an unexposed area are hardly separated.

A process of forming a color-image by making use of leuco dyes is described in U.S. Patent Nos. 3,985,565 and 4,022,617, respectively. Wherein, however, it is difficult to incorporate the leuco dyes stably into a photographic material. This process has, therefore, a defect that a color is gradually tinted.

Meanwhile, such a process that diffusible dyes are released by a heat-development with the use of a reducible dye-providing material and a reducing agent is described in Japanese Patent O.P.I. Publication Nos. 179840/1982 and 198458/1982, respectively, and another process is described in Japanese Patent O.P.I. Publication Nos. 186744/1982 and 207250/1982, respectively, in which a transfer image is obtained on an image receiving layer by coupling to the oxidant of a developer in place of the above-mentioned reducible dye-providing material and then releasing diffusible dyes from the coupling position. And, a further process is described in Japanese Patent O.P.I. Publication No. 149046/1983 in which dyes are formed by the oxidant of a developer and couplers and the dyes formed by heat are then transferred.

These processes have been improved in various aspects.

For example, in an improvement, color is not made turbid by a silver-image and a color-image is obtained in a simple

operation because released dyes are heat-transferred.

In such a process as disclosed in the above-mentioned Japanese Patent O.P.I. Publication No. 149046/1983, in which color-forming dyes are heat-transferred by making use of colorless biequivalent couplers, there is an advantage particularly in sensitivity among various photographic characteristics, because it is unnecessary to contain a colored color-providing material in a heat-developable photo-sensitive layer.

On the other hand, in an ordinary silver halide color photo-sensitive material, it is well-known that the component layers are multilayered. The typical examples of the layer arrangements include such an arrangement that is provided on a support in order from the support side with a silver halide panchromatic emulsion layer which is sensitive to red-light, a silver halide orthochromatic emulsion layer sensitive to green-light and, on the uppermost, a silver halide regular emulsion layer sensitive to blue-light.

In such a color photo-sensitive material as mentioned above, the silver halide panchromatic emulsion and silver halide orthochromatic emulsion are spectrally sensitized by making use of such an optical sensitizer as usually called a sensitizing dye, and besides these spectrally sensitized layers, there is provided with the so-called blue-sensitive silver halide emulsion layer having the inherent sensitivity of

silver halide itself, that is also called a regular layer.

In a color photo-sensitive material being popularly used, a blue-sensitive silver halide emulsion layer is arranged to the farthest position from a support to serve as the uppermost layer as described above, a color turbidity is caused by overlapping the spectra thereof. Accordingly, in the case of a negative photo-sensitive material, for example, it is usual that the color turbidity is prevented from occurring by interposing a blue-light-absorbing filter layer between a blue-sensitive silver halide emulsion layer and a green-sensitive silver halide emulsion layer.

As for the above-mentioned blue-light-absorbing filter layers, these are used, a layer comprising silver colloids of the order of from 0.001 to 0.05 µm in the particle size, a layer containing such a dye stuff or a dye as flowed into a processing liquid in course of a developing process.

Such a blue-light-absorbing filter layer as mentioned may therefore be present only when exposing or sensitizing a photo-sensitive material to light, and if it still remains after completing a development process, an unnecessary absorption will be caused thereby, that is not desirable from the viewpoint of color-reproduction.

From this aspect, a silver colloidal layer is advantageous to an ordinary color negative development process because it can readily be removed in a bleaching or fixing step after

completing the development process.

If multilayered color layers are taken into consideration to arrange to such a heat-development type color photo-sensitive material as is relative to the invention, it is required to provided thereto with a blue-light absorbing filter layer mentioned above.

In a heat-developable photo-sensitive material, however, such a silver colloid layer as used in the above-mentioned color negative photo-sensitive material cannot be used.

Because, in the case of a heat-developable photo-sensitive material, the silver colloid works as a physical developing nucleus for a heat-development as it has the property of a physical developing nucleus, and a reducing agent is oxidized and an organic silver salt is then so reduced as to deposit a metallic silver on the colloidal silver. Resultantly, the oxidants of the reducing agent are diffused into the adjacent layer to cause an undesirable color formation, the increase in fogginess and the lowering of contrast. It is, therefore, not preferable to make the silver colloid layer serve as a blue-light absorbing filter layer.

Objects of the Invention

It is the first object of the invention to provide a heat-developable multilayered color photo-sensitive material in which color turbidity is improved.

The second object of the invention is to provide a

heat-developable multilayered color photo-sensitive material in which fogs are rarely to be caused and the contrast is not lowered.

The third object of the invention is to provide a heat-developable multilayered color photo-sensitive material of diffusion-transfer type in which a stain and contrast are improved.

Summary of the Invention

The above-mentioned objects of the invention can be achieved with a heat-developable multilayered color photo-sensitive material comprising a support having thereon a blue-sensitive layer, a green-sensitive layer and a red-sensitive layer respectively containing at least one selected from (a) a light-sensitive silver halide, (b) an organic silver salt, (c) a developer and, (d) a dye-providing compound (another substance may be contained), wherein a layer containing a diffusionproof blue-light absorbing organic substance is interposed between said blue-sensitive layer and said green-sensitive layer or between said blue-sensitive layer and said red-sensitive layer.

DETAILED DESCRIPTION OF THE INVENTION

It is preferred embodiment to contain all of (a) to (b) above-mentioned in each light-sensitive layer.

It is preferred to provide a layer containing the

blue-light absorbing organic substance to the side of a blue-sensitive emulsion layer opposite to the side thereof to be exposed to light when the photo-sensitive material is exposed to light.

In this case, the order of arranging a green-sensitive layer and a red-sensitive layer is not always fixed, but is allowed to arranged in reverse order. It is also allowed that only a blue-sensitive layer is also used for a blue-light absorbing filter layer as to a blue-light absorbable organic substance that is a yellow-dye releasing material.

As for the blue-light absorbing organic substances to be used in the invention (hereinafter called BAOS), the preferable thereof are those having an absorption property in a visible spectral range of from 400nm to 500nm. It is, further, preferred that they are not diffused to other layers when a photo-sensitive layer is multilayered or preserved, and they do not stain any image when heat-developing or heat-transferring.

The characteristics required for the above-mentioned BAOS may somewhat become different in accordance with the conditions of a heat-development process, a post-processing made after the development process, or the like.

As for the dye which does not stain the heat-developed image if it is used for the heat-developable multilayered color photo-sensitive material of the invention, either the one which is low in heat-diffusibility to a binder, or the one which is

rather high in heat-diffusibility to the binder, but is decolorized by heat or light is cited. The one which is rather high in heat-diffusibility, but has little affinity to the image receiving layer, and therefore does not substantially stain the layer is cited as well.

The term, "diffusionproof", of a BAOS means such a degree of diffusion that the BAOS may remain at the most in an adjacent layer even if the BAOS may move out of a layer containing the BAOS itself through a heat-development is made at a usual heat-developing temperature of from 110°C to 170°, and preferably it means such a degree of diffusion that the BAOS will remain in the layer containing the very BAOS. The measurement thereof may be made with the eye.

On the other hand, the thickness of a photo-sensitive layer to be used in a heat-developable photo-sensitive material of the invention is from 1µm to 15µm and preferably from 2µm to 10µm, and the thickness of a layer containing BAOS of the invention is from 0.5µm to 10µm and more preferably from 1µm to 5µm. When providing with other non-photo-sensitive layer, the thickness thereof is from 0.1µm to 20µm and preferably from 0.3µm to 5µm.

As for dyes which are decolorized by heat or light, descriptions have been made, for example, in U.S. Patent Nos. 3,745,009; 3,769,019; 3,615,432; 3,821,001; 4,088,497; 4,197,131; 4,260,676; and 4,283,487. However, since such dyes,

even though some use of decolorizable color may be available, cannot always prevent the image receiving layer from staining according to treating conditions, then, as further preferable BAOS, those which do not diffuse into the image receiving layer because the low heat-diffusibility are cited.

As for the BAOS to be used in the invention, the preferable thereof are those each having a maximum absorption in a range of from 400nm to 500nm. And, as for the BAOS which are not diffused to other layers when a photo-sensitive layer is multilayered or preserved, and are low in heat-diffusibility in a binder during heat-developing. It is preferable that the molecule of such BAOS has at least one hydrophilic group selected from the group consisting of sulfo, carboxy, sulfino, sulfeno, thiosulfo, dithiosulfo, hydroxysulfonyloxy, hydroxysulfonylthio, thiocarboxy, carboxyimido, hydrazoic acid, carbohydrazoic acid, hydroxime acid, carbohydroxime acid, hydroxame acid, carbohydroxame acid, sulfinimide acid, sulfonimide acid, sulfinohydroxime acid, sulfonohydroxime acid, and sulfamoyl group. Among these hydrophilic group, a sulfo, sulfino, sulfeno, thiosulfo, dithiosulfo, hydroxysulfonyloxy, hydroxysulfonylthio, carboxy and thiocarboxy group are preferable and a sulfo group and a carboxy group are especially preferable.

On the other hand, as for the substances for lowering the diffusibility in a binder, a BAOS having a ballast group is

given as an example. Such a preferable BAOS includes those having a large molecular ballast group which are, for example, hydrophobic groups such as a straight or branched alkyl group having not less than 8 carbon atoms, a group containing the above-mentioned alkyl group, an aryl group having a straight or branched alkyl group having not less than 4 carbon atoms and a group containing the above-mentioned aryl group.

The ballast groups are satisfactorily useful if they have 30 carbon atoms.

In addition, BOAS having a hydrophobic or hydrophilic chain polymer are preferable in the invention.

In this invention, when comparing the above-mentioned dyes having a hydrophilic group with the dyes having a ballast group, the latter is preferable, and the dyes having both of the hydrophilic group and a highly hydrophobic ballast group are more preferable.

The alkyl group having not less than 8 carbon atoms may be either one of the straight-chained or the branch-chained, and preferable ones have not more than 30 carbon atoms, and more preferable ones have not more than 27 carbon atoms. They include, for example, an n-octyl group, a tert-octyl group, an n-dodecyl group, an n-octadecyl group and the like.

As for the groups each containing the alkyl group, there may be given as the examples, an alkoxy group such as dodecyloxy group, an alkylthio group such as dodecylthio group,

the like. The alkyl groups useful in the invention shall not be limited thereto.

The groups each containing an aryl group having an alkyl

The groups each containing an aryl group having an alkyl group having not less than 4 carbon atoms include, for example, an aryloxy group substituted by an alkyl group having not less than 4 carbon atoms, and such an arylamide group as 3-palmitoylamidobenzamide group, substituted thereof. The groups useful in the invention shall not be limited thereto.

As for the BAOS to be used in the invention, those having an absorption in a visible spectral range of 400nm to 500nm are arbitrarily selected out of generally known dyes including azo dyes, azomethyne dyes, cyanine dyes, merocyanine dyes, oxonol dyes, styryl dyes, and the like.

Typical compounds of such BAOS can be those represented by the following Formula (1) or (2) and the polymers each having a unit induced from monomer represented by the Formula (3); among them, the polymers are more preferable because of the excellent dispersion proof property thereof;

Formula (1)

(*: Enol type is sometimes tautomerized to Keto type and vice versa.)

Formula (2)

where each of R_1 to R_5 is a hydrogen atom, a halogen atom, or a substituted or unsubstituted alkyl, alkoxy, alkylamido, aryl, aryloxy, or arylamido group with 1 to 22 carbon atoms, and any group is also allowed to have a carboxy or sulfo substituent;

 R_6 is a hydrogen atom, or an alkyl, alkoxy, alkylamido, aryl, anilino, aryloxy, or arylamido group with 1 to 22 carbon atoms, and any group is also allowed to have a substituent.

Each of R_7 to R_{11} is a hydrogen atom, a halogen atom; or a cyano, nitro, hydroxy, carboxy, or sulfo group; further or a substituted or unsubstituted alkyl, alkoxy, dialkylamino, acyl, alkylamido, or carboalkoxy group with 1 to 22 carbon atoms; R_7 and R_8 are also allowed to combine with each other to form a benzene ring;

Each of R_{12} and R_{13} is a substituted or unsubstituted alkyl group with 1 to 22 carbon atoms such as a methyl, ethyl, propyl, butyl, hydroxyethyl, methoxyethyl, carboxyethyl, sulfopropyl or methanesulfonamidoethyl group; R_{12} and R_{13} are also allowed to combine with each other to form a piperidine, pyrrolidine or morphorino ring, or the like;

Each of R_{14} to R_{17} is a hydrogen atom, a halogen atom, or a substituted or unsubstituted alkyl, alkoxy, or alkylamido group with 1 to 4 carbon atoms; R_{18} is a substituted or unsubstituted alkyl or aryl group; Each of R_{19} to R_{23} is a hydrogen atom, a halogen atom, a carboxy group, a sulfo group, or a substituted or unsubstituted alkyl, alkoxy, alkylamino, or alkylamido group with 1 to 22 carbon atoms.

As for the BAOS to be used in the invention which are represented by General Formula (1) or (2) above-cited, those whose molecule has one or more hydrophilic groups, a greatly hydrophobic alkyl group with 8 or more carbon atoms, or an aryl group having an alkyl group with 4 or more carbon atoms are preferable. Further, those whose molecule has both the above hydrophilic groups and the above hydrophobic group are especially preferable. In addition, compounds whose whole BAOS is polymeric are preferable as well.

Concrete samples of BAOS having Formula (1) or (2) to be used in the invention are given below, although the range of the invention is not limited thereto.

(Exemplified Compounds)

(1)

(2)

$$\begin{array}{c|c} & & & \\ & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\$$

(3)

(4)

(5)

(7)

(8)

(9)

$$N = C - C_{17} H_{35}$$
 $C - CH - N = N - OH$

(11)

(12)

(13)

(14)

(15)

(16)

(t)
$$C_4H_9$$
 O-O-N N=C-NHCOC₉H₁₉ OH SO₃Na O SO₃Na

(17)

(19)

(20)

(21)

C1
$$N=C-NHCO$$
NHCOCH₂O
(t) C_5H_{11}
C1 $C-CH-N=N$
COCH₃

(23)

(24)

(25)

C1
$$N=C-NHCO$$
 $N+COC_{15}^{H}_{31}$
 $C-CH-N=N$
 $C_{2}^{H}_{5}$

C1
$$N=C-NHCO N+COCH_2O N$$

(27)

(28)

(29)

$$\begin{array}{c|c} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & &$$

(31)
$$CH_3 \sim N - N = N - SO_3 Na$$

(32)
$$C_{2}^{H_{5}} \sim N - COOH$$

$$C_{2}^{H_{5}} \sim N - COOH$$

$$C_{3}^{COCH_{3}} \sim COOH$$

$$C_{4}^{COCH_{3}} \sim COOH$$

(33)
$$\begin{array}{c} CO - NO_2 \\ C_2H_5 \\ C_2H_5 \end{array}$$

$$\begin{array}{c} CO - NO_2 \\ N = C - CONH - COOH \end{array}$$

(34)
$$\begin{array}{c} C_{2}H_{5} \\ C_{2}H_{5} \end{array}$$

$$\begin{array}{c} C_{2}H_{5} \\ \end{array}$$

$$\begin{array}{c} C_{2}H_{5} \\ \end{array}$$

$$\begin{array}{c} C_{2}H_{5} \\ \end{array}$$

(35)

$$\begin{array}{c} CH_{3} \\ CO-C-CH_{3} \\ CH_{3} \\ CH_{4} \\ CH_{3} \\ CH_{4} \\$$

$$\begin{array}{c|c} & & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & &$$

(37)

(38)

$$C_{2}^{H_{5}}$$
 $C_{2}^{H_{5}}$
 $C_{2}^{H_{5}}$
 $C_{3}^{C_{18}^{H_{37}}}$
 $C_{3}^{C_{18}^{H_{37}}}$

(39)

$$C_2^{H_5}$$
 N- C_2^{COH} COOH

(40)

(43)

(44)
$$\begin{array}{c} \text{CO-} \\ \text{HOCOCH}_2\text{CH}_2\\ \text{C}_2\text{H}_5 \end{array} \\ \text{N-} \\ \text{N-$$

(49)

(50)

Formula (3)

X-Dye

Wherein, X represents an ethylenicaly unsaturated group or a group having an ethylene unsaturated group; and Dye

represents a residual group of a blue-light absorbing dye.

In Formula (3), Dye represents a residual group of anyone of generally known dyes having its spectral absorption in a visible spectral range between 400nm and 500nm such as oxonol dyes, styryl dyes and the like including azo dyes, azomethine dyes, cyanine dyes, merocyanine dyes and the like.

In Formula (3), X represents an ethylenicaly unsaturated group or a group having an ethylenicaly unsaturated group, and preferably those represented by the following Formula (4); Formula (4)

$$CH_{2} = \left\{ \begin{array}{c} R_{24} \\ C \\ C \\ \end{array} \right. \left. \left(X_{1} \right)_{m_{1}} \left(X_{2} \right)_{m_{1}} \left(X_{2} \right)_{m_{2}} \left(X_{2} \right)_{m_{2}} \right\}_{k}$$

Wherein, R_{24} represents hydrogen, a carboxy or alkyl group including, for example, methyl group, ethyl group and the like; the alkyl group is allowed to have such a substituent as a halogen, e.g., fluorine, chlorine and the like, a carboxy group or the like. The carboxy group or the carboxy group of a substituent may be allowed to form a salt; J_1 and J_2 represent a divalent bonding group, respectively, including, for example, -NHCO-, -CONH-, -COO-, -OCO-, -SCO-, -COS-, -O-, -S-, -SO-, -SO₂-, and the like; X_1 and X_2 represent a divalent hydrocarbon group, respectively, including for example, the divalent hydrocarbon groups include, for example, an alkylene group, an

arylene group, an aralkylene group, an alkylenearylene group and an arylenealkylene group; the alkylene groups include, for example, methylene group, ethylene group, propylene group and the like; the arylene groups include, for example, phenylene group and the like; the aralkylene groups include for example, phenylmethylene group and the like; the alkylenearylene groups include, for example, methylenephenylene group and the like; and the arylenealkylene groups include, for example, phenylenemethylene group and the like. k, ℓ_1 , m_1 , ℓ_2 , and m_2 are 0 or 1, respectively.

Among the monomeric compounds of the blue-light absorbing dyes represented by Formula (3), the preferable ones are represented by the following Formula (5) or (6); Formula (5)

Formula (6)

Wherein, R_{25} through R_{47} represent respectively hydrogen atom, an alkyl group, an alkenyl group, an cycloalkyl group, an aryl group, an aralkyl group, an alkoxy group, an aryloxy group, an amyl group, an acyloxy group, an acylamino group, an alkoxyalkyl group, an aryloxyalkyl group, an alkoxycarbonyloxyl group, an alkoxycarbonylamino group, an alkoxycarbonyl group, an carbamoyl group, a substituted carbamoyl group, a sulfamoyl group, a substituted sulfamoyl group, an amino group, an alkylamino group, a dialkylamino group, an arylamino group, a cycloalkylamino group, a halogen atom, cyano group, a acyloxyalkyl group, nitro group, an alkylsulfonyl group, an arylsulfonyl group, hydroxy group, carboxy group, sulfo group, ureido group, a substituted ureido group, sulfamoylamino group, a substituted sulfamoyamino group, an alkylsulfonyloxy group, an arylonfonyloxy group, an alkylsulfonylamino group, an arylsulfonylamino group, an alkylthio group, an arylchio group, a heterocyclic residual group, imido group, and a quaternary ammonium group, and the like, and among them, at least one of from R_{25} through R_{35} and at least one of from R_{36} through R_{47} are an ethylene unsaturated group represented by X in the Formula (3) or a group having the ethylene unsaturated group.

Each group represented by R_{25} through R_{47} may further be allowed to have a substituent. Also, in Formulas (5) and (6) each, two groups adjacent to each other on the benzene ring may be bound to form a carbon ring, and further, R_{36} and R_{37} may be

bound each other to form a piperidino ring, a pyrrolidino ring or a morpholino ring.

The following compounds are the typical examples of the monomeric compounds of the invention represented by the Formula (3) given above, and the invention shall not be limited thereto.

Exemplified Monomers:

M-1

$$\begin{array}{c} \text{CH}_3\\ \text{NHCOC=CH}_2\\ \text{HO}_3\text{S} & \begin{array}{c} \text{N=C-CH}_3\\ \text{C-C-N=N-OCH}_3\\ \end{array}$$

M-2

$$\begin{array}{c|c} & & & & CH_3 \\ & & & & \\ & & & & \\ &$$

M-3

M-6

M-7

M-10

M-11

M-14

M-15

$$t-C_{4}H_{9} \longrightarrow O \longrightarrow N$$

$$C-CH-N=N \longrightarrow OH$$

$$SO_{3}Na$$

M-18

M-19

M - 20

M-21 ,

M-22

M - 24

M-25

M-26

M-28

M-29

$$\begin{array}{c} \text{CH}_3 \\ \text{NHCOC=CH}_2 \\ \text{CH}_3 \\ \text{N} \\ \text{CH}_3 \\ \text{N} \\ \end{array} \\ \begin{array}{c} \text{CH}_3 \\ \text{NHCOC=CH}_2 \\ \\ \text{SO}_2 \\ \text{N} \\ \end{array} \\ \begin{array}{c} \text{C}_2 \\ \text{H}_5 \\ \\ \text{C}_2 \\ \text{H}_5 \end{array}$$

M-30

$$\begin{array}{c} \text{CH}_3 \\ \text{NHCOC=CH2} \\ \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \\ \text{N=C-CONH-} \\ \end{array} \begin{array}{c} \text{COCH}_3 \\ \text{N=C-CONH-} \\ \end{array}$$

$$\begin{array}{c|c} & & \text{CH}_3 \\ & & \text{CO-NHCOC=CH}_2 \\ & & \text{C}_2\text{H}_5 \\ & & \text{C}_2\text{H}_5 \end{array}$$

M-32

$$\begin{array}{c|c} & & & & CH_3 \\ & & & & & NHCOC=CH_2 \\ \hline & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & &$$

M-33

$$\begin{array}{c} \text{CH}_3\\ \text{NHCOC=CH}_2\\ \text{C}_2\text{H}_5\\ \text{C}_2\text{H}_5 \end{array}$$

M - 34

$$\begin{array}{c|c} & & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & &$$

M-36

M-37

$$\begin{array}{c} \text{CH}_3\\ \text{CO-NHCOC=CH}_2\\ \text{CH}_3 \text{SO}_2 \text{NHCH}_2 \text{CH}_2\\ \text{C}_2 \text{H}_5 \end{array}$$

M-38

M - 40

M - 41

$$CH_2-CH = CH_2$$

$$CH_2-CH = CH_3$$

$$CH_3$$

$$CH_3$$

$$CH_3$$

The polymers each having a unit, which are derived from the monomeric compounds of the invention represented by the Formula (3), may be the so-called homopolymers each having a unit, which comprise only one kind of the monomers represented by the Formula (3), or they may be the copolymers each comprising a combination of not less than two kinds of the monomers having the Formula (3), or they may further be copolymers each comprising one or more kinds of other comonomers each having copolymerizable ethylene unsaturated group.

As for the comonomers each having the above-mentioned ethylene unsaturated group, which are capable of forming a copolymer with the monomers of the invention having the

Formula (3), there may be an ester acrylate, an ester methacrylate, a vinyl ester, an olefin, a styrene, an ester crotonate, a diester itaconate, a diester maleate, a diester fumarate, an acrylamide, an allyl compound, a vinyl ether, a vinyl ketone, a heterocyclic vinyl compound, a glycidyl ester, an unsaturated nitrile, a polyfunctional monomer, a variety of unsaturated acids and the like.

These comonomers are more concretely exemplified as follows; the esters acrylate include, for example, methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, sec-butyl acrylate, tert-butyl acrylate, amyl acrylate, hexyl acrylate, 2-ethyl acrylate, octyl acrylate, tert-octyl acrylate, 2-chloroethyl acrylate, 2-bromoethyl acrylate, 4-chlorobutyl acrylate, cyanoethyl acrylate, 2-acetoxyethyl acrylate, dimethylaminoethyl acrylate, benzyl acrylate, methoxybenzyl acrylate, 2-chlorocyclohexyl acrylate, cyclohexyl acrylate, furfryl acrylate, tetrahydrofurfuryl acrylate, phenyl acrylate, 5-hydroxypentyl acrylate, 2,2-dimethyl-3-hydroxypropyl acrylate, 2-methoxyethyl acrylate, 3-methoxybutyl acrylate, 2-ethoxyethyl acrylate, 2-iso-propoxy acrylate, 2-butoxyethyl acrylate, 2-(2-ethoxyethoxy)ethyl acrylate, ω -methoxypolyethyleneglycol acrylate, (added mol number n = 9), 1-bromo-2-methoxyethyl acrylate, 1,1-dichloro-2-ethoxyethyl acrylate, 1,1-dichloro-2-ethoxyethyl acrylate.

The esters methacrylate include, for example, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, sec-butyl methacrylate, tert-butyl methacrylate, amyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, chlorobenzyl methacrylate, actyl methacrylate, sulfopropyl methacrylate, N-ethyl-N-phenylaminoethyl methacrylate, 2-(3-phenylpropyloxy)ethyl methacrylate, dimethylaminophenoxyethyl methacrylate, furfuryl methacrylate, tetrahydrofurfuryl methacrylate, phenyl methacrylate, cresyl methacrylate, naphthyl methacrylate, 2-hydroxyethyl methacrylate, 4-hydroxyethyl methacrylate, triethyleneglycol monomethacrylate, dipropyleneglycol monomethacrylate, 2-methoxyethyl methacrylate, 3-methoxybutyl methacrylate, 2-acetoxyethyl methacrylate, 2-iso-propoxyethyl methacrylate, 2-butoxyethyl methacrylate, 2-(2-methoxyethoxy)ethyl methacrylate, 2-(2-ethoxyethoxy)ethyl methacrylate, 2-(2-butoxyethoxy)ethylmethacrylate, w-methoxypolyethyleneglycol methacrylate (added mol number n-6), allyl methacrylate, methacrylic acid dimethylaminoethyl methacrylchrolide salt.

The vinyl esters include, for example, vinyl acetate, vinyl propionate, vinyl butylate, vinyl isobutylate, vinyl caproate, vinyl chloroacetate, vinyl methoxyacetate, vinyl phenylacetate, vinyl benzoate, vinyl salicylate.

The olefins include, for example, dicyclopentadiene,

ethylene, propylene, 1-butene, 1-pentene, vinyl chloride, vinylidene chrolide, isoprene, chloroprene, butadiene, 2,3-dimethylbutadiene.

The styrenes include, for example, styrene, methylstyrene, dimethylstyrene, trimethylstyrene, ethylstyrene, isopropylstyrene, chloromethylstyrene, methoxystyrene, acetoxystyrene, chlorostyrene, dichlorostyrene, bromostyrene, methyl vinylbenzoate.

The crotonic acid esters include, for example, butyl crotonate, hexyl crotonate and the like.

The diesters itaconate include, for example, dimethyl itaconate, diethyl itaconate, dibutyl itaconate and the like.

The diesters maleate include, for example, diethyl maleate, dimethyl maleate, dibutyl maleate and the like.

The diesters fumarate include, for example, diethyl fumarate, dimethyl fumarate, dibutyl fumarate and the like.

The examples of the other comonomers may be given as follows.

An acrylamide such as acrylamide, methylacryl, ethylacrylamide, propylacrylamido, butylacrylamide, tert-butylacrylamide, cyclohexylacrylamide, benzylacrylamide, hydroxymethylacrylamide, methoxyethylacrylamide, dimethylaminoethylacrylamide, phenylacrylamide, dimethylacrylamide, diethylacrylamide, -cyanoethylacrylamide, N-(2-acetoacetoxyethyl)acrylamide;

A methacrylamide such as methacrylamide methylmethacrylamide, ethylmethacrylamide, propylmethacrylamide, butylmethacrylamide, tert-butylmethacrylamide, cyclohexylmethacrylamide, benzylmethacrylamide, hydroxymethylmethacrylamide,
methoxyethylmethacrylamide, dimethylaminoethylmethacrylamide,
dimethylmethacrylamide, β -cyanoethylmethacrylamide,
N-(2-acetoxyethyl)methacrylamide.

An allyl compound, such as allyl acetate, allyl caproate, allyl laurate, allyl benzoate;

A vinylether, such as methylvinylether, butylvinylether, hexylvinylether, methoxyethylvinylether, dimethylaminoethylvinylether;

A vinylketone, such as methylvinylketone, phenylvinylketone, methoxyethylvinylketone;

A vinylheterocyclic compound, such as vinylpyridine, N-vinylimidazole, N-vinyloxazolidone, N-vinyltriazole, N-vinylpyrolydone;

A glycidyl ester, such as glycidyl acrylate, glycidyl methacrylate;

A multi functional monomer, such as divinylbenzene, methylenebisacrylamide, ethyleneglycol dimethacrylate.

Further, the monomer are given as acrylic acid, methacrylic acid, itaconic acid, maleic acid and a monoalkyl itaconate, such as monomethyl itaconate, monoethyl itaconate, monobutyl itaconate; a monoalkyl maleate such as monomethyl

meleate, monoethyl maleate, monobutyl maleate; citraconic acid, stylenesulfonic acid, vinylbenzylsulfonic acid, vinylsulfonic acid, an acryloyloxyalkylsulfonic acid such as acryloyloxymethylsulfonic acid, acryloyloxypropylsulfonic acid; a methacryloxyalkylsulfonic acid such as methacryloyloxymethylsulfonic acid, methacryloyloxyethylsulfonic acid, methacryloylpropylsulfonic acid; an acrylamidoalkylsulfonic acid such as 2-acrylamide-2-methylethanesulfonic acid, 2-acrylamide 2-methylpropanesulfonic acid, 2-acrylamido-2--methylbutanesulfonic acid; a methacrylamidoalkylsulfonic acid such as 2-methacrylamido-2-methylethanesulfonic acid, 2-methacrylamido-2-methylpropanesulfonic acid, an acryloyloxyalkylphosphate such as acryloyloxyethylphosphate, 3-acryloyloxypropyl-2-phosphate; a methacryloyloxyalkylphosphate such as methacryloyloxypropy1-2-phosphate; a 3-allyoxy-2-hydroxypropanesulfonic acid having two hydrophilic groups, such as 3-alloxy-2-hydroxypropanesulfonic acid. acids may also be such an alkaline metal as Na, K and the like, or an ammonium ion salt. As for the other comonomers, such a bridged monomer as described in U.S. Patent Nos. 3,459,790, 3,438,708, 3,554,987, 4,215,195 and 4,247,673, and Japanese Patent O.P.I. Publication No. 205735/1982 may be used. To be more concrete, they include, for example, N-(2-acetacetoxyethyl)acrylamide, N-{2-(2-acetacetoxyethoxy)ethyl}acrylamide, and the like.

In the case of forming a copolymer by making use of a

monomer of the invention having the Formula (3) and the aforementioned comonomer, a preferable case thereof is that the contents of the repetition unit comprising a monomer having the Formula (3) are from 10 wt% to 90 wt% of the whole polymer, and more preferable case is that the contents thereof are 30 wt% to 70 wt% of the whole polymer.

In general, a polymer is prepared in an emulsion-polymerization process or in a solution-polymerization
process. The same processes may be applied to the blue-light
absorbing dye polymers of the invention having the repetition
unit derived from the monomers of the invention having the
Formula (3). As for the emulsion-polymerization processes,
those described in U.S. Patent Nos. 4,080,211 and 3,370,952 may
be applied, and as for the processes in which hydrophobic
polymers are dispersed to serve as the latex into an aqueous
solution of gelatin, those described in U.S. Patent
No. 3,451,820 may be applied.

These processes may also be applied to form a homopolymer or copolymer. In the latter case, the comonomers thereof may be liquid comonomers which may serve, in a normal state, as a solvent for a stationary monomer, when emulsification—polymerizing.

As for the emulsifying agents to be applicable to the emulsification-polymerization process, these include a surface active agent, a macromolecular protective colloid, and a

copolymeric emulsifying agent. As for the surface active agents, there include, for example, an anionic active agent, a nonionic active agent, a cationic active agent, and an amphoteric active agent.

As for the anionic active agent, there are given as the examples, a soap, sodium dodecylbenzene sulfonate, sodium laurylsulfate, sodium dioctylsulfosuccinate, and a sulfuric acid salt of a nonionic active agent.

As for the nonionic active agents, there include, for example, a polyoxyethylene nonylphenyl ether, a polyoxyethylene stearic acid ester, a polyoxyethylene sorbitan monolaurylic acid ester, a polyoxyethylene-polyoxypropylene block copolymer, and the like. As for the cationic active agents, there include, for example, an alkylpyridium salt, tertiary amine and the like.

As for the amphoteric active agents there include, for example, a dimethyl alkyl betaine, an alkyl glycine and the like. As for the macromolecular protective colloids, there include, for example, a polyvinyl alcohol, hydroxyethyl cellulose and the like. They may be used independently to serve as an emulsifying agent and may also be used in combination with the other surface active agents. The various kinds and functions of these active agents are described in "Belgische Chemische Industrie, 28, 16 - 20 (1963).

How to disperse a lipophilic polymer synthesized in a

solution polymerization process into an aqueous gelatin solution so that the polymer may be dispersed therein in the form of a latex, the lipophilic polymer is dissolved in an organic solvent first and the solution thereof is then dispersed latexwise in an aqueous gelatin solution, with the aid of a dispersing agent, by means of a supersonic colloid-mill or the like. The processes of dispersing a lipophilic polymer in the form of a latex into an aqueous gelatin solution are described in U.S. Patent No. 3,451,820. As for the organic solvents for dissolving the lipophilic polymers, there include, for example, methyl acetate, ethyl acetate, propyl acetate, and the like, and an alcohol, a ketone, a halogenated hydrocarbon, an ether, and the like. These organic solvents may be used independently or in combination with two or more kinds of them.

In the case of preparing a polymer having a unit derived from a monomer having Formula (3), that is a blue-light absorbing dye polymer relating to this invention, it is desired that the solvents to be used in a polymerization process are a monomer and a well-qualified solvent for blue-light absorbing dye polymers to be produced, and are relatively low in reactivity with a polymerization starting agent. To be more concrete, there include, for example, water, toluene, an alcohol (e.g., methanol, ethanol, iso-propanol, tert-butanol and the like), acetone, methyl ethyl ketone, tetrahydrofuran,

dioxane, ethyl acetate, dimethyl formaldehyde, dimethyl sulfoxide, acetonitrile, methylene chloride, and the like; and these solvents may be used independently or in a mixture of two or more kinds thereof.

The temperatures for a polymerization process are normally within the range of from 30°C to 120°C, though it is necessary to take the kinds of the polymerization starting agents and the solvents into consideration.

As for the polymerization starting agents to be used in the emulsification-polymerization process or the solution-polymerization process for preparing a blue-light absorbing dye polymer of this invention, there include the following ones:

As for a water-soluble polymerization starting agent, there include, for example, a persulfate such as potassium persulfate, ammonium persulfate, sodium persulfate and the like; a water-soluble azo compound such as 4,4'-azobis-4-sodium cyanovalerate, 2,2'-azobis(2-amidinopropane) chloride and the like; and hydrogen peroxide.

As for the lipophilic polymerization starting agents to be used in the solution-polymerization process, there include, for example, a azo compound such as azobisisobutylonitryl,

2,2'-azobis-(2,4-dimethylvaleronitryl), 2,2'-azobis-(4-methoxy--2,4-dimethlvaleronitryl), 1,1'-azobis(cyclohexanon-l--carbonitryl), 2,2'-azobisisocyanolactic acid, dimethyl-2,2'--azobisisolactate, 1,1'-azobis(cyclohexanone-l-carbonitryl),

4,4'-azobis-4-cyanovaleric acid; a peroxide compound such as benzoyl peroxide, lauryl peroxide, chlorobenzyl peroxide, diisopropyl peroxycarbonate, di-t-butyl peroxide. The preferable ones among the above are benzoyl peroxide, chlorobenzyl peroxide, lauryl peroxide and the like.

These polymerization starting agents may be contained in the range of from 0.01 wt% to 10 wt% and more preferably from 0.1 wt% to 5 wt% to the aggregate quantity of monomers in the emulsification-polymerization process or in the solution-polymerization process.

Besides the above-mentioned processes, the other processes such as a suspension-polymerization process, a block-polymerization and the like may also be applied. In other words, in this invention, there contains every one of the homopolymer of the monomers of the invention having the Formula (1), a copolymer comprising two or more of the monomers in combination, or a copolymer comprising the monomers and at least one kind of the other polymerizable comonomers as the copolymeric components. The synthesizing processes shall not limit to the invention.

The following blue-light absorbing dye polymers of the invention are given as the typical examples. It is, however, to be understood that the invention shall not be limited thereto.

Exemplified blue-light absorbing dye polymers:

- PM-1 Copolymer of Exemplified monomer M-3 and butyl acrylate (Polymerization proportion: 50:50)
- PM-2 Copolymer of Exemplified monomer M-3 and butyl acrylate (Polymerization proportion: 60:40)
- PM-3 Copolymer of Exemplified monomer M-3 and butyl acrylate (Polymerization proportion: 70:30)
- PM-4 Copolymer of Exemplified monomer M-3 and methyl methacrylate (Polymerization proportion: 60:40)
- PM-5 Copolymer of Exemplified monomer M-5 and butyl acrylate (Polymerization proportion: 50:50)
- PM-6 Copolymer of Exemplified monomer M-6 and butyl acrylate (Polymerization proportion: 50:50)
- PM-7 Copolymer of Exemplified monomer M-9 and vinyl acetate (Polymerization proportion: 60:40)
- PM-8 Copolymer of Exemplified monomer M-13 and styrene (Polymerization proportion: 70:30)
- PM-9 Copolymer of Exemplified monomer M-18 and acrylamide (Polymerization proportion: 50:50)
- PM-10 Copolymer of Exemplified monomer M-20 and butyl acrylate (Polymerization proportion: 60:40)
- PM-11 Copolymer of Exemplified monomer M-23 and butyl acrylate (Polymerization proportion: 60:40)
- PM-12 Copolymer of Exemplified monomer M-28 and propylene (Polymerization proportion: 50:50)
- PM-13 Copolymer of Exemplified monomer M-29 and butyl acrylate

(Polymerization proportion: 60:40)

- PM-14 Copolymer of Exemplified monomer M-31 and isopropyl methacrylate (Polymerization proportion: 50:50)
- PM-15 Copolymer of Exemplified monomer M-35 and butyl acrylate (Polymerization proportion: 40:60),

provided that the polymerization proportion represents the proportion by weight.

Next, how to synthesize a blue-light absorbing dye polymer of the invention will be described.

Generally speaking blue-light absorbing dye polymers of the invention are synthesized in the following two processes;

- (1) Synthesis of blue-light absorbing dye compound having an ethylene unsaturated group or an ethylene unsaturated group → polymerization.
- (2) The polymerization reaction product Dye coloring through the introduction of a chromophore (e.g., a diazo coupling reaction).

Some of the synthesis examples of the blue-light absorbing dye polymers of the invention will be described below:

° Synthesis Example-1 (Synthesis of PM-10):

Synthesis of Copolymer (PM-10) of 1-(2,4,6-trichloro-phenyl)-3-methacryloylamino-4-(4-cyanophenylazo)-5-pyrazolone and butyl acrylate:

A solution was prepared by dissolving 40g of 1-(2,4,6-tri-chlorophenyl)-3-amino-4-(4-cyanophenylazo)-5-pyrazolone and 24g

of pyridine into 800ml of acetonitrile and the resulting solution was cooled to 5°C and stirred. Whereinto, a solution prepared by dissolving 13g of methacrylic acid chloride into 100ml of acetonitrile was dropped. The resulting solution was stirred for 30 minutes of room temperature and was then poured into a chloric acid solution (0.5N), and the resulting crystals were filtrated. Thereby, 45g of Compound (A) were obtained.

This Compound (A) of 60g were dissolved in 500ml of dioxane at 80°C. The system of reaction was applied with a nitrogen substitution, and 40g of butyl acrylate and 2.7g of azobisisobutylonitrile were added thereto and the resulting solution was stirred for two hours at 80°C. Further, 1.3g of azobisisobutylonitrile were added thereto and stirred for two hours at 80°C. The resulting mixture was poured into 5 ℓ of water and was filtrated. Then, 95g of Polymer PM-10 were obtained.

The weight-average molecular weight thereof $M\overline{w}$ was 11,000. Synthesis Example-2 (Synthesis of PM-1):

Synthesis of Copolymer (PM-1) of 1-phenyl-3-methacrylic acid amide-4-(4-methoxyphenylazo)-5-pyrazolone and butyl acrylate:

A solution was prepared by dissolving 50g of 1-pheny1-3-methacrylic acid amide-4-amino-5-pyrazolone into 500ml of
dioxane at 80°C. The system of reaction was applied with a
nitrogen substitution, and 50g of butyl acrylate and 2.7g of

azobisisobutylonitrile were added. The resulting solution was stirred for two hours at 80°C. Further, 1.3g of azobisisobutylonitrile were added therein and were then stirred for two hours at 80°C. The resulting mixture was poured into 5£ of water and the resulting polymers were filtrated. Then, 95g of Polymer (A) were obtained.

Next, a mixture was prepared by mixing 18g of p-methoxy aniline, 32ml of concentrated chloric acid and 450ml of water. The resulting solution was cooled to 0°C and was then dropped therein with a solution of 10.5g of sodium nitrite disslolved in 60ml of water. The resulting solution was stirred for 30 minutes at 0°C was. A solution of a diazonium salt was thus obtained.

Meanwhile, 73g the above-described Polymer (A) were mixed together with 450ml of water, 450ml of DMF and 27g of sodium hydroxide, and the resulting mixture was cooled and kept at a temperature of not higher than 10°C. Then, the aforementioned solution of a diazonium salt was dropped thereinto and thereafter the resulting solution was stirred for one hour at room temperature. The resulting mixture was poured into a chloric acid solution (0.1N), and 88g of Polymer (PM-1) were obtained. The weight-average molecular weight Mw was 8,500.

It is preferred that the molecular weight of a blue-light absorbing dye polymer of the invention is within the range of from 1,500 to 100,000 in term of weight-average molecular

weight (Mw).

According to the invention, such dyes as above cited are contained by a layer interposed between a blue-sensitive layer and a green-sensitive layer, or between a blue-sensitive layer and a red-sensitive layer.

However, the dyes are ordinarily contained by the layer interposed between the blue-sensitive layer and the green-sensitive layer as shown in the following layer arrangement.

(Typical layer arrangement)

- (a) Support
- (b) Red-sensitive heat-developable photo-sensitive layer.
- (c) Green-sensitive heat-developable photo-sensitive layer.
- (d) Layer containing blue-light-absorbing dyes.
- (e) Blue-sensitive heat-developable photo-sensitive layer.

Such a layer arrangement as shown above sometimes has, in addition, various other layers (hereinafter called intermediate layer) interposed between the above layers for various specific purposes.

In a heat-developable multilayered color photo-sensitive material, the red-sensitive heat-developable photo-sensitive layer is composed of red-sensitive silver halide, an organic silver salt, a developer, a cyan dye-providing compound, and a binder. Similarly, the green-sensitive heat-developable photo-sensitive layer is composed of green-sensitive silver

halide, an organic silver salt, a developer, a magenta dye-providing compound, and a binder. The blue-sensitive heat-developable photo-sensitive layer is composed of blue-sensitive silver halide, an organic silver salt, a developer, a yellow dye-providing compound, and a binder.

A heat-developable multilayered color photo-sensitive material of the invention which is arranged in such a way as described above, releases and forms dyes in course of a heat-developing process, and transfers the dyes onto an image receiving layer. In this case, it is necessary to cut off the blue-light from the green-sensitive layer and the red-sensitive layer because both layers are sensitive also to the inherent sensitive range (400nm to 500nm). The above layer containing BAOS functions effectively for this purpose.

Because the BAOS of the invention have not only the property of effectively absorbing the blue light but also an excellent diffusion-resistance as aforementioned, diffusion of the BAOS into farther layers than adjacent layer is prevented substantially. Therefore, not only any fogginess or lowering of contrast, but also any stain are not caused.

The above BAOS relevant to the invention are applied ranging from 0.01g/m^2 to 10g/m^2 , preferably from 0.05g/m^2 to 1.5g/m^2 . They can be added to the blue-light-absorbing layer of the heat-developable multilayered color photo-sensitive material by various means according to their structure and

properties. As for such means, for example, there are the method that the BAOS, together with a binder are dissolved in a certain solvent, and ground with the use of a ball mill, the protect dispersing method that a dispersion is made with the use of a high boiling-point solvent or its combination with a low boiling-point solvent, similarly to the case of dispersion of ordinary couplers, and the Fischer dispersing method that the BAOS are dissolved in a alkaline solution, and then dispersed into a hydrophilic binder.

Particularly, as for the processes which may be applied to contain a blue-light absorbing dye polymer of the invention in the photographic component layers of a heat-developable color photo-sensitive material, there are such a process as a latex-dispersion process in which the polymers of the invention may be contained in the component layer in such a manner that the polymers are dissolved in a low-boiling solvent such as methanol, ethanol, ethyl acetate or the like, or a high-boiling solvent such as dibutyl phthalate, dioctyl phthalate, tricresyl phosphate, or the like and the resulted solution is then dispersed by ultrasonic waves; a process in which an polymers are dissolved in an aqueous alkali solution such as an aqueous solution of 10% sodium hydroxide or the like and the resulted solution is neutralizing by a mineral acid such as hydrochloric acid, nitric acid or the like; or a process in which the polymers are dispersed together with an aqueous solution of a

suitable polymer such as polyvinyl butyral, polyvinyl pyrrolidone, or the like, by making use of a ball-mill.

Any blue-light absorbing dye polymer of the invention may be used independently or in combination. The amount thereof to be used is not limited but may be depended upon the kinds of the polymers or whether they are to be used independently or in combination with two or more of them. For example, an amount to be used is from 0.01g to 10g and preferably from 0.05g to 1.5g per square-meter of a support.

The photo-sensitive silver halide to be used in the invention include, for example, silver chloride, silver bromide, silver iodide, silver chlorobromide, silver chloroiodobromide, and the like. These photo-sensitive silver halide can be prepared in such an arbitrary process in the photographic technical field as a single-jet process, a double-jet process and the like. In the invention, the desired results are obtained with the use of photo-sensitive silver halide emulsions containing a photo-sensitive silver halide prepared in accordance with an ordinary preparation process of a silver halide gelatin emulsion.

They have particle size ranging from 0.01µm to 1.0µm, preferably from 0.05µm to 0.5µm. The shape of the silver halide particle is allowed to be a regular tetrahedron, regular octahedron, or tetradecahedron, but preferably has at least

(1, 1, 1) faces. The particle is allowed to be of core-shell type that the interior and exterior ports are different than each other in halogen composition.

Such photo-sensitive silver halide emulsions may preferably be chemically sensitized in an arbitrary process used in the photographic technical field. As for such sensitizing processes, there are various processes including, for example, a gold, platinum or palladium sensitization, a sulphur sensitization, a gold-sulphur sensitization, a reduction sensitization, and the like, which may be applied independently or in combination.

The photo-sensitive silver halide emulsions prepared as mentioned above can be most preferably applied to a heat-developable photo-sensitive layer that is a component layer of the photo-sensitive materials of this invention.

As for a process of preparing the other photo-sensitive silver halide, it is possible, in this invention, to form a photo-sensitive silver halide in a portion of an organic silver salt by making a photo-sensitive silver salt forming component co-exist with an organic silver salt which will be described later. As for the photo-sensitive silver salt forming components to be used in this preparing process, an inorganic halide may be given as the example thereof, including, for example; a halide represented by MXn in which M represents hydrogen, NH_A group or a metal atom, X represents Cl, Br or I

and n is 1 when the M is hydrogen or NH_A group, and when M is a metal atom, n is the valence thereof, and the metal atoms include those of lithium, sodium, potassium, rubidium, cecium, copper, gold, beryllium, magnesium, calcium, strontium, barium, zinc, cadmium, mercury, aluminum, indium, lanthanum, ruthenium, thalium, germanium, tin, lead, antimony, bismuth, chromium, molybdenum, wolfram, manganese, rhenium, iron, cobalt, nickel, rhodium, paradium, osmium, iridium, platinum, cerium; a halide-containing metal complex, such as K2PtCl6, K2PtBr6, $HAuCl_4$, $(NH_4)_2$ $IrCl_6$, $(NH_4)_3$ $IrCl_6$, $(NH_4)_2$ $RuCl_6$, $(NH_4)_3$ $RuCl_6$, $(NH_4)_3$ RhCl₆, $(NH_4)_3$ RhBr₆; an onium halide e.g., a quantanary ammonium halide such as tetramethylammonium bromide, trimethylphenylammonium bromide, cetylethyldimethylammonium bromide, 3-methylazolium bromide and trimethylbenzylammonium bromide; a quartanary phosphonium halide, e.g., tetraethylphosphonium bromide; a tertiary sulfonium halide, e.g., benzylethylmethylsulfonium bromide and 1-ethylthiazolium bromide; a halogen substituted hydrocarbon, e.g., iodoform, bromeform, carbontetrachloride and 2-bromo-2-methylpropan; an N-halogen compound, e.g., N-chlorosuccinimide, N-bromosuccinimide, N-bromophthalimide, N-bromoacetamide, N-iodosuccinimide, N-bromophthaladinone, N-chlorophthaladinone, N-bromoacetanilide, N,N-dibromobenzensulfonamide, N-bromo--N-methylbenzensulphonamide and 1,3-dibromo-4,4-dimethylhydantoin; and the other halogen containing compounds, e.g.,

triphenylmethyl chloride, triphenylmethylbromide, 2-bromolactic acid, and 2-bromoethanol.

These photo-sensitive silver halide and the photo-sensitive silver salt forming components may be used in combination in various processes. A preferable amount used thereof is from 0.00lg to 50g per sq. meter, and a more preferable amount is from 0.1g to 10g per sq. meter.

The heat-developable color photo-sensitive materials may also comprise each of blue-light-sensitive, green-light-sensitive and red-light-sensitive layers, namely, a multiple-layer comprising a heat-developable blue-light-sensitive layer, a heat-developable green-light-sensitive layer and a red-light-sensitive layer, and the same light-sensitive layer thereof may be divided into two or more layers such as a high sensitive layer and a low sensitive layer.

Each of the blue-light sensitive silver halide emulsion, green-light sensitive silver halide emulsion and red-light silver halide emulsion to be used in the above-mentioned case may be prepared by adding various kinds of spectral sensitization dyes to the silver halide emulsions.

It is preferred that the spectral sensitization is made by making use of a sensitizing dye.

The spectral sensitization dyes which may typically be used in this invention include, for example, cyanine,

merocyanine, a trinuclear or tetranuclear complex cyanine, holopolar cyanine, styryl, hemicyanine, oxonole and the like. Among the cyanine dyes, those each having a basic nucleus such as thiazoline, oxazoline, pyrroline, pyridine, oxazole, thiazole, selenazole, and imidazole are preferred to use. Such a nucleus may have an enamine group capable of producing an alkyl group, alkylene group, hydroxyalkyl group, sulfalkyl group, carboxyalkyl group, aminalkyl group, or a condensed carbocyclic or heterocyclic color ring. Also, it may be in the symmetric or unsymmetric form, and the methine chain or the polymethine chain thereof may have an alkyl group, a phenyl group, an enamine group, a heterocyclic substituent.

The merocyanine dyes may also have, for example, such an acid nucleus as a thiohydantoin nucleus, a rhodanine nucleus, an oxazolyl acid nucleus, a thiazolinethione nucleus, a malononitrile nucleus, and a pyrazolone nucleus. These acid nuclei may also be substituted by either of an alkyl, alkylene, phenyl, carboxyalkyl, sulfalkyl, hydroxyalkyl, alkoxyalkyl or alkylamine group, or a heterocylic ring nucleus. If required, these dyes may further be used in combination. It is still further possible to jointly use such a supersensitive additive incapable of absorbing any visible rays of light as an ascorbic acid derivative, an azaindene cadmium salt, an organic sulfonic acid and the like including, for example, those described in U.S. Patent Nos. 2,933,390, and 2,937,089.

The amount of these dyes to be added is from 1×10^{-4} mole to 1 mole per mol of a silver halide or a silver halide forming component, and more preferably, from 1×10^{-4} mole to 1×10^{-1} mole.

In the heat-developable color photo-sensitive materials of the invention, various kinds of organic silver salts may be used if required for increasing the sensitivity and improving the developability of the materials.

As for the organic silver salts to be used to the heat-developable color photo-sensitive materials of the invention, there may be given as the examples thereof the following; an aliphatic carboxylic acid silver salt such as silver laurate, silver myristate, silver palmitate, silver stearate, silver arachidonate, silver behenate, silver -(1-phenyltetrazolethio) acetate and the like, as described in Japanese Patent Examined Publication Nos. 4924/1968, 26582/1969, 18416/1970, 12700/1970, and 22185/1970, Japanese Patent O.P.I. Publication No. 52626/1974, 31728/1977, 137321/1977, 141222/1977, 36224/1978 and 37610/1978, and U.S. Patent Nos. 3,330,633, 3,794,496, 4,105,451, 4,123,274 and 4,168,980, and the like; an aromatic carboxylic acid silver such as silver benzoate, silver phthalate and the like; and silver salts of an imino group, e.g., those of benzotrizole, 5-nitrobenzotriazole, 5-chlorobenzotrizole, 5-methoxybenzotriazole, 4-sulfobenzotriazole, 4-hydroxybenzotriazole,

5-aminobenzotriazole, 5-carboxybenzotriazole, imidazole, benzimidazole, 6-nitrobenzimidazole, pyrazole, urazol, 1,2,4-triazole, 1H-tetrazole, 3-amino-5-benzylthio-1,2,4--triazole, saccharin, phthalazinone, phthalimide, 2-mercaptobenzoxazole, mercaptoxydiazole, 2-mercaptobenzothiazole, 2-mercaptobenzimidazole, 3-mercapto-4-phenyl-1,2,4--triazole, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, and 5-methyl-7-hydroxy-1,2,3,4,6-pentazaindene. There may also be used such a silver compound as those described in Research Disclosure, (hereinafter called RD), Nos. 16966 and 16907, and British Patent Nos. 1,590,956 and 1,590,957. Among the above-mentioned organic silver salts, silver salts of an imino group are preferred to use, especially silver salts of a benzotriazole derivative are preferred, and further, silver salts of a sulfobenzotriazole derivative are more preferred to use.

As for such benzotriazole silver salts, there are cited alkyl substitute-bearing benzotriazole silver salts such as, for example, methylbenzotriazole silver; halogen-bearing benzotriazole silver salts such as, for example, bromobenzotriazole silver, and chlorobenzotriazole silver; amido group-bearing benzotriazole silver such as, for example, 5-acetamidobenzotriazole silver, and the compounds described in the specifications of British Patent Nos. 1,590,956 and 1,590,957, such as, for example, N-[6-chloro-4-N-(3,5-dichloro-4-N-(3

-4-hydroxy phenyl)imino-1-oxo-5-methyl-2,5-cyclohexadiene-2-yll--5-carbamoylbenzotriazole silver salt, 2-benzotriazole-5-ylazo--4-methoxy-1-naphthol silver salt, 1-benzotriazole-5-ylazo-2--naphthol silver salt, and N-benzotriazole-5-yl-4-(4-dimethyl-aminophenylazo)benzamide silver salt.

The organic silver salts especially useful in the invention are those having a hydrophilic group, for example, those in Japanese Patent O.P.I. Publication No. 118638/1983.

For example, the following organic salts are cited: 4-hydroxybenzotriazole silver, 5-hydroxybenzotriazole silver, 4-sulfobenzotriazole silver, 5-sulfobenzotriazole silver, benzotriazole silver-4-sulfonic acid sodium, benzotriazole silver-5-sulfonic acid sodium, benzotriazole silver-4-sulfonic acid potassium, benzotriazole silver-5-sulfonic acid potassium, benzotriazole silver-4-sulfonic acid ammonium, benzotriazole silver-5-sulfonic acid ammonium, 4-carboxybenzotriazole silver, 5-carboxybenzotriazole silver, benzotriazole silver-4--carboxylic acid sodium, benzotriazole silver-5-carboxylic acid sodium, benzotriazole silver-4-carboxylic acid potassium, benzotriazole silver-5-carboxylic acid potassium, benzotriazole silver-4-carboxylic acid ammonium, benzotriazole silver-5--carboxlic acid ammonium, 5-carbamoylbenzotriazole silver, 4-sulfamoylbenzotriazole silver, 5-carboxy-6-hydroxybenzotriazole silver, 5-carboxy-7-sulfobenzotriazole silver, 4-hydroxy-5-sulfobenzotriazole silver, 4-hydroxy-7-sulfobenzo-

triazole silver, 5,6-dicarboxybenzotriazole silver, 4,6-dihydroxybenzotriazole silver, 4-hydroxy-5-chlorobenzotriazole silver, 4-hydroxy-5-methoxybenzotriazole silver, 4-hydroxy-5-nitrobenzotriazole silver, 4-hydroxy-5-cyanobenzotriazole silver, 4-hydroxy-5-aminobenzotriazole silver, 4-hydroxy-5-acetamidobenzotriazole silver, 4-hydroxy-5-benzenesulfonamedobenzotriazole silver, 4-hydroxy-5-hydroxycarbonylmethoxybenzotriazole silver, 4-hydroxy-5-ethoxycarbonylmethoxybenzotriazole silver, 4-hydroxy-5-carboxymethylbenzotriazole silver, 4-hydroxy-5-ethoxycarbonylmethylbenzotriazole silver, 4-hydroxy-5-phenylbenzotriazole silver, 4-hydroxy-5-(p-nitrophenyl)benzotriazole silver, 4-hydroxy-5-(p-sulfophenyl)benzotriazole silver, 4-sulfo-5-chlorobenzotriazole silver, 4-sulfo-5-methylbenzotriazole silver, 4-sulfo-5-methoxybenzotriazole silver, 4-sulfo-5-cyanobenzotriazole silver, 4-sulfo-5-aminobenzotriazole silver, 4-sulfo-5-acetamidobenzotriazole silver, 4-sulfo-5-benzenesulfonamidobenzotriazole silver, 4-sulfo-5-hydroxycarbonylmethoxybenzotriazole silver, 4-sulfo-5-ethoxycarbonylmethoxybenzotriazole silver, 4-hydroxy-5-carboxybenzotriazole silver, 4-sulfo-5-carboxymethylbenzotriazole silver, 4-sulfo-5-ethoxycarbonylmethylbenzotriazole silver, 4-sulfo-5-phenylbenzotriazole silver, 4-sulfo-5-(p-nitrophenyl)benzotriazole silver, 4-sulfo-5--(p-sulfophenyl)benzotriazole silver, 4-sulfo-5-methoxy-6--chlorobenzotriazole silver, 4-sulfo-5-chloro-6-carboxybenzo

triazole silver, 4-carboxy-5-chlorobenzotriazole silver,
4-carboxy-5-methylbenzotriazole silver, 4-carboxy-5-nitrobenzotriazole silver, 4-carboxy-5-aminobenzotriazole silver,
4-carboxy-5-methoxybenzotriazole silver, 4-carboxy-5-acetamidobenzotriazole silver, 4-carboxy-5-ethoxycarbonylmethoxybenzotriazole silver, 4-carboxy-5-carboxymethylbenzotriazole silver,
4-carboxy-5-phenylbenzotriazole silver, 4-carboxy-5-(p-nitrophenyl)benzotriazole, and 4-carboxy-5-methyl-7-sulfobenzotriazole. These compounds are allowed to use singly or in dual
or more comination with each other.

As for organic silver salts relevant to the invention, the salt may be isolated, and dispersed into a binder for the photo-sensitive layers by an appropriate means for its use. Alternatively, the salt may be prepared in such a binder for the photo-sensitive layers, and directly used without isolation.

The applying amount of the organic silver salt ranges preferably from 0.05g to 10.0g per sq. meter of the support or from 0.01 mole to 500 mole per mole of a photo-sensitive layer halide, and more preferably from 0.2g to 5.0g per sq. meter of the support or from 0.1 mole to 100 mole per mole of the photo-sensitive silver halide.

As for developers to be used in a heat-developable color photo-sensitive material of the invention, such developing agents as described, for example, in the specifications of U.S.

Patent Nos. 3,531.286; 3,761,270; and 3,764,328; in RD
Nos. 12146, 15108, and 15127; and in Japanese Patent O.P.I.
Publication No. 27132/1981; that is, developing agents of
p-phenylenediamine type, p-aminophenol type, phosphoroamidophenol type, and sulfonamidophenol type; and color developing
agents of hydrazone type are advantageously applicable in the
case of heat-transferable dye-providing materials described,
for example, in Japanese Patent O.P.I. Publication
No. 186744/1982; in Japanese Patent Application
Nos. 122596/1982, 160698/1982, and 126054/1982; a Japanese
Patent O.P.I. Publication Nos. 12431/1984, 48765/1984 and
15941/1984.

In this case, diffusible dyes by oxidative coupling of the developer with these heat-transferable dye-providing materials are released or formed. Precursors of color developing agent described in U.S. Patent Nos. 3,342,599 and 3,719,492; and Japanese Patent O.P.I. Publication Nos. 135628/1978 and 79035/1979 also are advantageously used.

The particularly preferable reducing agents may be given those represented by the following Formula (23) appeared in Japanese Patent O.P.I. Publication No. 146133/1981:

Formula (7)

Wherein, R_{48} and R_{49} each represent hydrogen or an alkyl group which is allowed to have a substituent and has one to 30 carbon atoms and preferably one to four carbon atoms, and the R_{48} and R_{49} may close a ring so as to form heterocyclic ring; R_{50} , R_{51} , R_{52} and R_{53} each represent hydrogen, a halogen, a hydroxy group, an amino group, an alkoxy group, an acylamide group, a sulfonamide group, an alkylsulfonamide group, or an alkyl group which is allowed to have a substituent and has one to 30 carbon atoms, and preferably, one to four carbon atoms, and the R_{50} and R_{48} , and the R_{52} and R_{49} each may close a ring so as to form a heterocyclic ring, respectively; and M represents an alkaline metal atom or a compound containing an ammonium group, a nitrogen-containing organic base or a quaternary nitrogen atom.

The nitrogen-containing organic base in the Formula (7) is an organic compound containing a nitrogen atom which is capable of producing an inorganic acid and a salt and displays a basicity. The particularly essential organic bases include, for example, an amine compound. Chain amine compounds include,

for example, primary amine, secondary amine, and tertiary amine, and cyclic amine compounds include pyridine, quinoline, piperidine, imidazole and the like as the famous examples of the typical heterocyclic organic bases. Besides the above, such a compound as hydroxylamine, hydrazine, amidine and the like is also useful for a chain amine. As for the salts of nitrogen-containing organic bases, such an inorganic acid salt as a chloride, a sulfate, a nitrate or the like of the organic bases is preferably used.

On the other hand, as for the compounds each containing quaternary nitrogen in the formula above, there include, for example, a salt or hydroxide of a nitrogen compound having a quatrivalent covalent bond.

Next, some preferred examples of the reducing agents represented by Formula (7) above will be given below:

(R-2)

(R-3)

$$C_2H_5$$
 N-NHSO₃Na C_2H_5

(R-4)

(R-5)

$$\begin{array}{c} \text{OCH}_3 \\ \text{C}_5\text{H}_{11} \\ \text{C}_5\text{H}_{11} \end{array} \\ \begin{array}{c} \text{NHSO}_3 \\ \end{array} \\ \begin{array}{c} \text{NH} \left(\text{C}_2\text{H}_5\right)_3 \\ \end{array}$$

(R-6)

(R-7)

(R-8)

(R-9)

$$\begin{array}{c} {}^{\mathrm{C_2H_5}} \\ \mathrm{CH_3SO_2NHC_2H_4} \end{array} \\ \begin{array}{c} \mathrm{NHSO_3Na} \\ \\ \mathrm{CH_3} \end{array}$$

(R-10)

$$C_2^{H_5}$$
HO $(C_2^{H_4})$
 $C_3^{H_5}$
 $C_3^{H_5}$

(R-11)

(R-12)

(R-13)

(R-14)

(R-15)

(R-16)

(R-17)

(R-20)

(R-21)

$$C_2H_5$$

(R-23)

The reducing agents represented by Formula (7) may be synthesized in such a well-known process as described in, for example, Houben-Weyl, Methoden der Organischen Chemie, B and XI/2, pp. 645 - 703.

As for other developing systems, there are cited, for example, phenols, including p-phenylphenol, p-methoxyphenol, 2,6-di-tert-butyl-p-cresol, and N-methyl-p-aminophenol; sulfonamidophenols, for example, 4-benzenesulfonamidophenol, 2-benzenesulfonamidophenol, 2,6-dichloro-4-benzenesulfonamidophenol, and 2,6-dibromo-4-(p-toluenesulfonamido)phenol; polyhydroxybenzenes, for example, hydroquinone, tert-butylhydroquinone, 2,6-dimethylhydroquinone, chlorohydroquinone, carboxyhydroquinone, catechol, and 3-carboxycatechol; naphthols, for example, α -naphthol, β -naphthol, 4-aminonaphthol, and 4-methoxynaphthol; hydroxybinaphthyls and methylenebisnaphthols, for example, 1,1'-dihydroxy-2,2'--binaphthyl, 6,6'-dibromo-2,2'dihydroxy-1,1'-binaphthyl, 6,6'-dinitro-2,2'-dihydroxy-1,1'-dihydroxy-2,2'-binaphthyl, and bis(2-hydroxy-l-naphthyl)methane; methylenebisphenols, for example, 1,1-bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane, 1,1-bis(2-hydroxy-3-tert-buty1-5-methylphenol)methane, 1,1-bis(2-hydroxy-3,5-di-tert-butylpheny1)methane, 2,6-methylene-bis(2-hydroxy-3-tert-butyl-5-methylphenyl)-4--methylphenol, X-phenyl-X,X-bis(2-hydroxy-3,5-di-tert-butylphenyl) methane, α -phenyl- α - α -bis(2-hydroxy-3-tert-butyl-5-methylphenyl)methane, 1,1-bis(2-hydroxy-3,5-dimethylphenyl)-2-methylpropane, 1,1,5,5-tetrakis(2-hydroxy-3,5-dimethylphenyl)-2,4-ethylpentane, 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane, 2,2-bis(4-hydroxy-3-methyl-5-tert-butylphenyl)propane, and 2,2-bis(4-hydroxy3,5-di-tert-butylphenyl)propane; ascorbic acids; 3-pyrazolidones; pyrazolones;
hydrazones, and para-phenylenediamines are cited.

These developers can be employed either separately or in combination of two or more types. The applying amount depends on types of organic silver salt, photo-sensitive silver salt and other ingredients to be used, or the like, but ranges ordinarily from 0.05 moles to 10 moles, preferably from 0.1 mole to 3 moles per mole of organic silver salts, respectively.

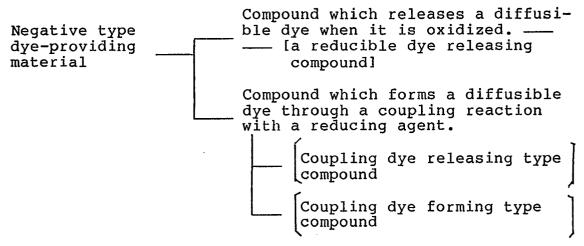
As for dye-providing compounds to be used in a heat-developable color photo-sensitive material of the invention, the ones of both dye-releasing type and dye-forming type are applicable, and there are cited compounds described, for example, in Japanese Patent O.P.I. Publication

Nos. 179840/1982, 186744/1982, 123533/1983, 149046/1983, and 149047/1983, 12431/1984, 716648/1984, 95529/1984, 116740/1984, 124327/1984, 124329/1984, 159159/1984 and the like.

As for especially preferable dye-providing compounds described in the specifications of the above Japanese Patent O.P.I. Publication Nos. 124339/1984 and 1591591984, it is

preferable that, their molecule has either a hydrophilic groups such a sulfo or carboxy group, or a ballast group as a large-molecular hydrophobic group, and thereby can be immobilized in photo-sensitive layers, and that the dyes formed therefrom are heat-transferable.

As for the dye-providing materials capable of being used in the invention, those may be used for, provided that they may be able to take part in the reduction reaction of a photo-sensitive silver halide and/or an organic silver salt usable as required and also be able to form or release a diffusible dye, as a function of the reaction. The dye-providing materials may be classified, depending on the reaction forms, into two types, that is, one is a negative type dye-providing material which works on a positive function, namely, thereby a negative dye image is formed when the negative type silver halide is used; and the other is a positive type dye-providing material which works on a negative fuction, namely, thereby a positive dye image is formed when a negative type silver halide is used. Further, the negative type dye-providing material may be classified in the following;



Various types of dye-providing materials will now further be described.

As for the reducible dye releasing compounds, there may be given a compound represented by Formula (5) as the example thereof.

Formula (5)

Wherein, Car represents a reducible substrate, i.e., the so-called Carrier, which is capable of releasing an oxidized dye when a photo-sensitive silver halide and/or an organic silver salt to be used if required; and Y represents a diffusible dye residual group.

The concrete examples of the above-mentioned reducible dye releasing compounds include those described in Japanese Patent O.P.I. Publication Nos. 179840/1982, 116537/1983, 60434/1984, 65839/1984, 71046/1984, 87450/1984, 88730/1984, 123837/1984, 165054/1984 and 165055/1984, which are namely given as follows;

Exemplified dye-providing materials:

(1)

(2)

(3)

As for the other reducible dyes, there may be given a compound represented by Formula (9) below, as the example; Formula (9)

Wherein, A₁ and A₂ each represent hydrogen or a hydroxy or amino group; and Y is similar to the Y previously represented in Formula (8). Some concrete examples thereof are described in Japanese Patent O.P.I. Publication No. 124329/1984.

As for the coupling dye releasing type compounds, there includes a compound represented by Formula (10) below; Formula (10)

$$Cp_1 \{J\}_n Y$$

Wherein, Cp₁ represents an organic group, i.e., the so-called coupler residual group, which is capable of releasing a diffusible dye upon reacting with the oxidation products of a reducing agent; J represents a divalent coupling group, and the coupling of Cp₁ to J is cleaved by the reaction of J with the oxidation product of the reducing agent; n is an integer of 0 or 1; and Y is similar to the Y represented in Formula (8). It

is preferred that Cp_1 is substituted by one of various ballast groups so as to make the coupling dye releasing type compound non-diffusible. The ballast groups are an organic group having not less than 8 carbon atoms and more preferably not less than 12 carbon atoms; a hydrophilic group such as a sulfo group, a carboxy group or the like; and a group having not less than 8 carbon atoms and more preferably not less than 12 carbon atoms, and a hydrophilic group such as a sulfo group, a carboxy group or the like, together, which are suitably used according to characters of photo-sensitive materials. The other ballast groups which are particularly preferable may include a chain polymer.

The examples of the compounds represented by Formula (10) are described in Japanese Patent O.P.I. Publication

Nos. 186744/1982, 122596/1982, 160698/1982, 174834/1984,

224883/1982, and 159159/1984, and Japanese Patent Application

No. 104901/1984. They include, namely;

Exemplified dye-providing materials:

(4)

(5)

As for coupling dye forming compounds, a compound represented by Formula (11) or (17) below may be given as the example thereof;

Formula (11)

where A' represents a hydrophobic coupler residue. A' has no group such as a sulfo, carboxy or thiosulfo group, which makes the dye-providing compound immobile in heat-developable

photo-sensitive layers. B' represents a group releasible from a coupler by a coupling reaction. B' has a sulfo, carboxy, or thiosulfo group; a large-molecular hydrophobic group, for example, an alkyl group having 8 or more carbon atoms, or an aryl group having an alkyl group with 4 or more carbon atoms; a group which can make dye-providing compounds such as hydrophilic and hydrophobic polymer residues immobile in heat-developable photo-sensitive layers.

Such a dye-providing compound is that which yeilds a hydrophilic heat-transferable dye through coupling reaction with the oxidant of a color developing agent in course of heat-development. A' in the above General Formula (11) can be represented, for example, by the following General Formulas (12) to (16).

Formula (12)

Formula (13)

Formula (14)

Formula (15)

Formula (16)

where each of R₅₄, R₅₅, R₅₆ and R₅₇ is a hydrogen atom, a halogen atom (preferably a chlorine, bromine or iodine atom), an alkyl group (preferably an alkyl group with 1 to 24 carbon atoms, for example, a methyl, ethyl, butyl, t-octyl, n-dodecyl, n-pentadecyl, or cyclohexyl group; or an alkyl group with an aryl substituent, for example, a benzyl or phenethyl group as well), a substituted, or unsubstituted aryl group, (for example, a phenyl, naphthyl, tolyl, or methyl group), an acyl group (for example, an acetyl, tetradecanoyl, or pivaloyl group, or a substituted or unsubstituted benzoyl group), an alkyloxycarbonyl group (for example, a methoxycarbonyl, or

benzyloxycarbonyl group), an aryloxycarbonyl group (for example, a phenoxycarbonyl, p-tolyloxycarbonyl, or -naphthoxycarbonyl group), an alkylsulfonyl group (for example, a methylsulfonyl group), an arylsulfonyl group (for example, a phenylsulfonyl group), a carbamoyl group (for example, a substituted or unsubstituted alkylcarbamoyl group such as a methylcarbamoyl, butylcarbamoyl, tetradecylcarbamoyl, or N-methyl-N-dodecylcarbamoyl group; a substituted or unsubstituted phenoxyalkylcarbamoyl group such as a 2,4-di-tert-aminophenoxybutylcarbamoyl group; a substituted or unsubstituted phenylcarbamoyl group such as 2-dodecyloxyphenylcarbamoyl group or the like), a substituted or unsubstituted acylamino group (for example, a substituted or unsubstituted A-phenoxyethylamido group, a phenoxyacetamide group, a substituted or unsubstituted benzamide group, a methanesulfonamidoethylamide group, or a -methoxyethylamide group), an alkoxy group (preferably an alkoxy group with 1 to 18 carbon atoms, for example, a methoxy, ethoxy, or octadecyloxy group), a sulfamoyl group (for example, a methylsulfamoyl, or n-dodecylsulfamoyl group, or a substituted or unsubstituted phenylsulfamoyl group such as a dodecylphenylsulfamoyl group), a sulfonylamino group (for example, a methylsulfonylamino or tolylsulfonylamino group), or a hydroxyl group. R_{54} and R_{55} are allowed to combine with each other to form a saturated or unsaturated, 5- or 6-membered

ring.

Each of R₅₈, R₅₉ and R₆₀ is a hydrogen atom, a halogen atom (preferably a chlorine, bromine or iodine atom), an alkyl group (preferably an alkyl group with 1 or 2 carbon atoms, that is, a methyl or ethyl group), an alkoxy group (preferably an alkoxy group with 1 or 2 carbon atoms, that is, a methoxy or ethoxy group), a substituted or unsubstituted alkylamido group (for example, a laurylamido group or the like), a substituted or unsubstituted phenoxyacetamido group (for example, a phenoxyacetamido group with an alkyl substituent, or the like), or a substituted or unsubstituted arylamido group.

R₆₁ is an alkyl group (preferably an alkyl group with 1 to 24 carbon atoms, for example, a methyl, butyl or heptadecyl group), an alkoxy group (preferably an alkoxy group with 1 to 18 carbon atoms, for example, a methoxy, ethoxy or octadecyloxy group), an arylamino group (for example, an anilino group, or further an anilino group with a halogen atom, or an alkyl, amido or imido group as substituent), a substituted or unsubstituted alkylamido group (for example, a laurylamido group, a substituted or unsubstituted phenoxyacetamido group, or a phenoxybutaneamido group), or a substituted or unsubstituted arylamido group (for example, a benzamido group, or a benzamido group with a halogen atom, or an alkyl, or alkoxyamido group, or the like as substituent).

 R_{62} is an alkyl group (preferably an alkyl group with 1 to

18 carbon atoms), or a substituted or unsubstituted aryl group (for example, a phenyl, tolyl, or methoxyphenyl group, or the like).

 R_{63} is an arylamino group (for example, an anilino group, or an anilino group with a halogen atom, or an alkyl, alkoxy, alkylamido, arylamido, or imido group, or the like as substituent).

Each of R_{64} and R_{65} represents the same group as the one represented by above-mentioned R_{54} , R_{55} , R_{56} or R_{57} .

In General Formula (11), each of the substituents R_{54} to R_{56} as coupler residues which are represented by A' are desirable to have an aryl group having either an alkyl group with 8 or more carbon atoms, or an aryl group with an alkyl group of 4 or more carbon atoms so as not to hinder the heat-transferability of formed dyes.

In General Formula (11), B' represents a hydrophilic group such as a sulfo group or a carboxyl group, or a group represented by -J-Y (where J is a divalent combined group, and Y is a substituted or unsubstituted alkyl or aryl group).

Further concretely, as for the divalent combined group represented by J, -O-, -S-, -OCO-, -OC-NH-, -OC-, -N=N-,

-NHCO-, -NHSO-, or the like is cited. As for the alkyl or aryl group represented by Y, it is preferable to be an alkyl or aryl group having a hydrophilic substituent such as a sulfo or

carboxy group. It is especially preferable to be an alkyl group having a substituted or unsubstituted alkylcarbamoyl or arylcarbamoyl substituent; an alkyl group having a carboalkoxy, or carboaryloxy substituent; an alkyl group having a halogen substituent; an aryl group having a alkylamido, alkylsulfonamido, arylamido, or arylsulfonamido substituent; an aryl group having a substituted or unsubstituted alkylcarbamoyl, alkylsulfamoyl, arylcarbamoyl, or arylsulfamoyl substitutent or a substituted or unsubstituted alkyl substitutent with 1 to 22 carbon atoms; an aryl group having a substituted or unsubstituted alkyl substituent with 1 to 22 carbon atoms; an aryl group having an alkylamino substituent with 1 to 22 carbon atoms; or an aryl group having a halogen, hydroxyl, sulfo, carboxyl, or sulfamoyl substituent.

As for the active-position substituent represented by B' in Formula (11), it is preferable to have an alkyl group or the like having a hydrophilic group such as a sulfo or carboxy group, an alkyl group with 8 or more carbon atoms, or an aryl group with an alkyl group of 4 or more carbon atoms as a group immobilizable against heat in the heat-developable photo-sensitive layer. It is especially preferable to have both the hydrophilic group and the hydrophobic group mentioned above.

As for the especially preferable hydrophilic group, a sulfo, sulfino, sulfeno, thiosulfo, dithiosulfo,

hydroxylsulfonyloxy, hydroxysulfonylthio, carboxy, or thiocarboxy group is cited.

Formula (17)

$$Cp_2-(x_3)-(Q)$$

Wherein, Cp₂ represents an organic group capable of forming a diffusible dye upon reaction with, i.e., coupling to, the oxidation product of a reducing agent, that is, the so-called coupler residual group; X₃ represents a divalent coupling group; and Q represents a ballast group.

The molecular weight of the coupler residual group represented by Cp_2 is preferably not more than 700 and more preferably not more than 500, because of the diffusivity of the formed dye.

A preferable ballast group is the one similar to the ballast groups defined by Formula (10), and more preferable one is a group having not less than 8 carbon atoms and more preferably not less than 12 carbon atoms and a hydrophilic group such as a sulfo group, a carboxy group or the like together, and a further preferable one is a chain polymer.

As for the coupling dye forming compounds each having the above-mentioned chain polymer, the preferable ones are those having a repetition unit, which are represented by Formula (18) below;

Formula (18)

$$Cp_2 - (X_3) - (X_4) - (L)$$

Wherein, Cp_2 and X_3 each represent the same reference characters defined in Formula (17); X_4 represents an alkylene, allylene or aralkylene group, or a divalent organic group; and L represents an ethylene unsaturated group or a group having the ethylene unsaturated group; and each of L and ℓ_3 is 0 or 1.

The examples of the coupling dye forming compounds represented by Formulas (17) and (18) are described in Japanese Patent O.P.I. Publication Nos. 124339/1984 and 181345/1984. They include the following compounds, namely;

Exemplified dye-providing materials (6)

(7)

(8)

1

Polymer

(9)

x: 60 wt%

y: 40 wt%

(10)

(11)

(12)

(14)

$$\begin{array}{c} \text{CH}_3 \\ \text{C-CH}_2 \\ \text{CONHCH}_2 \text{CH}_2 \text{CHCOOH} \\ \text{CH}_3 \\ \text{Y: 50 wt} \\ \text{W} \end{array}$$

A further detailed description will now be made on the coupler residual groups defined by ${\rm Cp}_1$ and ${\rm Cp}_2$ each in Formulas (10), (17) and (18) above. The groups represented by the formulas below are preferable.

Formula (19)

Formula (21)

Formula (23)

Formula (25)

Formula (27)

Formula (20)

Formula (22)

Formula (24)

Formula (26)

Formula (28)

Wherein, R₆₆, R₆₇, R₆₈ and R₆₉ represent hydrogen atom, a halogen atom, an alkyl group, a cycloalkyl group, an aryl group, an acyl group, an alkyloxycarbonyl group, an arylsulfonyl group, an arylsulfonyl group, carbamoyl group, sulfamoyl group, an acyloxy group, amino group, an alkoxy group, aryloxy group, cyano group, ureido group, an alkylthio group, an arylthio group, carboxy group, sulfo group, or a heterocyclic residual group, and they may further be substituted with hydroxy group, carboxy group, sulfo group, an alkoxy group, cyano group, nitro group, an alkyl group, an aryl group, an aryloxy group, an acyloxy group, an acyl group, sulfamoyl group, carbamoyl group, imido group and a halogen atom.

These substitutions may be selected in accordance with the purposes of Cp_1 and Cp_2 , and in Cp_1 , as described above, it is preferred that one of the substituents is a ballast group, and in Cp_2 , it is preferred to select a substituent so that the molecular weight thereof may be not more than 700 and more preferably not more than 500, because the diffusibility of dyes to be formed is to be improved.

As for the positive type dye-providing materials, there are given the oxidation dye releasing compounds represented by Formula (29) below, as the examples.

Formula (29)

Wherein, W_1 represents a group of atoms necessary for forming a quinone ring on which a substituent may be taken place; R_{70} represents an alkyl group or hydrogen; E represents

-SO₂- or -N-C-(R₇₂)- in which R₇₁ represents an alkyl group or
$$^{\rm R}_{0}$$
 N-C-(R₇₂)- in which R₇₁ represents an alkyl group or $^{\rm R}_{1}$ hydrogen, and R₇₂ represents oxygen or -N-; r is 0 or 1; and Y

hydrogen, and R₇₂ represents oxygen or -N-; r is 0 or 1; and Y is synonymous with the Y previously defined in Formula (8). The examples of the compounds are described in Japanese Patent O.P.I. Publication Nos. 166954/1984, 154445/1984 and the like. They include, for example, the following compounds; Exemplified dye-providing materials:

Exemplified dye-providing materials:

(15)

(16)

As for the other positive type dye-providing materials, there includes a compound which is deprived of a dye releasing function when it is oxidized, that is typified by the compound represented by Formula (30) below; Formula (30)

Wherein, W represents a group of atoms necessary for forming a benzene ring on which a substitutent may be taken place; and R₇₀, E, and Y each are synonymous with those defined in Formula (29), respectively. The examples of these compounds are described in Japanese Patent O.P.I. Publication Nos. 124329/1984, 154445/1984 and the like. The following compounds are given as the examples;

Exemplified dye-providing materials:

(17)

(18)

$$\begin{array}{c|c} & & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\$$

As for the still other positive type dye-providing materials, the compounds represented by Formula (31) below may be given;

Formula (31)

Wherein, W, R₇₀ and Y each are synonymous with those defined in Formula (30). The examples of the compounds are described in Japanese Patent O.P.I. Publication
No. 154445/1984, and the following compounds are given as the examples;

Exemplified dye-providing materials:

(19)

(20)

There will now be a further detailed description of the diffusible dye residual groups represented by Y in the above-given Formulas (8), (9), (10), (29), (30) and (31). The preferable residual groups of such diffusible dyes are of not more than 800 in molecular weight and more preferably not more than 600 because of improving the diffusibility of the dyes, and the examples of such residual groups are given these of an azo dye, azomethine dye, anthraquinone dye, napthoquinone dye, styryl dye, nitro dye, quinoline dye, carbonyl dye, phthalocyanine dye and the like. These residual groups of dyes may also be in the recolorable and temporarily short-waved form when heat-developing or image-transferring. Among these residual groups of dyes, a chelatable dye residual group is in

the preferable form to answer the requirements for improving light resistance of an image. These are described, for example, in Japanese Patent O.P.I. Publication Nos. 48765/1984 and 124337/1984.

These dye-providing materials may be used independently or in combination with two or more of them. The amount was is not limited but may be determined according to the kinds of dye-providing materials, whether they are used independently or in combination, or whether the photographic component layer of a photo-sensitive material of the invention comprises a single layer or two or more multilayers. The amount thereof to be used is, for example, 0.005g to 50g per square-meter and preferably from 0.1g to 10g per square meter.

Any arbitrary process may be applied to contain dye-providing material to be used in the invention in the photographic component layers of a heat-developable color photo-sensitive material. For example, the polymers of the invention may be contained in the component layer in such a manner that the polymers are dissolved in a low-boiling solvent such as methanol, ethanol, ethyl acetate or the like, or a high-boiling solvent such as dibutyl phthalate, dioctyl phthalate, tricresyl phosphate, or the like and the resulted solution is then dispersed by ultrasonic waves; that the polymers are dissolved in an aqueous alkali solution such as an aqueous solution of 10% sodium hydroxide or the like and the

resulted solution is neutralized by a mineral acid such as chloric acid, nitric acid or the like; or that the polymers are dispersed together with an aqueous solution of a suitable polymer such as polyvinyl butyral, polyvinyl pyrolidone, or the like, by making use of a ball-mill.

To the heat-developable multilayered color photo-sensitive material of the invention, various other additives components mentioned above can be added as occasion calls. For example, as development accelerators, alkali-releasing agent described in the specifications of U.S. Patent Nos. 3,220,846; 3,531,285; 4,012,260; 4,060,420; 4,088,496; and 4,207,392; and in RD Nos. 15733, 15734, and 15776; organic acids described in Japanese Patent Examined Publication No. 12700/1970; -CO-, -SO₂-, or -SO- group-bearing nonaqueous polar solvents described in U.S. Patent No. 3,667,959; melt-formers described in U.S. Patent No. 3,438,766; and polyalkyleneglycols described in U.S. Patent No. 3,438,776, and in Japanese Patent O.P.I. Publication No. 19525/1976 may be added. As image tone control agent, there are cited compounds, for example, described in Japanese Patent O.P.I. Publication Nos. 4928/1971, 6077/1971, 5019/1974, 5020/1974, 91215/1974, 107727/1974, 2524/1975, 67132/1975, 67641/1975, 114217/1975, 33722/1977, 99813/1977, 1020/1978, 55115/1978, 76020/1978, 125014/1978, 156523/1979, 156524/1979, 156525/1979, 156526/1979, 4060/1980, 4061/1980, and 32015/1980; in the specifications of West German Patent

Nos. 2,140,406; 2,147,063; and 2,220,618; and in the specifications of U.S. Patent Nos. 3,080,254; 3,847,612; 3,782,941; 3,994,732; 4,123,282; and 4,201,582; that is, including phthalazinone, phthalimide, pyrazolone, quinazolinone, N-hydroxynaphthalimide, benzoxazines, naphthoxazinediones, 2,3-dihydro-1,3-oxazine-2,4-dione, oxypyridines, aminopyridines, hydroxyquinolines, aminoquinolines, isocarbostyrylsulfonamides, 2H-1,3-benzothiazine-2,4-(3H)dione, benzotriazines, mercaptotriazoles, dimercaptotetrazapentalenes, phthalic acids, naphthalic acids; mixtures of the above one or more compounds and imidazole compounds; mixtures of at least one of naphthalic acids and their anhyrides, and phthalazine compounds; and combinations of phthalazines and maleic acid, itaconic acid, quinolinecarboxylic acids or gentisic acid. In addition, compounds described in the specifications of Japanese Patent O.P.I. Publication Nos. 189628/1983 and 193460/1983, including 3-amino-5-mercapto-1,2,4-triazoles, and 3-acylamino-5--mercapto-1,2,4-triazoles are effective as well.

As anti-fogging agents, there are cited compounds for example, described in Japanese Patent Examined Publication No. 11113/1974; in Japanese Patent O.P.I. Publication Nos. 90118/1974, 10724/1974, 97613/1974, 101019/1975, 130720/1974, 123331/1975, 47419/1976, 57435/1976, 78227/1976, 104338/1976, 19825/1978, 20923/1978, 50725/1976, 3223/1976,

42529/1976, 81124/1976, 51821/1979, and 93149/1980; in the specification of British Patent No. 1,455,271; in the specifications of U.S. Patent Nos. 3,885,968; 3,700,457; 4,137,079; and 4,138,265; and in the specification of West German Patent No. 2,617,907; that is, mercuric salts; oxidizing agents (for example, N-halogenoacetamides, N-halogenosuccinimides, perchloric acid and its salts, inoraginic peroxides, and persulfuric acid salts); acids and their salts (for example, sulfinic acid, lithium laurate, rosin, diterpene acid, and thiosulfonic acid); sulfur-containing compounds (for example, mercapto compound-releasing compounds, thiouracil, disulfides, elemental sulfur, mercapto-1,2,4-triazole, thiazolinethione, and polysulfide compounds); oxazolines; 1,2,4-triazoles, and phthalimide.

For stabilizers, a printout inhibiting agent is allowed to be used in combination especially against printout after the heat-developing treatment. There are cited halogenated hydrocarbons described in, for example, Japanese Patent O.P.I. Publication Nos. 45288/1973, 119624/1975, 120328/1975, and 46020/1978; that is, tetrabromobutane, tribromoethanol, 2-bromo-2-tolylacetamide, 2-bromo-2-tolysulfonylacetamide, 2-tribromomethylsulfonylbenzothiazole, and 2,4-bis(tribromomethyl)-6-methyltriazine.

It is also allowed to conduct a post-treatment making use of a sulfur-containing compound as described in Japanese Patent

Examined Publication No. 5393/1971; and in Japanese Patent O.P.I. Publication Nos. 54329/1975 and 27034/1975.

Further, it is also allowed to contain the precursors of isothiuronium-type stabilizers described in the specifications of U.S. Patent Nos. 3,301,678; 3,506,444; 3,824,103; and 3,844,788; or the precursors of activator/stabilizers described in the specifications of U.S. Patent Nos. 3,669,670; 4,012,260; and 4,060,420.

To a heat-developable multilayered color photo-sensitive material of the invention, besides the components mentioned above, varied ingredients or coating auxiliaries including spectral sensitizing dyes, anti-halation dyes, fluorescent sensitizers, film-hardening agents, anti-static agents, plasticizers, and extenders at need.

As binders to be used in a heat-developable multilayered color photo-sensitive material of the invention, hydrophilic binders are usually preferable. However, certain hydrophobic binders are allowed to be used in partial combination of such hydrophilic binders. Binders in the invention are referred to as binders soluble in water, or in mixtures of water and freely water-soluble organic solvents. There are preferably cited proteins such as gelatine and gelatine derivatives; cellulose derivatives; polysaccharides such as dextran; natural substances such as gum arabic; and synthetic polymers such as polyvinyl acetals (for example, polyvinyl butyral, preferably

acetalized by 20% or less), polyacrylamide, polyvinyl pyrrolidone, ethyl cellulose, and polyvinyl alcohol (preferably saponified by 75% or more). However, binders to be used in the invention are not limited thereto. These may be used in combination of two or more types if necessary, and the combination of gelatine and other water-soluble polymers which is described in the specifications of Japanese Patent O.P.I. Publication Nos. 124331/1984, and 229656/1984, is especially preferable. In particular, it is preferable to use gelatin or the derivatives thereof and such a hydrophilic polymer as polyvinyl pyrrolidone, polyvinyl alcohol or the like in combination, and it is more preferable to use the under-mentioned binder described in Japanese Patent Application No. 104249/1983.

This binder contains gelatin and vinyl pyrrolidone polymer. The vinyl pyrrolidone polymer may be a polyvinyl pyrrolidone which is a homopolymer of vinyl pyrrolidone or may be a copolymer, including a graft copolymer, of vinyl pyrrolidone and one or two of the other monomers capable of polymerizing with the vinyl pyrrolidone. These polymers may be used regardless of any polymerization degree thereof. The polyvinyl pyrrolidone may be a substituted polyvinyl pyrrolidone, and a preferred polyvinyl pyrrolidone has a molecular weight of from 1,000 to 400,000. As for the other monomers capable of copolymerizing with vinyl pyrrolidone,

there are vinyl monomers including, for example, a (metha) acrylic ester such as acrylic acid, methacrylic acid and the alkyl esters thereof, a vinyl alcohol, a vinyl imidazol, a (metha) acrylamide, a vinyl carbinol, a vinyl alkyl ether and the like. It is preferred that at least 20% by weight of the composition thereof (hereinafter a percentage by weight will be referred simply to as "%") is polyvinyl pyrrolidone. In the preferred examples of such polymers, their molecular weight each are from 5,000 to 400,000.

The gelatines may be treated in a liming or acidizing process, and they may also be an ossein gelatin, a pig-skin gelatin, a hide gelatin or a denatured gelatin in which the above-mentioned gelatin is esterified, or phenylcarbamoylated.

In the above-mentioned binders, a gelatin amount to the total binder amount is preferably from 10% to 90% and more preferably from 20% to 60%, and a vinyl pyrrolidone amount thereto is preferably from 5% to 90% and more preferably from 10% to 80%.

The above-mentioned binders may contain other high molecular substances, and the preferred binders comprise, for example, gelatin and a mixture of vinyl pyrrolidone of from 1,000 to 400,000 in molecular weight and one or more than two of other high molecular substances, or they comprise gelatin and a mixture of a vinyl pyrrolidone copolymer of from 5,000 to 400,000 in molecular weight and one or more than two of other

high molecular substances. As for the other high molecular substances to be used therein, there may be given as the examples, polyvinyl alcohol, polyacrylamide, polymethacrylamide, polyvinyl butyral, polyethylene glycol, a polyethylene glycol ester, or a natural substance including, for example, a protein such as a cellulose derivative, and a polysaccharide such as starch and gum arabic. The contents thereof may be from 0 to 85% and preferably from 0 to 70%.

In addition, the above-mentioned vinyl pyrrolidone polymers may also be a cross-linked polymers, and if this is the case, it is preferred to make them cross-link after they are coated on a support. This case include the case where a cross-linking reaction is progressed in nature.

The amount of the binders used therein is normally from 0.05g to 50g per square meter of each layer, and more preferably from 0.1g to 10g. The binders are to be used preferably in the amount of from 0.1g to 10g per gram of a dye-providing material monomer, and more preferably in the amount of from 0.25g to 4g. Photo-sensitive layer ranges from 1/10 to 10 weight parts, preferably 1/4 to 4 weight parts per weight part of organic silver salt.

As for binders to be used in every layer (hydrophilic colloid) other than photo-sensitive layers of a heat-developable multilayered color photo-sensitive material of the invention, there is no limitation, but varied binders are

applicable. However, the arbitrary use of certain hydrophilic or hydrophobic binders according to the purpose is preferable. Such binders include, for example, proteins such as gelatine, gelatine derivatives, casein, casein sodium, albumin; cellulose derivatives such as ethyl cellulose; polysaccharides such as dextran and agar-agar; natural substances such as gum arabic, and tragacanth gum; synthetic polymers such as polyvinyl alcohol, polyvinyl pyrrolidone, and water-soluble polyvinyl acetal; latex-state vinyl compounds which improve the dimentional stability of photographic material; and other synthetic polymers such as follows. As for suitable synthetic polymers, there are cited those described in the specifications U.S. Patent Nos. 3,142,586; 3,193,386; 3,062,674; 3,220,844; 3,287,289; and 3,411,911. As for effective polymers, there are cited water-insoluble polymers composed of alkyl acrylate or methacrylate, acrylic acid, or sulfoalkyl acrylate or methacrylate. As for suitable high-polymeric substances, there are cited polyvinyl butyral, polyacrylamide, cellulose acetate butyrate, cellulose acetate propionate, polymethyl methacrylate, polyvinylpyrrolidone, polystyrene, ethyl cellulose, polyvinyl chloride, chlorinated rubber, polyisobutylene, butadiene-styrene copolymer, vinyl chloride--vinyl acetate copolymer, vinyl acetate-vinyl chloride-maleic acid copolymer, polyvinyl alcohol, polyvinyl acetate, benzyl cellulose, cellulose acetate, cellulose propionate, and

cellulose acetate phthalate. They may be used in combination of two or more types if necessary.

The heat-developable photo-sensitive multilayer of a heat-developable multilayered color photo-sensitive material of the invention is basically constituted three layers which is photo-sensitive in the blue color range, the green color range, and the red color range, respectively, that is, a blue-sensitive layer, a green-sensitive layer, and a red-sensitive layer. These individual layers release and form dyes which correspond to the three primary colors of yellow, magenta, and cyan, respectively.

Although formed dyes are principally yellow for the blue-sensitive layer, magenta for the green-sensitive layer, and cyan for the red-sensitive layer, respectively, they are not always limited to such correspondence. In addition, each of the above individual photo-sensitive layers may be divided into two layers — a high-sensitive layer and a low-sensitive layer — which are applied separately, or further may be divided into three or more layers, and applied.

As elemental layers in a heat-developable multilayered color photo-sensitive material of the invention, there are provided, in addition to the photo-sensitive layers, with varied photograph-constituting layers such as an overcoating layer, an undercoating layer, a backing layer, intermediate layers and filter layers according to purposes.

The heat-developable photo-sensitive layers and other photograph-constituting layers relevant to the invention are applied on varied supports. As for material to be used as a support in the invention, there are cited plastic films such as cellulose nitrate film, cellulose ester film, polyvinyl acetal film, polyamide film, polyethylene film, polyethylene terephthalate film, and polycarbonate film; metals such as aluminum; baryta paper and synthetic paper.

Among these supporting materials, those with relatively low shrinkage/expansion ratio are preferable.

A heat-developable multilayered color photo-sensitive material of the invention gives color images to an image-receiving element through heat-transfer onto the image-receiving element which is layed under the heat-developable photo-sensitive material.

In a heat-developable multilayered color photo-sensitive material of the invention a certain, known thermal solvent is allowed to be added for the purpose of balancing of the above solution physical development ratio, color development reaction ratio and diffusion transfer ratio. As for such thermal solvents, there are cited urea derivatives, amide derivatives, polyethylene glycols, and polyhydric alcohols.

As for polyethyleneglycols, these having a molecular weight between 62 to 10,000 are preferable.

As for concrete samples of the urea derivatives, there are

cited, besides urea itself, thiourea, 1,3-dimethylurea,
1,3-diethylurea, diethyleneurea, 1,3-diisopropylurea,
1,3-dibutylurea, 1,1-dimethylurea, 1,3-dimethoxyethylurea,
1,3-dimethylthiourea, 1,3-dibutylthiourea, tetramethylthiourea,
phenylurea, tetramethylurea, and tetraethylurea.

As for concrete instances of the amide derivatives, there are cited acetamide, propionamide, n-butylamide, i-butylamide, benzamide, diacetamide, dimethylformamide, acetanilide, ethylacetamidoacetate, malonamide, 2-chloroproionamide, 3-chloropropionamide, phthalimide, succinimide, and N,N-dimethylacetamide.

As for concrete samples of polyhydric alcohols, there are cited 1,10-decanediol, ethyleneglycol, and diethylene glycol.

As for such compounds, there are described in U.S. Patent Nos. 3,347,675 and 3,667,959; and RD No. 176643.

To a heat-developable multilayered color photo-sensitive material of the invention, an encapsulated, water-immiscible auxiliary agent for diffusion described in Japanese Patent O.P.I. Publication No. 174949/1983 can be added.

As for an image receiving layer to be used in the invention, any layer may do, so long as it is composed of a substance which receives the diffusible black dye released or formed through heat-development. However, it is preferable that the layer is formed by a mordant used in a photo-sensitive material of diffusion-transfer type, and a heat-resistant

organic polymer having a glass transition point between 40°C and 250°C, described in Japanese Patent O.P.I. Publication No. 207250/1982, etc.

As concrete instances of the above mordant, nitrogen-containing secondary and tertiary amines, nitrogen-containing
heterocyclic compounds, and their quaternary cationic compounds
are well-known, and effectively applicable to the invention as
well.

Polymer of vinylpyridine, and polymer or vinylpyridinium cation are disclosed in U.S. Patent Nos. 2,548,564; 2,484,430; 3,148,061; and 3,756,814.

The use of dialkylamino group-containing polymer as mordant is disclosed in U.S. Patent No. 2,675,316.

Aminoguanidine derivatives are disclosed in U.S. Patent No. 2,882,156.

Mordants crosslinkable with gelatine or the like are disclosed in U.S. Patent Nos. 3,625,694 and 3,859,096; and British Patent Nos. 1,277,453 and 2,011,012.

Mordants of aqueous sol type are disclosed in U.S. Patent Nos. 3,958,995 and 2,721,852.

Water-insoluble mordants are disclosed in Japanese Patent O.P.I. Publication No. 61228/1975.

Further various mordants are disclosed in U.S. Patent Nos. 3,709,690 and 3,788,855; West German Patent Application (O.L.S) No. 2,843,320; Japanese Patent O.P.I. Publication

Nos. 30328/1978, 155528/1977, 125/1978, 1024/1978, 74430/1979, 124726/1979, and 22766/1980; U.S. Patent Nos. 3,642,482; 3,488,706; 3,557,066; 3,271,147; and 3,271,148; Japanese Patent Examined Publication Nos. 29418/1980, 36414/1981, and 12139/1982; and RD No. 12045 (1974).

As for instances of the above heat-resistant organic polymeric substances, there are cited polystyrenes with 2000 to 85,000 molecular weight; derivatives of poly-styrene bearing a substituent with 4 or less carbon atoms; polyvinylcyclohexane, polydivinylbenzene, polyvinylpyrrolidone, polyvinylcarbazole, polyallylbenzene, polyvinylalchol; polyvinylacetals such as polyvinylformal and polyvinylbutyral; polyvinyl chloride, chlorinated polyethylene, polytrichlorofluoroethylene, polyacrylonitrile, poly-N, N-dimethylacrylamide; polyesters, whose unit bears a p-cyanophenyl, pentachlorophenyl, or 2,4-dichlorophenyl group, such as polyacrylate, polyacryl chloroacrylate, polymethyl methacrylate, polyethyl methacrylate, polypropyl methacrylate, polyisopropyl methacrylate, polyisobutyl methacrylate, poly-tert-butyl methacrylate, polycyclohexyl methacrylate, polyethyleneglycol dimethacrylate, and polyethylene terephthalate; polyanhydrides; polyamides; and celllose acetates. In addition, the synthetic polymers with a glass transition temperature of 40°C or lower described in "Polymer Handbook," 2nd ed. (edited by J. Brand and E.H. Immergut. John Wiley & Sons.) also are useful. These

polymeric substances may be used either singly or as a copolymer in combination of them.

As for especially useful polymers, there are cited cellulose acetates such as triacetate and diacetate; polyamides, for example, by combination of heptamethylenediamine and terephthalic acid, fluorenedipropylamine and adipic acid, hexamethylenediamine and diphenic acid, or hexamethylendiamine and isophthalic acid; polyesters, for example by combination of diethylene glycol and diphenylcarboxylic acid, or bis-p-carboxyphenoxybutane and ethylene glycol; polyethylene terephthalate, and polycarbonate. These polymers are allowed to be modified ones. For example, polyethylene terephtalate modified making use of cyclohexanedimethanol, isophthalic acid, methoxypolyethylene glycol, or 1,2-dicarbomethoxy-4-benzenesulfonic acid also effective.

The polymer may be either applied on a support such as paper, glass and metal to form an image-receiving layer, or processed in the form of film or sheet to function also as a support in itself. In the latter case, the support may be formed by either a single layer, or several layers. The support may have a titanium white-containing part or layer as a white color-reflecting layer therein or thereon. In addition, the compound to be used as the mordant afore-mentioned also is applied on an appropriate support singly or in combination with

another polymer.

For a heat-developable multilayered color photo-sensitive material of the invention, various exposing means are applicable. The latent image is obtained with image exposure to a radiation including visible rays. Generally, light sources for the ordinary color printing such as a tungsten lamp, mercury lamp, xenon lamp, laser, CRT and LED are available as light source.

As original drawings, not only line drawing images such as draftings but also gradational photographic images are applicable. Printing from an original drawing may be done through contact printing as well.

Further, it is possible that images which are cast by a video camera or the like, and image information which is transmitted from a TV station are directly produced by CRT or OFT, and that such images are formed on a heat-developable photo-sensitive material by means of contact or lens.

Further, LEDs which have been markedly improved in recent years, are being used as exposing or displaying means in various instruments. However, it is difficult to obtain an LED which emits the blue light effectively. For the purpose of reproducing a color image, it may be useful that a system is designed so that LEDs may emit the green light, the red light, and the infrared radiation, respectively, and layers which are sensitive to such lights and radiation, may provide yellow,

magenta, and cyan dyes, respectively. That is, the green-, red- and infrared-sensitive layers may be to contain yellow, magenta, and cyan dye-providing compounds, respectively.

Besides the above method of direct contacting or casting of the original drawing, there is a method that the original drawing is read by a light-receiving element such a phototube and CCD, and inputted into a memory of a computer or the like, and that such information is image-treated at need, reproduced by CRT, and then utilized as a image-like light source, or, on the basis of the treated information, the three LEDs are made to emit and expose.

The heat-transfer from a heat-developable multilayered color photo-sensitive material of the invention to an image receiving layer (element) for heat-transfer is conducted when the heat-developable multilayered color photo-sensitive material of the invention is heat-developed or is reheated after the completion of the heat-development. Heating for heat-transfer may be conducted making use of any means applicable to ordinal heat-developable photo-sensitive materials. For example, it may be useful to make the material contact with a heated block or blade, to make use of high-frequency heating, and further to provide a conductive layer within the heat-developable multilayered color photo-sensitive material of the invention, or within the image-receiving layer (element), and ultilize Joule heat

generated by conduction or an intensive magnetic field therefrom. As for the heating pattern, there is no special limitation, but it is possible to reheat after preheating, to heat for a short time at high temperature or for a long time at low temperature, including continuously raising or lowering the temperature, repeatedly if necessary, or to heat discontinuously. However, certain simple heating patterns are preferable. Usually, the heating termperature for heat-transfer ranges from 80°C to 200°C, preferably from 100°C to 180°C, and the heating time ranges from 1 second to 5 minutes, preferably from 5 seconds to 3 minutes.

In heat-transfer with the use of a heat-developable multilayered color photo-sensitive material, most of heat-developing apparatuses on the market — for example, "Image Forming Model 4634" (Sony Techtronics), "Developer Module 277" (3M), and "Video Hard Copy Unit NWZ-301" (Japan Radio) — are readily applicable.

Examples of the invention are given below, although functioning modes of the invention can not be limited thereto.

Example 1

A coating liquid compound of the below components was prepared, and applied onto a 100µm-thick support of transparent polyethylene terephthalate film provided with treatment of photographic undercoating:

Red-sensitive silver halide emulsion (An aged silver

iodobromide emulsion, containing 4 mol% of silver iodide, composed of cubic particles with an average particle size of 0.15µm, and added to with 520mg per mole of Ag of 3,3'-carboxy-ethyl-5,5'-dichloro-9-ethyl-4-thiacarbocyanine.)

....(as Ag) 0.2g

A compound obtained by an equimolar reaction between 4-sulfobenzotriazole and silver nitrate in an aqueous solution of poly(4-vinylpyrrolidone), with adjusted pH of 6.0.

....(as Ag) 0.2g

1,6-hexanediol

1.6q

4-diethylamino-2-methylphenylsulfamic acid sodium 0.4g

2-actamido-4-(1-carboxy-tridecyloxy)-5-methyl-6-chlorophenyl

(as dye-providing compound)

0.52q

3-amino-4-allyl-5-mercapto-1,2,4-triazole

6mq

In addition, Gelatine, Surface active agent, and Gelatin-hardening agent.

The applying amounts of main components were $1.2g/m^2$ for Ag, $1.25g/m^2$ for gelatine, and $2.9g/m^2$ for poly(4-vinyl--pyrrolidone), respectively.

Next, over the above layer, an intermediate layer (I) composed of polyvinylpyrrolidone and gelatine was applied. The applying amounts were $0.4g/m^2$ for gelatine, and 1.0g for polyvinyl-pyrrolidone, but, besides, $0.7g/m^2$ of 1.6-hexanediol was added to.

Further, over the above layer (I), another coating liquid

having the same composition as the above coating liquid, except for substituting a green-sensitive silver halide emulsion (An aged silver iodobromide emulsion, containing 4 mole% of silver iodide, composed of cubic particles with an average grain size of 0.15 μ , and added to with 500mg per mole% Ag of 3,3'--carboxyethyl-5,5'dichloro-oxacarbocyanine.) for the said red-sensitive silver halide emulsion, and using 0.63g of κ , κ ,- κ ', κ '-tetrakis(l-phenyl-3-isopropanamido-pyrazoline-5-one-4-yl)-m-xylene as dye-providing material, was applied.

Furthermore, over the above second emulsion layer, another intermediate layer (II) composed of polyvinylpyrrolidone and gelatine was applied. The applying amounts were $0.4g/m^2$ for gelatine, $1.0g/m^2$ for polyvinylpyrrolidone, but, besides, $0.7g/m^2$ of 1.6-hexanediol was added to.

Finally, over the above layer (II), another coating liquid having the same composition as the above second coating liquid, except for substituting a blue-sensitive silver halide emulsion (An aged silver iodobromde emulsion, containing 4 mole% of silver iodide, composed of cubic particles with an average grain size of 0.15µm) for the said green-sensitive silver halide emulsion, and using 0.65g of K-benzoyl-K-(1-phenyl-2-[4--{2-octadecenyl-3-carboxypropanamido} benzyll-1,2,4-triazine-3,5-dione-4-yl)-2-chloro-acetanilide, was applied. The obtained photo-sensitive material was designated as control I.

Then, various samples were prepared in order by adding to

the above intermediate layer (II) blue-light absorbing materials described in Table 1, respectively. The adding amounts of the materials were adjusted so that the concentration in the intermediate layer (II) falled on 1.5 in transmission concentration units. The adding method was described in Table 1.

Table 1

Test No.	Samp:	le	blue-light absorbing material to be adde	g d	adding method
1	contro	l I	nil		
2	11	II	colloidal silver (average grain size 0	.01µm)	ball mill
3	π	III	HO—N=N—OCH ₃		11
4	11	IV	N=C-CH ₃ C-CH-N=N-	⊢осн ₃	tt
5	ŧī	V	C ₂ H ₅ N-N-CCCO-C ₄ CONH-C	H ₉ (t)	11
6	Invent	ion I	Exemplified compound	(1)	tř
7	11	II	п	(35)	Ħ
8	n	III	11	(19)	protection dispersion
9	Ħ	IV	11	(40)	tr
10	11	V	11	(15)	tr
11	11	VI	11	(16)	17

The obtained samples 1 to 11 of heat-developable multilayered color photo-sensitive materials were exposed to the blue light and then the green light through a step wedge, respectively.

On the other hand, an image-receiving element was prepared by applying a solution of polyvinyl chloride (polymerization degree: about 1100; mfd. by Wako Pure Chemical Industries) in tetrahydrofuran so that the thickness of the formed layer of polyvinyl chloride may fall on 15 µm. Then the image-receiving element was laid over the above heat-developable multilayered color photo-sensitive material, heated for 1 minute at 140°C, and immediately stripped. Thus a diffusion-transfer image was produced on the image-receiving layer. Obtained results are shown in Table 2 at every sample.

Table 2

			blue-light exposure			green-light exposure					
Test	Sa	Sample	Е	В		G		В		G	
No.			Dmax	Dmin	Dmax	Dmin	Dmax	Dmin	Dmax	Dmin	
1	Co.		1.54	0.31	1.32	0.23	0.24	0.21	1.08	0.12	
2	п	II	1.48	0.53	0.52	0.50	0.55	0.52	1.11	0.38	
3	11	III	2.23	0.95	0.25	0.21	1.10	1.00	1.10	0.12	
4	11	IV	2.45	0.99	0.27	0.22	1.08	0.98	1.05	0.10	
5	11	V	2.53	1.10	0.26	0.23	1.15	1.08	1.03	0.07	
6	Inv	ven- on I	1.80	0.25	0.22	0.19	0.28	0.24	1.10	0.08	
7	11	II	1.68	0.28	0.23	0.20	0.30	0.26	1.05	0.09	
8	IT	III	1.65	0.23	0.27	0.23	0.26	0.23	1.11	0.10	
9	If	IV	1.58	0.23	0.25	0.22	0.27	0.24	1.10	0.11	
10	11	V	1.70	0.21	0.24	0.20	0.23	0.21	1.10	0.08	
11	11	VI	1.72	0.19	0.24	0.21	0.23	0.19	1.08	0.09	

As seen in Table 2, the transfer image of the Control II was evenly developed, being low in contrast with high Dmin of both yellow and magenta images. (The reason of this is presumably that colloidal silver contained in the intermediate layer as blue light-absorbing layer functioned as nucleus of physical development.) The transfer images of the Controls III to V was stained, having high Dmin of the yellow component of the magenta image. (The reason of this is presumably that the dyes in the blue-light-absorbing dye layer were diffused to transfer to the image receiving layer.) By contraries, the transfer images of the Samples I to VI by the invention were not stained with good filter effects, being low in Dmin and Dmax of the yellow component of the magenta image, because dyes were not diffusion-transferred.

Example 2

Samples prepared for the above Example 1 were exposed to the red light through a step wedge, and treated in the same way as in Example 1. Obtained results of diffusion-transferred images are shown in Table 3.

Table 3

			red-light exposure					
	Sample	9	В		R			
Test No.			Dmax	Dmin	Dmax	Dmin		
12	Control	I	0.23	0.20	1.01	0.13		
13	11	II	0.50	0.48	0.93	0.11		
14	17	III	1.08	1.05	0.92	0.10		
15	11	IV	1.03	1.05	0.88	0.09		
16	11	V	1.05	1.00	0.85	0.08		
17	Inventi	on I	0.23	0.23	0.92	0.09		
18	11	II	0.26	0.27	0.98	0.10		
19	11	III	0.23	0.23	0.88	0.12		
20	11	ΙV	0.23	0.21	0.85	0.11		
21	17	٧	0.20	0.21	0.90	0.09		
22	11	ΛΙ	0.19	0.20	0.89	0.10		

As seen in Table 3, similarly to the case of Example 1, the existence of colloidal silver in the intermediate layer of the Control II functioned as nucleus of physical development, and the Controls III to V were stained without any filter effect. By contraries, the transfer images of the Samples I to VI by the invention were found to have excellent filter effects.

Example 3

A coating liquid compound of the below components was prepared, and applied onto a 100µm-thick support of transparent polyethylene terephthalate film provided with treatment of photographic undercoating:

Red-sensitive silver halide emulsion (An aged silver iodobromide emulsion, containing 4 mol% of silver iodide, composed of cubic particles with an average particle size of 0.15 μ , and added to with 520mg per mol of Ag of 3,3'-carboxy-ethyl-5,5'-dichloro-9-ethyl-4-thiacarbocyanine.)

....(as Aq) 0.2q

A compound obtained by an equimolar reaction between 4-sulfobenzotriazole and silver nitrate in an aqueous solution of poly(4-vinylpyrrolidone), with adjusted pH of 6.0.

....(as Aq) 0.2q

1,6-Hexanediol

1.6g

4-diethylamino-2-methylphenylsulfamic acid sodium 0.4g exemplified dye-providing material (13) as a dye-providing

compound 0.98g

3-amino-4-allyl-5-mercapto-1,2,4-triazole 6mg
In addition, Gelatine, Surface active agent, and Gelatin-hardening agent.

The applying amounts of main components were $1.2g/m^2$ for Ag, $1.25g/m^2$ for gelatine, and $2.9g/m^2$ for poly(4-vinyl--pyrrolidone), respectively.

Next, over the above layer, an intermediate layer (I) composed of polyvinylpyrrolidone and gelatine was applied. The applying amounts were $0.4g/m^2$ for gelatine, and $1.0g/m^2$ for polyvinyl-pyrrolidone, but, besides, $0.7g/m^2$ of 1.6-hexanediol was added to.

Further, over the above layer (I), another coating liquid having the same composition as the above coating liquid, except for substituting a green-sensitive silver halide emulsion (An aged silver iodobromide emulsion, containing 4 mole% of silver iodide, composed of cubic particles with an average grain size of 0.15µm, and added to with 500mg per mole of Ag of 3,3'-carboxyethyl-5,5'dichloro-oxacarbocyanine.) for the red-sensitive silver halide emulsion, and using 1.47g of exemplified dye-providing material (12) as a dye-providing material, was applied.

Furthermore, over the above second emulsion layer, another intermediate layer (II) composed of polyvinylpyrrolidone and gelatine was applied. The applying amounts were 0.4g/m^2 for

gelatine, $1.0g/m^2$ for polyvinylpyrrolidone, but, besides, $0.7g/m^2$ of 1,6-hexanediol was added to.

Finally, over the above layer (II), another coating liquid having the same composition as the above second coating liquid, except for substituting a blue-sensitive silver halide emulsion (An aged silver iodobromide emulsion, containing 4 mole% of silver iodide, composed of cubic particles with an average grain size of 0.15µm) for the green-sensitive silver halide emulsion, and using 1.3g of exemplified dye-providing material (10) as a dye-providing material was applied. The obtained photo-sensitive material was designated as Control I.

Then, various samples were prepared in order by adding to the above intermediate layer (II) blue-light absorbing material described in Table 4, respectively. The adding amounts of dyes were adjusted so that the concentration in the intermediate layer (II) falled on 1.5 in transmission concentration units. The adding method was described in Table 4.

Table 4

Test No.	Sample	blue-light absorbing material to be added	adding method
23	control VI	nil	
24	control VII	colloidal silver (average grain size 0.01µm)	ball mill
25	" VIII	HO-N=N-OCH3	11
26	" IX	N=C-CH-N=N-OCH3	11
27	" X	C ₂ H ₅ N-N=C CO-C ₄ H ₉ (t)	11
28	Invention VII	Exemplified compound PM-1 ($M\overline{w} = 8500$)	Latex dispersion
29	" VIII	" $PM-2$ ($M\overline{W} = 7000$)	11
30	" IX	" $PM-5$ ($M\overline{W} = 10000$)	11
31	n X	" $PM-10 (M\overline{W} = 11000)$	11
32	" XI	" PM-13 (Mw = 15000)	17
33	. " XII	$PM-15 (M\overline{w} = 12000)$	11

The obtained samples 23 to 33 of heat-developable multilayered color photo-sensitive materials were exposed to the blue light and then the green light through a step wedge, respectively.

On the other hand, an image-receiving element was prepared by applying a solution of polyvinyl chloride in tetrahydrofuran so that the thickness of the formed layer of polyvinyl chloride may fall on 15um. Then the image-receiving element was laid over the above heat-developable multilayered color photo-sensitive material, heated for 1 minute at 140°C, and immediately stripped. Thus a diffusion-transfer image was produced on the image-receiving layer. Obtained results are shown in Table 5 at every sample.

Table 5

		blue-light exposure		green-light exposure					
	Sample	В		G		В		G	
Test No.		Dmax	Dmin	Dmax	Dmin	Dmax	Dmin	Dmax	Dmin
23	Con- trol VI	1.68	0.30	1.30	0.23	0.24	0.21	1.09	0.11
24	" VII	1.53	0.51	0.51	0.49	0.54	0.51	1.13	0.38
25	" VIII	2.26	0.90	0.24	0.21	1.13	0.99	1.11	0.12
26	" IX	2.45	0.98	0.26	0.22	1.12	0.96	1.06	0.10
27	n X	2.61	1.02	0.26	0.21	1.16	1.04	1.04	0.07
28	Inven- tion VII	1.85	0.14	0.18	0.16	0.21	0.18	1.29	0.07
29	" VIII	1.75	0.21	0.17	0.14	0.24	0.22	1.10	0.09
30	" IX	1.70	0.21	0.24	0.22	0.22	0.19	1.21	0.10
31	" X	1.63	0.21	0.21	0.17	0.24	0.23	1.21	0.10
32	n XI	1.80	0.20	0.21	0.18	0.21	0.21	1.22	0.06
33	u XII	1.75	0.16	0.20	0.19	0.21	0.19	1.15	0.09

As seen in Table 5, the transfer image of the Control

II was evenly developed, being low in contrast with high Dmin
of both yellow and magenta images. (The reason of this is
presumably that colloidal silver contained in the intermediate
layer as blue light-absorbing layer functioned as nucleus of
physical development.) The transfer images of the Controls

III to V was stained, having high Dmin of the yellow component
of the magenta image. (The reason of this is presumably that
the dyes in the blue-light-absorbing dye layer were transferred
in themselves.) By contraries, the transfer images of the
Samples I to VI by the invention were not stained with good
filter effects, being low in Dmin and Dmax of the yellow
component of the magenta image, because dyes were not
diffusion-transferred.

Example 4

Samples prepared for the above Example 3 were exposed to the red light through a step wedge, and treated in the same way as in Example 1. Obtained results of diffusion-transferred images are shown in Table 5.

Table 6

		red-light exposure					
\ 	Sample	В		R			
Test No.		Dmax	Dmin	Dmax	Dmin		
34	Control V	7 I	0.21	0.20	1.01	0.13	
35	" VI	I	0.49	0.46	0.93	0.11	
36	" VII	I	1.06	1.01	0.92	0.10	
37	"]	V	1.01	0.91	0.88	0.09	
38	п	V	1.00	0.96	0.85	0.08	
39	Invention VI	ΞI	0.17	0.15	0.99	0.07	
40	" VII	I	0.17	0.15	0.98	0.09	
41	"]	ΙX	0.19	0.17	0.93	0.08	
42	11	х	0.19	0.16	0.91	0.09	
43	11 >	ΚΙ	0.18	0.16	0.93	0.08	
44	" X]	ΙΙ	0.19	0.16	0.94	0.09	

As seen in Table 6, similarly to the case of Example 3, the existence of colloidal silver in the intermediate layer of the Control VII functioned as nucleus of physical development, and the Controls VIII to X were stained without any filter effect. By contraries, the transfer images of the Samples VII to XII by the invention were found to have excellent filter effects.

A heat-developable multilayered color photo-sensitive material in which an intermediate layer containing a blue-light absorbing dye relevant to the invention, which is a compound represented by Formula (1) or (2) or a polymer having a unit derived rom a monomer represented by Formula (3) is interposed between the blue-sensitive layer and its adjacent layer does not cause fogs and lowering of contrast, and enables diffusion-transferred unturbid images.

WHAT IS CLAIMED IS:

- 1. A heat-developable multilayered color photo-sensitive material comprising a support having thereon a blue-light-sensitive layer, a green-light-sensitive layer and a red-light-sensitive layer each containing at least one selected from (a) a photo-sensitive silver halide, (b) an organic silver salt, (c) a developer and (d) a dye-providing compound wherein a layer containing a diffusion proof blue-light absorbing organic substance is interposed between said blue-sensitive layer and said green-sensitive layer or between said blue-sensitive layer and said red-sensitive layer.
- 2. A heat-developable multilayered color photo-sensitive material according to claim 1, wherein said dye-providing compound is a compound capable of forming or releasing a diffusible dye through a heat-development.
- 3. A heat-developable multilayered color photo-sensitive material according to claim 1, wherein said blue-light absorbing organic substance is a compound having a hydrophilic group in the molecules thereof.
- 4. A heat-developable multilayered color photo-sensitive material according to claim 1, wherein said blue-light absorbing organic substance is a compound having a ballast

group in the molecules thereof.

5. A heat-developable multilayered color photo-sensitive material according to claim 1, wherein said blue-light absorbing organic substance is at least one kind of the compounds represented by Formulas (1) and (2) below; Formula (1)

Formula (2)

Wherein, each of R_1 to R_5 is a hydrogen atom, a halogen atom, or alkyl, alkoxy, alkylamido group with 1 to 22 carbon atoms, or an aryl, aryloxy, or arylamido group,

 R_6 is a hydrogen atom, or an alkyl, alkoxy, alkylamido group with 1 to 22 carbon atoms, or an aryl, anilino, aryloxy, or arylamido group,

each of R_7 to R_{11} is a hydrogen atom, a halogen atom,

or a cyano, nitro, hydroxy, carboxy, or sulfo group or alkyl, alkoxy, dialkylamino, acyl, alkylamido, or alkoxycarbonyl group with 1 to 22 carbon atoms;

 R_7 and R_8 are allowed to combine with each other to form a benzene ring;

each of R_{12} and R_{13} is alkyl group with 1 to 22 carbon atoms and being allowed to combine with each other to form a piperidine, pyrrolidine or morphorino ring;

each of R_{14} to R_{17} is a hydrogen atom, a halogen atom, or alkyl, alkoxy, or alkylamido group with 1 to 4 carbon atoms;

 R_{18} is alkyl or aryl group,

each of R_{19} to R_{23} is a hydrogen atom, a halogen atom, a carboxy group, a sulfo group, or alkyl, alkoxy, alkylamino, or alkylamido group with 1 to 22 carbon atoms,

- 6. A heat-developable multilayered color photo-sensitive material according to claim 1, wherein said blue-light absorbing organic substance is contained in the amount within the range of from 10g to 0.01g per square meter.
- 7. A heat-developable multilayered color photo-sensitive material according to claim 1, wherein said blue-light absorbing organic substance is a polymer having a unit derived from a monomer represented by Formula (3) below;

Formula (3)

X-Dye

Wherein, X represents an ethylene unsaturated group or a group having an ethylene unsaturated group; and Dye represents a residual group of a blue-light absorbing dye.

8. A heat-developable multilayered color photo-sensitive material according to claim 7, wherein said X denoted in said Formula (3) is represented by Formula (4) below; Formula (4)

$$\mathbf{CH_2} = \left\{ \begin{array}{c} \mathbf{R_{24}} \\ \mathbf{C} \\ \mathbf{C} \\ \mathbf{J_1} \\ \mathbf{\ell_1} \end{array} \right. \\ \left. (\mathbf{X_1})_{\mathbf{m_1}} \\ \left. (\mathbf{J_2})_{\mathbf{\ell_2}} \\ \left. (\mathbf{X_2})_{\mathbf{m_2}} \right]_{\mathbf{k}} \\ \end{array}$$

Wherein, R_{24} represents hydrogen, or carboxy or alkyl group; J_1 and J_2 represent a divalent bonding group; X_1 and X_2 represent a divalent hydrocarbon group; and k, \mathcal{L}_1 , m_1 , \mathcal{L}_2 , and m_2 are 0 or 1, respectively.

9. A heat-developable multilayered color photo-sensitive material according to claim 7, wherein said monomer denoted in said Formula (3) is represented by Formula (5) or (6) below;

Formula (5)

Formula (6)

Wherein, R₂₅ through R₄₇ represent respectively a hydrogen atom, an alkyl group, an alkenyl group, an cycloalkyl group, an aryl group, an aralkyl group, an alkoxy group, an aryloxy group, an amyl group, an acyloxy group, an acylamino group, an alkoxyalkyl group, an aryloxyalkyl group, an alkoxycarbonyloxyl group, an alkoxycarbonylamino group, an alkoxycarbonyl group, a carbamoyl group, a sulfamoyl group, an amino group, an alkylamino group, a dialkylamino group, an arylamino group, a cycloalkylamino group, a halogen atom, a cyano group, a acyloxyalkyl group, a nitro group, an alkylsulfonyl group, an arylsulfonyl group, a hydroxy group, a carboxyl group, a sulfo group, ureido group, sulfamoylamino group, an alkylsulfonyloxy group, an arylsulfonyloxy group, an alkylsulfonylamino group, an

arylsulfonylamino group, an alkylthio group, an arylthio group, a heterocyclic group, an imido group, and a quaternary ammonium group; at least one of from R_{25} through R_{35} and at least one of from R_{36} through R_{47} are an ethylene unsaturated group represented by X in the Formula (3) or a group having an ethylene unsaturated group,

in Formulas (5) and (6) each, two groups adjacent to each other on the benzene ring may be bound to form a carbon ring, and further, R_{36} and R_{37} may be bound each other to form a piperidino ring, a pyrrolidino ring or a morpholino ring.

10. A heat-developable multilayered color photo-sensitive material according to claim 7, wherein the weight average molecular weight of said blue-light absorbing organic substance is from 1,500 to 100,000.