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(19) THE PATENT OFFICE LONDON

(54) PHOTOGRAPHIC SILVER HALIDE DEVELOPING PROCESS

(71) We, AGFA-GEVAERT AKTIENGESELLSCHAFT, a Body Corporate organised under the laws of Germany of 509 Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of photographic images and to a photographic material suitable for this purpose, which material contains diffusion resistant, oxidizable compounds which contain in their molecule a photographically useful fragment and which in their non-oxidized form, as compared with the oxidized form have an increased capability of releasing said photographically useful fragment. Where this fragment is diffusible, it may diffuse into other layers to exert therein a desired effect. In one aspect of the invention the photographically useful fragment may be a diffusible dye and in this case the oxidizable compound may be of particular use as colour providing compound in colour photographic dye diffusion transfer process. Such compounds in their non oxidized form are capable of releasing diffusible dyes whereas such release is inhibited from the oxidized form of the compounds.

Among the previously known processes for the production of coloured photographic images by dye diffusion transfer, those based on colour providing compounds which are incorporated in a diffusion-fast form and from which diffusible dyes or dye precursor products are split off imagewise during development to be transferred to an image receiving layer have recently become of increasing importance.

Among the colour providing compounds suitable for this purpose may be included, for example, the non-diffusible colour couplers described in German Patent No. 1,095,115, which, during development, react with an oxidation product of a colour developer compound consisting of a primary aromatic amine to release, in a diffusible form, either a preformed dye or a dye which is produced in the colour coupling reaction. The choice of developer compounds is, of course, in this case restricted to colour developers.

Other suitable non-diffusible colour providing compounds have been described in German Offenlegungsschrift No. 1,930,215. These compounds contain a preformed, latently diffusible dye residue attached by a removable hydrazone group to a residue which confers diffusion resistance. These compounds should not be regarded as colour couplers and it has, in fact, been found that the choice of developer compounds suitable for releasing the diffusible dye residue is by no means limited to the usual colour developers but may very well include black and white developers, e.g. pyrocatechols.

Non-diffusible colour providing compounds have also been described in German Offenlegungsschrift No. 1,772,929. These compounds contain a special group and undergo an oxidative ring closure reaction during development, thereby releasing a preformed dye residue in a diffusible form. The compounds described in the said Offenlegungsschrift may be divided into two groups. The compounds of one group require a conventional colour developer compound for development; they undergo a coupling reaction with the oxidation products of the colour developer compound and release the preformed dye residue in a diffusible form in a subsequent ring closure reaction. The compounds of the other group are themselves silver halide developers and are therefore capable, in their oxidized form, to enter into the above mentioned ring closure reaction to release the diffusible dyes even in the absence of other developer compounds.

Lastly, the non-diffusible colour providing compounds according to German Offenlegungsschrift No. 2,242,762 should be mentioned in this connection. These compounds are sulphonamidophenols or sulphonamidoanilines which, after the oxidation reaction which takes place during development, are split by the action of the alkali of the developer to release a diffusible dye which has a free sulphamoyl group.

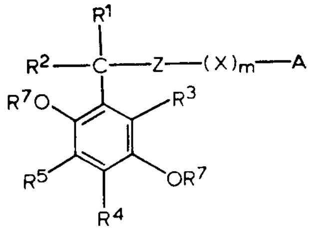
All the colour providing compounds mentioned above operate negatively, that is to say that when they are used with the usual (negative) silver halide emulsions, they release the photographically useful fragment which in most of these cases is a diffusible dye in imagewise distribution corresponding to the negative silver image produced by development. Production of positive dye images therefore requires the use of direct positive silver halide emulsions or the application of a suitable reversal process.

Non-diffusible colour providing compounds have also been disclosed in German Offenlegungsschriften Nos. 2,402,900 and 2,543,902. These compounds are capable of undergoing a splitting reaction under alkaline development conditions to release a photographically useful fragment such as a diffusible dye whereas in their oxidized form the above mentioned splitting reaction is difficult or impossible. Compounds of this type may suitably be used in combination with conventional negative emulsions to produce positive transfer colour images.

Among the colour providing compounds hitherto known, it is difficult to select any which are satisfactory in all respects, that is to say both sufficiently reactive and sufficiently stable. They should not release the diffusible dyes at the very beginning of alkaline development but only after imagewise oxidation has been effected by the silver halide which has been developed in imagewise distribution. On the other hand, release of the diffusible dyes, either from the oxidized form or from the non-oxidized form of the colour providing compounds, must take place sufficiently rapidly and rapid transfer of the diffusible dyes is also necessary.

A class of non-diffusible, oxidizable compounds has now been found which, in their non-oxidized form, are subject to a splitting reaction under the influence of the developer alkali to release a photographically useful fragment, in particular, a diffusible dye, but which do not undergo this splitting reaction, or to only a much less extent, when they are oxidized.

The present invention relates to a photographic process for the production of images, in which a photographic material having at least one light-sensitive silver halide emulsion layer and a non-diffusible, oxidizable compound associated with this layer, which compound is subject to a splitting reaction under alkaline development conditions when in its nonoxidized form, thereby releasing a photographically useful fragment, e.g. a diffusible dye, and which in its oxidized form is not subject to this splitting reaction or only to a much less extent than in its non-oxidized form, is exposed imagewise and developed with a silver halide developer, the oxidized form of the silver halide developer oxidizing the non-diffusible, oxidizable compound, thereby converting it into a form which cannot be split by alkali or only to a slight extent, whereas the residual non-oxidised, oxidizable compound releases the photographically useful fragment as a result of being split under the influence of the alkaline medium. In cases where the photographically useful fragment is a diffusible dye, this may be transferred to an image receiving layer to provide therein a dye image. The non-diffusible compounds used in such cases are referred to hereinafter as colour providing compounds. The process is characterised in that the non-diffusable, oxidizable compound used is a compound represented by the following formula:



in which

A either alone or together with the connecting members X (when present) and Z represents the residue of a photographically useful fragment, in particular the residue of a diffusible dye or dye precursor;

X represents a bivalent linking member having the formula —R—$(L)_p$—$(R)_q$—, in which R represents an alkylene group preferably having from 1 to 6 carbon atoms or a substituted or unsubstituted arylene or aralkylene group and the two groups R may be the same or different; R may be, for example an unsubstituted phenylene group or a phenylene group substituted by one or more substituents selected from alkyl, alkoxy, halogen, acylamino, acyl such as —$COCH_3$ or alkoxycarbonyl;

L represents —O—, —CO—, —$CONR^6$—, —NR^6CO—, —SO_2NR^6—, —NR^6SO_2—, —O—CO—NR^6—, —NR^6—CO—O—, —S—, —SO— or —SO_2—, in which R^6 represents hydrogen or an alkyl group;

p=0 or 1;

q=0 or 1; q=1 when p=1;

R^7 represents hydrogen or a photographically inert group which is capable of being hydrolysed under alkaline development conditions;

Z represents a bivalent connecting group which is electro-negative with respect to the carbon-atom shown, in particular —SO_2—, —S—, —O— or —NH—SO_2—;

R^1 and R^2 which may be the same or different represent hydrogen or a substituted or unsubstituted hydrocarbon group, e.g. an alkyl group having from 1 to 18 carbon atoms such as a methyl, ethyl, n-hexyl, n-octyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl or n-heptadecyl group, an aralkyl group such as a benzyl group, or an aryl group such as a phenyl group;

R^3, R^4 and R^5 which may be the same or different represent hydrogen, halogen, e.g. chlorine or bromine, alkyl or alkoxy preferably having up to 18 carbon atoms, or acylamino in which the acyl group is derived from aliphatic or aromatic carboxylic or sulphonic acids; or R^5 together with R^4 may represent the residue required to complete a condensed, substituted or unsubstituted benzene ring;

m=0 or 1;

at least one of the substituents R^1, R^2, R^3, R^4 and R^5 contains a residue which confers diffusion resistance.

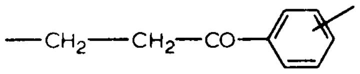
The photographically useful fragment that is released from the non-oxidized oxidizable compound includes the connecting member —Z—$(X)_m$— and may be diffusible and may include a development inhibitor, a developing agent, a silver halide solvent and more particularly a dye or dye precursor. The photographically useful fragment after release from the non-oxidized oxidizable compound may come into effect in the same layer where it was released or, after diffusion, in another layer of the photographic material.

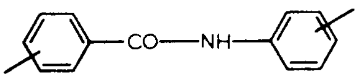
The dye residues may in principle be residues from any series of dyes, provided that they are sufficiently diffusible to be able to diffuse through the layers of the light-sensitive material to the image receiving layer. The dye residues may be equipped with one or more water-solubilizing groups for this purpose. Suitable water-solubilizing groups include, inter alia, carboxyl groups, sulpho groups, sulphonamide or sulphamoyl groups and aliphatic as well as aromatic hydroxyl groups. The sulphamoyl group which in some cases remains attached to the dye after the splitting reaction, for example in cases where Z represents —NH—SO_2—, may in itself impart to the dye molecule a considerable tendency to diffuse in an alkali medium, so that in these cases the presence of an additional water-solubilizing group is not essential. The following are examples of dyes which are particularly suitable for the process according to the invention: Azo dyes, azomethine dyes, anthraquinone dyes, phthalocyanine dyes, indigoid dyes, triphenylmethane dyes, metal complex dyes and coloured metal complexes.

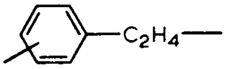
By residues of dye precursors are meant residues of compounds which are converted into dyes by any of the usual steps or by additional steps during photographic processing, whether it be by oxidation or by coupling or by exposure of an auxochromic group in a chromophoric system, for example by saponification. Dye precursors in this sense may be leuco dyes, couplers or dyes which are converted into other dyes during processing. Where it is not important to distinguish between dye residues and residues of dye precursors, it is to be understood that the term "dye residue" is also used to cover such residues of dye precursors.

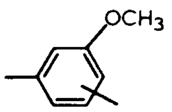
The bivalent linking member X represented in the general formula may represent, for example, a residue represented by one of the following formulae:

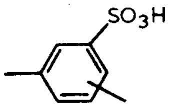
$—CH_2—CH_2—O—CH_2—CH_2—$











$—CH_2—CH_2—SO_2—C_6H_{12}—$

and

$—C_3H_6—NH—CO—C_2H_4—$

R^7 preferably represents a hydrogen atom, but it should be noted that the two substituents R^7 need not necessarily be the same. Due to their configuration, the compounds used according to the invention are capable of being oxidized to form a p-quinoid system which includes the substituents OR^7. An important function of the compounds used in the present invention, besides the oxidizability, is the hydrolysability in their non-oxidized form. Hydrolysis in the alkaline developer medium should proceed rather quickly to provide a rapid release of the photographically useful fragment. On the other hand the onset of hydrolysis should be delayed until the imagewise oxidation by the developer oxidation products or by developable silver halide has been substantially completed so that an imagewise transfer of the photographically useful fragment, for example of a diffusible dye can be obtained. Thus it is evident that the velocity of hydrolysis must be adapted suitably to the velocity of oxidation and this can easily be done by variation of those substituents having a strong influence on the hydrolysability. The hydrolysobility is strongly influenced by the nature of the connecting group Z apparently depending on its degree of electronegativity. Selection of a particular connecting group Z may also require varying other substituents and in particular R^1 and R^2 within the claimed range of substituents to have them co-operate with the connecting group Z in order to provide the desired degree of hydrolysability. When, for example, Z represents $—SO_2—$ at least one of R^1 and R^2 should be hydrogen and the other of R^1 and R^2 may be hydrogen or an optionally substituted alkyl or aralkyl group; when Z represents —S—, R^1 and R^2 additionally both may be alkyl and when Z represents $—NH—SO_2—$ it is preferred to have R^1 and R^2 both being hydrogen.

It should be noted that the colour producing compounds used according to the invention should not be diffusible through the layers of a photographic material when they are present as intact molecules. For this purpose they carry a residue which renders them diffusion resistant, for example in one of the substituents R^1 to R^5 or in a substituent present on the condensed benzene ring which is completed by R^5 together with R^4.

The colour providing compounds may be sufficiently resistant to diffusion even when the above mentioned substituents do not contain long alkyl residues, because the molecule of the dye residue may itself be sufficiently large even under these circumstances. In other cases, the colour providing compounds may be rendered sufficiently resistant to diffusion by providing them with sufficiently large residues.

Residues which confer diffusion resistance are residues which allow the compounds used according to the invention to be incorporated in a diffusion resistant form in the hydrophilic colloids normally used in photographic materials. Organic residues which generally carry straight or branched chain aliphatic groups and which may also carry carboxylic or heterocyclic or aromatic groups generally having from 8 to 20 carbon atoms are preferably used for this purpose. These residues are attached to the remainder of the molecule either directly or indirectly, e.g. through one of the following groups: —NHCO—; —$NHSO_2$—; —NR—, in which R represents hydrogen or alkyl; —O—; —S—; or —SO_2—. The residue which confers diffusion resistance may in addition carry groups which confer solubility in water, e.g. sulpho groups or carboxyl groups, and these may also be present in an anionic form. Since the diffusion properties depend on the molecular size of the compound as a whole, it is sufficient in some cases, for example when the molecule as a whole is large enough, to use shorter chain groups as "groups which confer diffusion resistance".

Examples of oxidizable compounds of formula I are the following:

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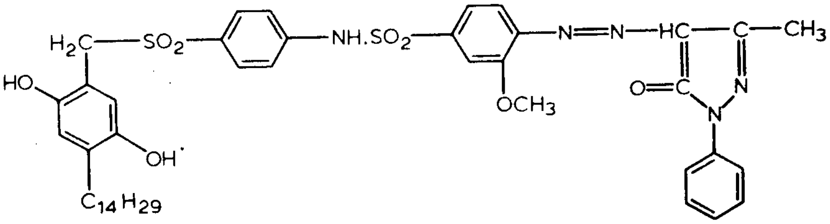

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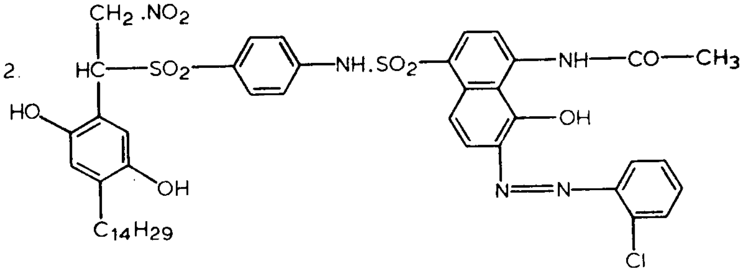

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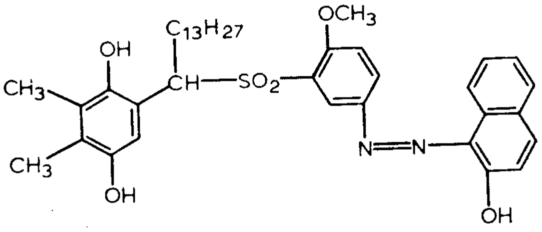

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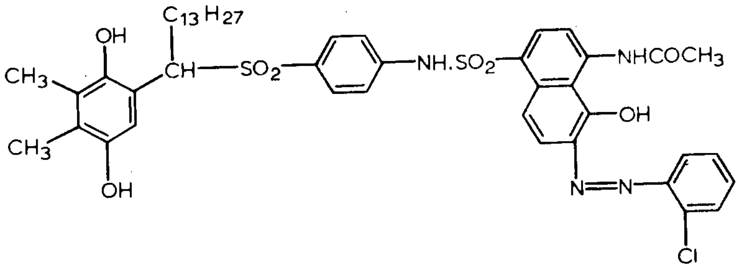

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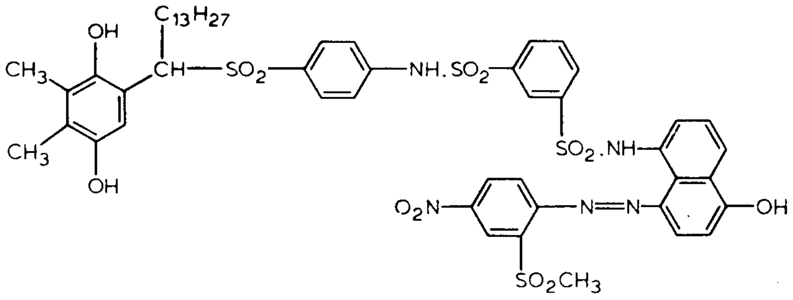

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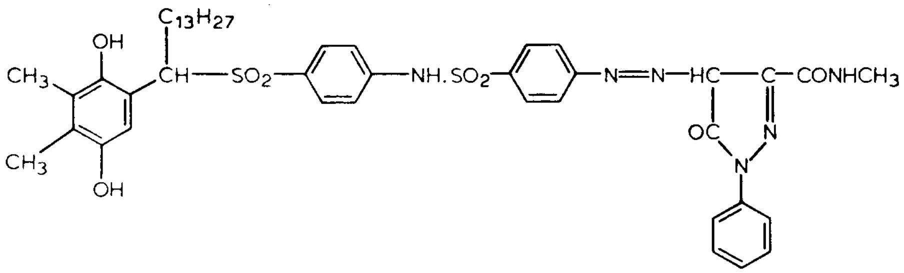

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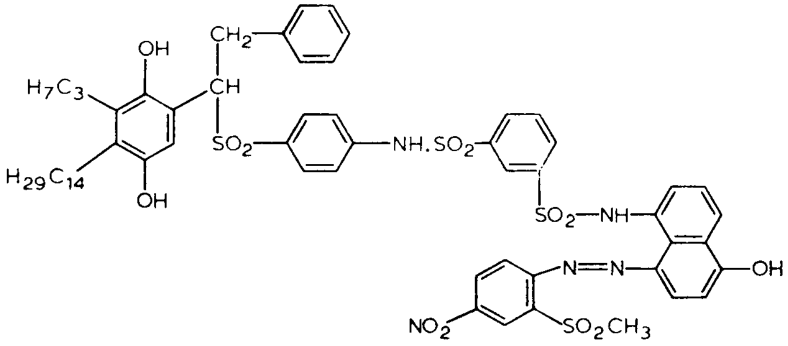

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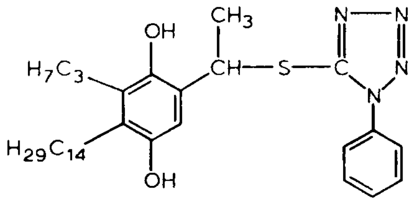

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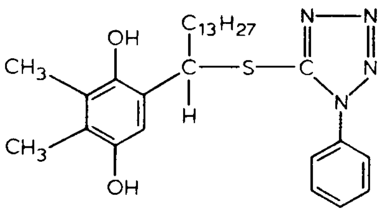

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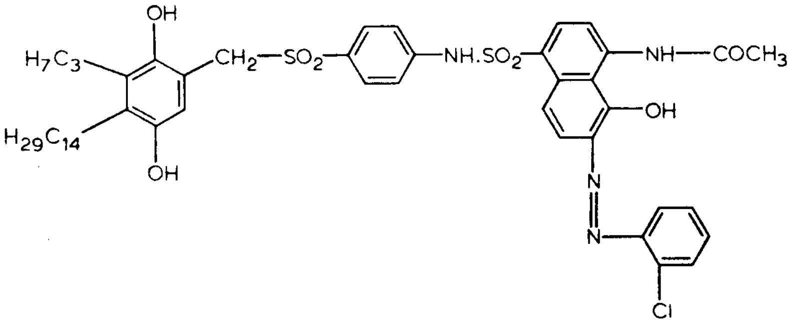

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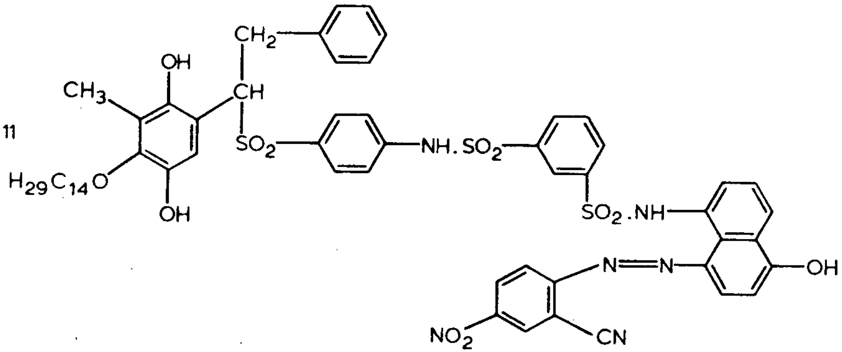

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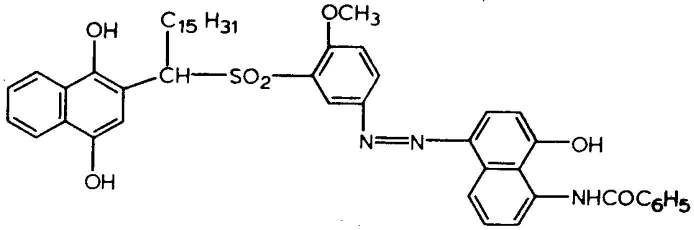

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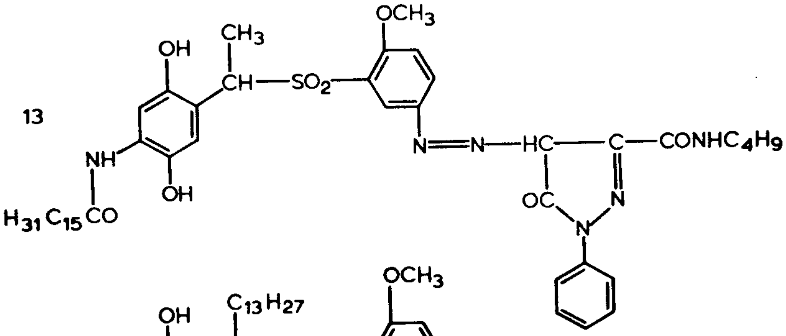

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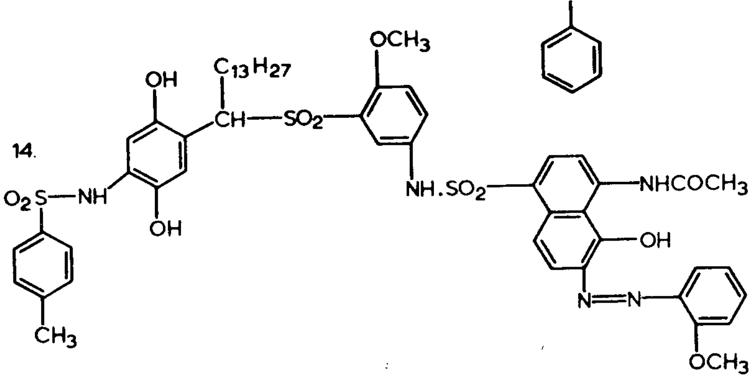


The preparation of some of the compounds listed above is described in the following. Others may be prepared using slightly modified procedures.

Compound No. 1

a) 2-Tetradecanoylhydroquinone may be prepared following a method described by Armstrong et al, J. Amer. Chem. Soc. *82*, 1928 (1960) for the case of 2-stearoylhydroquinone.

m.p. 101—103°C.

b) 2-Tetradecylhydroquinone

The carbonyl compound 1a was subjected to the Wolff-Kishner reduction: 64 g of 2-tetradecanoylhydroquinone was refluxed for two hours together with 30 g of hydrazine hydrate, 45 g of grinded KOH and 300 ml of triethyleneglycol. Thereafter the reflux condenser was replaced by a descinding cooler and the mixture was heated for four hours up to 195°C. When cool the mixture was poured into 800 ml of water and the suspension obtained was several times extracted with ether. The combined extracts were washed with water and evaporated. The residue crystallised from 250 ml of benzene.

Yield: 22 g m.p.: 108—109°C.

c) 2-Tetradecyl-5-formyl-hydroquinone

4.5 ml of titanium-IV-chloride were added at 5°C under a protective atmosphere of nitrogen to a suspension of 6.12 g of 1b in 120 ml of dichloromethane. 6.3 g of α,α-dichlorodimethylether were added without cooling. The obtained solution was stirred at 35°C until the evolution of hydrogen chloride was finished. The mixture was decomposed by the addition of some crushed ice and 120 ml of 5% hydrochloric acid and three times extracted with ether. The combined ether extracts were washed with 2% sodium carbonate solution and with water. The organic solution was dried with Na_2SO_4 and evaporated. The yellowish-brown residue was recrystallized from ligroin.

Yield: 3 g m.p. 66—69°C.

d) 2-Tetradecyl-5-hydroxymethyl-hydroquinone

A solution of 0.31 g of sodium borohydride in 2 ml of water were added with stirring at 40°C and under protective nitrogen to a solution of 2.45 g of the aldehyde 1 *c* in 30 ml of methanol. After 20 minutes the solution was poured out into 100 ml of 5% sulfuric acid. The precipitate formed was suction filtered and dried. Recrystallization was made from butyl chloride.

Yield: 1.95 g m.p. 106—108°C.

e) 4 - [4 - (1 - Phenyl - 3 - methyl - pyrazolone - (5) - yl - (4) - azo) - 3 - methoxy - benzenesulfonamido] - benzensulfinic Acid

4.07 g of 4 - (1 - phenyl - 3 - methyl - pyrazolone - (5) - yl - (4) - azo) - 3 - methoxy - benzenesulfochloride, 1.6 g of 4-aminobenzenesulfinic acid and 1.2 g of dimethylaniline were stirred in 6 ml of dimethylformamide for 3 hours at 20°C. The solution was poured out into 200 ml of 2 N hydrochloric acid. The dye was salted out as sulfinic acid.

Yield: 4 g.

f) Compound No. 1

A solution of 1.68 g of the carbinol compound 1 *d* in 90 ml of acetic acid was mixed with a solution of 2.64 g of the sulfinic acid 1 *e* and 0.56 g of sodium acetate in 25 ml of ethanol (80%). The mixture after addition of 0.2 ml of concentrated sulfuric acid was refluxed for 4 hours. The obtained solution was poured out into water and extracted with ethyl acetate. The combined extracts were washed with 5% sodium acetate solution and with water until the aqueous phase was colourless. After removal of the solvent by evaporation the residue was heated with a 1:1 mixture of butylchloride and ligroin. The residue crystallized on trituration with butyl chloride and was recrystallized from ethyl acetate.

Yield: 0.65 g m.p. 165—170°C.

Compound No. 3

a) 2,3-Dimethyl-5-tetradecanoyl-hydroquinone

A solution of 56 g 2,3-dimethylhydroquinone [Acta Pharm. Suecica *5*, 215 (1968)] and 147,5 g of myristic acid in 200 ml of dichloromethane was saturated at 35—40°C with boron trifluoride. After standing over night the solution was refluxed for 2 hours. The mixture was stirred into a solution of 113 g of sodium acetate in 1000 ml of water. After 30 minutes the layer of dichloromethane was separated and 2 times washed with 5% sodium carbonate. After removal of the organic solvent the residue was recrystallized from ligroin.

Yield: 80 g m.p. 101—102°C.

b) 2,3 - Dimethyl - 5 - α - hydroxytetradecyl - hydroquinone

6.4 g of sodium borohydride dissolved in 40 ml of water were added dropwise at 30°C with stirring to a solution of 70 g of the keto compound 3*a* in 600 ml of methanol. By cooling the temperature was kept below 30°C. After 30 minutes the mixture was diluted with 1 l of water and acidified with diluted sulfuric acid. The precipitate was taken up in ethylacetate and the organic layer was separated. After removal of the ethyl acetate the residue was purified by heating it with butyl chloride.

Yield: 60 g m.p. 132°C.

c) 2 - Methoxy - 5 - (β - hydroxynaphthylazo) - benzo - sulfinic Acid Sodium Salt

1.87 g of 2 - methoxy - 5 - amino - benzenesulfinic acid were dissolved in 18 ml of water together with 0.4 g of NaOH. After addition of 0.7 g of $NaNO_2$ and 15 g of ice 3 ml of concentrated hydrochloric acid were slowly added with stirring. The solution was stirred for another 15 minutes and then added dropwise slowly with stirring at 5—8°C to a solution of 1.44 g of β-naphthol and 2.5 of sodium carbonate in 30 ml of water. After stirring for one hour at 5—8°C the formed precipitate was suction filtered, washed with 10% sodium chloride solution and dried on clay.

Yield: 3.2 g.

d) Compound No. 3

1.75 g of the carbinol 3 *b* were dissolved in 60 ml of acetic acid at 60°C and a solution of 2 g of the dye sulfinate 3 *c* in 25 ml of water was added. The mixture was stirred at 50°C for 30 minutes and then cooled. The precipitate was separated from the solvent by decanting and taken up in ethyl acetatate. The concentrated ethyl acetate solution was washed with water several times and the compound No. 3 was precipitated by addition of ligroin.

Yield: 1.5 g m.p. 149—151°C.

Compound No. 4

a) 4 - [4 - Acetamido - 5 - hydroxy - 6 - (2 - chlorphenylazo) - naphthalene - (1) - sulphonamido]benzenesulfinic Acid

A mixture of 2.19 g of 4 - acetamido - 5 - hydroxy - 6 - (2 - chlorophenylazo) - naphthalene - (1) - sulfochloride, 0.79 g of 4-aminobenzenesulfinic acid and 0.6 g of dimethylaniline in 30 ml of dimethylformamide was stirred at 20°C for 2.5 hours and then stirred into 150 ml of 2 N hydrochloric acid. The precipitate was suction filtered, washed with diluted hydrochloric acid, pressed on clay and dried.

Yield: 2.4 g.

b) Compound No. 4

2.23 g of dye sulfinic acid 4 *a* were dissolved in 40 ml of 3 N acetic acid together with 0.5 g of anhydrous sodium acetate and mixed with a solution of 1.4 g of the carbinol 3 *b* in 50 ml of acetic acid. The mixture was stirred at 50°C for 1.5 hours. After cooling the precipitate was suction filtered, washed with acetic acid and dried. The raw material was then heated with 30 ml of ethyl acetate; undissolved was removed by filtration and the filtrate was concentrated. After standing for several hours the purple Compound No. 4 precipitated from the concentrated residue.

Yield: 0.9 g m.p. 167—170°C.

Compound No. 5

a) 4 - {3 - [5 - Hydroxy - 8 - (2 - methylsulfonyl - 4 - nitro - phenylazo) - naphthyl - (1) - aminosulfonyl] - benzenesulfonamido} - benzenesulfinic Acid

This compound was prepared similarly as compound 4 *a*. Instead of 2.19 g of 4 - acetamido - 5 - hydroxy - 6 - (2 - chlorophenylazo) - naphthalene - (1) - sulfochloride - 3.13 g of 3 - [5 - hydroxy - 8 - (2 - methylsulfonyl - 4 -

nitrophenylazo) - naphthyl - (1) - aminosulfonyl] - benzene sulfochloride were used.

Yield: 3.6 g.

b) Compound No. 5

This compound was prepared in an analogeous manner as compound No. 4. 3 g of dye sulfinic acid 5 *a* were used instead of 2.23 g of dye sulfinic acid 4 *a*. Yield: 0.95 g recrystallized from ethyl acetate/ligroin.

Compound No. 6

a) 4 - [4 - (1 - Phenyl - 3 - N - methylcarbamoyl - pyrazolon - (5) - yl - (4) - azobenzenesulfonamido] - benzene Sulfinic Acid

This compound was prepared similarly as sulfinic acid 4*a*. 2.1 g of 4 - (1 - phenyl - 3 - N - methylcarbamoyl - pyrazolone - (5) - yl - (4) - azo) - benzenesulfochloride were reacted with 0.79 g of 4-aminobenzene sulfinic acid.

b) Compound No. 6

This yellow dye was prepared in an analogous manner as compound 4, from 2.16 g of the dye sulfinic acid 6 *a* described above.

Yield: 0.93 g m.p. 128—131°C.

Compound No. 9

3.5 g of the carbinol 3 *b* described above and 1.9 of 1 - phenyl - 5 - mercaptotetrazole were dissolved in 100 ml of benzene. After the addition of 0.05 ml of concentrated sulfuric acid the solution was refluxed for 2 hours. The benzene solution was washed with water, dried and concentrated. The residue was taken up in butyl chloride filtered from unreacted 1 - phenyl - 5 - mercaptotetrazole and then purified by column-chromatography (stationary phase; silicagel; solvent mixture: benzene/ethylacetate 40:1).

Yield: 1.95 g oily (no m.p.).

The main aspect of the present invention is the case in which the oxidizable compound is a colour providing compound that is where the photographically useful fragment is a diffusible dye. This is the reason why, in the following, mainly reference is made to colour providing compounds. The invention, however, is not at all limited to this aspect and it should be kept in mind that for various other purposes other photographically useful fragment may be present in the oxidizable compounds instead of the dyes or dye precursors.

The colour providing compounds used according to the invention are incorporated in the casting solutions for the layers of photographic material by one of the usual methods. The quantity of colour providing compound used per litre of casting solution varies within relatively wide limits, and the most suitable concentration can be found with the aid of simple tests. For example, from 5 to 80 g, preferably from 20 to 40 g, of colour providing compound may be used per litre of casting solution. The association between diffusion resistant, colour providing compound and silver halide necessary for achieving the desired effect can be obtained, for example, by making use of the known emulsification processes. Processes of this kind have been described, for example, in British Patent Specifications Nos. 791,219; 1,099,415; 1,099,416 and 1,099,417. It is also possible to prepare aqueous dispersions of the colour providing compounds may be incorporated in the layers by one of the known emulsification processes. Processes of this kind have been described, for example, in British Patent Specifications Nos. 791,219 and 1,099,414 to 1,099,417. It is also possible to prepare aqueous dispersions of the colour providing compound and add them to the given casting solutions. In that case, aqueous slurries of the colour providing compound are finely milled, for example by intensive stirring with the addition of sharp edged sand or by using ultrasound. According to another method, it may be desired to incorporate the colour providing compounds in the layer in the form of so-called micro-capsules together with silver halide and optionally also developer substances. In that case, two or more differently sensitized light-sensitive silver halide emulsions and the appropriate diffusion resistant compounds may be combined in a single layer in the form of so-called mixed grain emulsions, for example as described in U.S. Patent No. 2,698,794. Methods of incorporation in which a compound is incorporated into a hydrophilic binder from an alkaline aqueous solution, however, are less preferred. As the compounds are hydrolysable under the alkaline development conditions and as this hydrolysability is a necessary feature of the compounds used in the invention, care should be taken that no premature hydrolysis will occur during the incorporation.

The non-diffusible, colour providing compounds may be accommodated in a light-sensitive layer or in a layer adjacent thereto. A compound which releases a cyan dye, for example, is associated with the red sensitive layer, a compound releasing a magenta dye with the green sensitive layer and a compound releasing a yellow dye with the blue sensitive layer.

By "association" and "associated" is meant that the silver halide emulsion and the colour providing compound are so arranged in relation to each other that they are capable of interacting with each other to produce an imagewise correspondence between the silver image formed and the imagewise distribution of oxidized, non-diffusible colour providing compound.

The associated colour providing compound is preferably incorporated in the silver halide emulsion itself or in a layer adjacent to the silver halide emulsion layer, this adjacent layer being preferably situated behind, viewed in the direction of incident light during exposure, the silver halide emulsion layer. The colour providing compounds used according to the invention are oxidized imagewise by developer oxidation products during development of the silver image; the non-oxidized portions of these compounds then undergo a splitting reaction under the influence of the developer alkali or activator alkali to release the dye residues in a diffusible form. The usual photographic silver halide developers are suitable for development, provided that they are capable, when in their oxidized form, of oxidizing the colour providing compounds used according to the invention.

The following are examples of suitable developers:
Hydroquinone,
aminophenols e.g.,
N-methylaminophenol,
1-phenyl-3-pyrazolidone,
1-phenyl-4,4-dimethyl-3-pyrazolidone,
1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone
1-phenyl-4,4-bis-hydroxymethyl-3-pyrazolidone,
N,N-diethyl-p-phenylenediamine,
N-ethyl-N-hydroxyethyl-p-phenylenediamine,
3-methyl-N,N-diethyl-p-phenylenediamine,
N,N,N',N'-tetraalkyl-p-phenylenediamine such as tetramethyl-p-phenylenediamine, triethylsulphobutyl-p-phenylenediamine, 1,4-bis-pyrrolidinobenzene, and reductones.

It should be particularly noted that the choice of developer substances in the process according to the invention is not restricted to colour developers but that the usual black-and-white developers may advantageously also be used. This is to be seen as an advantage in view of the lower tendency of the latter to discoloration.

The developers may be contained in the layers of the photographic material, in which they are activated by the alkaline activator liquid, or they may be contained in the alkaline processing liquid or paste. Since some of the colour providing compounds used according to the invention have developer properties, the use of auxiliary developer compounds may in some cases be dispensed with. In such cases, the colour providing compound is directly oxidized by the developable silver halide.

Since the imagewise distribution of the diffusible dye released during development corresponds to the imagewise distribution of undeveloped silver halide, the production of positive coloured transfer images does not require the use of direct positive silver halide emulsions or the application of suitable reversal process, but can be achieved with the usual negative emulsions.

The emulsions may be chemically sensitized, for example by the addition of sulphur compounds such as allyl isothiocyanate, allylthiourea or sodium thiosulphate during chemical ripening. Reducing agents may also be used as chemical sensitizers, for example the tin compounds described in Belgian Patent Specifications Nos. 493,464 and 568,687; polyamines such as diethylene triamine or aminomethanesulphinic acid derivatives, for example, according to Belgian Patent Specification No. 547,323.

Noble metals such as gold, platinum, palladium, iridium, ruthenium and rhodium and compounds of these metals are also suitable chemical sensitizers. This method of chemical sensitization has been described in the article by R. Koslowsky, Z. Wiss. Phot. 46, 65—72 (1951).

The emulsions may also be sensitized with polyalkylene oxide derivatives, e.g. with a polyethylene oxide having a molecular weight of between 1000 and 20,000, or with condensation products of alkylene oxides and aliphatic alcohols, glycols, cyclic dehydration productions of hexitols, alkylsubstituted phenols, aliphatic carboxylic acids, aliphatic amines, aliphatic diamines and amides. The condensation products should have a molecular weight of at least 700, preferably more than 1000. These sensitizers may, of course, be used in combination to achieve special effects, as described in Belgian Patent Specification No. 537,278 and in British Patent Specification No. 727,982.

The emulsions may also be spectrally sensitized, e.g. with the usual monomethine or polymethine dyes such as acid or basic cyanines, hemicyanines, streptocyanines, merocyanines, oxonoles, hemioxonoles or styrol dyes as well as trinuclear or higher nuclear methine dyes, for example rhodacyanines or neocyanines. Sensitizers of this kind have been described, for example, in the work by F. M. Hamer "The Cyanine Dyes and Related Compounds" (1964) Interscience Publishers, John Wiley and Sons, New York.

The emulsions may contain the usual stabilizers, e.g. homopolar compounds or salt compounds of mercury having aromatic or heterocyclic rings, such as mercaptotriazoles, or simple mercury salts, sulphonium mercury double salts and other mercury compounds. Azaindenes are also suitable stabilizers, particularly tetra- and penta-azaindenes and especially those which are substituted with hydroxyl or amino groups. Compounds of this type have been described in the article by Birr, Z. Wiss. Phot. 47, 2—27 (1952). Other suitable stabilizers include heterocyclic mercapto compounds, e.g. phenyl mercapto tetrazole, quaternary benzothiazole derivatives and benzotriazoles.

The binder used for the photographic layers is preferably gelatine although this may be partly or completely replaced by other natural or synthetic binders. Examples of natural binders include alginic acid and its derivatives such as its salts, esters or amides, cellulose derivatives such as carboxymethylcellulose, alkylcelluloses such as hydroxyethylcellulose, starch or its derivatives such as ethers or esters, or carrageenates. Polyvinyl alcohols, partially saponified polyvinyl acetate and polyvinyl pyrrolidone are examples of suitable synthetic binders.

The layers may be hardened in the usual manner, for example with formaldehyde or halogen substituted aldehydes containing a carboxyl group, such as mucobromic acid, diketones, methane sulphonic acid esters or dialdehydes.

Where the process according to the invention is a dye diffusion transfer process, the light-sensitive element used for carrying out the process invention contains one or more silver halide emulsion layers and non-diffusible colour providing compounds associated therewith, and an image receiving element in which the desired colour image is produced by the diffusible dyes which are transferred to it imagewise. To effect this transfer, firm contact must be established between the light-sensitive element and the image receiving element at least for a finite period of time during development so that the imagewise distribution of diffusible dyes produced in the light-sensitive element as a result of development can be transferred to the image receiving element. This contact may be established either after development has begun or even before development. The latter method may be employed, for example, in cases where the light-sensitive element and the image receiving element in the material used for carrying out the dye diffusion transfer process form an integral unit, hereinafter referred to as monosheet material, which is preserved even after completion of the development process, i.e. the light-sensitive element is not separated from the image receiving element even after colour transfer. Such an arrangement has been described, for example, in German Offenlegungsschrift No. 2,019,430.

A monosheet material suitable for carrying out the process according to the present invention where this is a dye diffusion transfer process may comprise, for example, the following layer elements:

1) a transparent substrate,
2) an image receiving layer,
3) a light impervious layer,
4) a light-sensitive element having at least one light-sensitive silver halide emulsion layer and at least one non-diffusible colour providing compound associated with this layer,
5) a retarding layer,
6) an acid polymer layer,
7) a transparent substrate.

The elements of the monosheet material may be so arranged that two different parts are prepared separately from each other, namely the light-sensitive part (layer elements 1 to 4) and the cover sheet (layer elements 5 to 7), these two parts being then placed together with their active surfaces in contact and bonded together, optionally with the interposition of spacer strips so that a space is left between the two parts for an accurately calculated quantity of processing liquid. The layer elements 5 and 6, which together form the neutralisation system, may also be arranged additionally or alternatively between the substrate and the image receiving layer of the light-sensitive part, but in this case their sequence would be reversed.

Means may be provided for introducing a processing liquid between the light-sensitive part and the cover sheet, for example in the form of a breakable container arranged at the side of the material so that it pours out its contents between two adjacent layers of the monosheet material when subjected to mechanical forces.

An essential part of the photographic material according to the present invention is the light-sensitive element which, in the case of a single dye transfer process, contains a light-sensitive silver halide emulsion layer and a non-diffusible colour providing compound associated therewith. This non-diffusible compound may be situated in a layer adjacent to the silver halide emulsion layer or in the silver halide emulsion layer itself. In the latter case, the colour of the image dye is preferably chosen so that the predominant absorption range of the colour providing compound does not correspond to the predominant sensitivity range of the silver halide emulsion layer.

To produce multicoloured transfer images in true-to-life colours, the light-sensitive element contains three such associations of colour providing compound with light-sensitive silver halide emulsion layer, and the absorption range of the colour providing compound in general substantially corresponds to the range of spectral sensitivity of the associated silver halide emulsion layer. In that case, in order to obtain the highest possible sensitivity it is necessary that the colour providing combination should be arranged in a separate layer of binder behind, viewed in the direction of incident light during exposure, the silver halide emulsion layer.

The action of the developer oxidation products produced by development of the silver halide emulsion must, of course be restricted to the associated colour providing compounds. Separating layers are therefore generally provided in the light-sensitive element to prevent diffusion of the developer oxidation products into other layers with which they are not associated.

These separating layers may, for example contain suitable substances which react with the developer oxidation products, for example, non-diffusible hydroquinone derivatives or, if the developer is a colour developer substance, non-diffusible colour couplers. In a preferred arrangement, therefore, the light-sensitive element has the following arrangement of components (from below upwards):

blue sensitive silver halide emulsion layer,
layer containing non-diffusible compound which releases a diffusible yellow dye,
separating layer,
green sensitized silver halide emulsion layer,
layer containing non-diffusible compound which releases a diffusible magenta dye,
separating layer,
red-sensitized silver halide emulsion layer,
layer containing non-diffusible compound which releases a diffusible cyan dye.

The silver halide emulsion layers may, of course, also be arranged in a different sequence, but in that case the associated layers must also be interchanged with the colour producing system so that the association is preserved.

The light impervious layer arranged under the light-sensitive element is permeable to aqueous alkaline treatment solutions and hence to diffusible dyes. It has two main functions: first, it serves to cover the image silver left in the originally light-sensitive element after development as well as the colour producing compounds left behind as colour negative so that when the photographic material is viewed through the transparent support layer of the light-sensitive part, only the positive transfer image is visible; second, it provides a lightproof cover for the light-sensitive element on the side facing the image receiving layer, from the bottom. The latter is particularly important in cases where the monosheet material is brought into contact with the alkaline processing mass while still in the camera after exposure and is then to be pulled out of the camera to be developed outside.

Layers which are sufficiently impervious to light but sufficiently permeable to diffusible dyes may be prepared, for example, from suspensions of inorganic or organic dark pigments, preferably black pigments, for example suspensions of carbon black, in suitable binders, e.g. in gelatine solutions. To ensure adequate exclusion of light during development, it is generally sufficient to use layers from 0.5 to 2 μ in thickness containing from 10 to 90% by weight (based on the total dry weight) of carbon black in gelatine. The particle size of the pigment used is relatively uncritical, provided that it is not substantially above 0.5 μ.

In addition to the black pigment layer, the light impervious layer preferably also includes a white pigment layer arranged underneath it. The purpose of this white pigment layer is to cover the black layer and provide a white background for the image. Any white pigments are suitable for this layer, provided that it is not necessary to use unduly thick layers to obtain the necessary covering power. Examples of such pigments include barium sulphate, oxides of zinc, titanium, silicon, aluminium and zirconium, barium stearate and kaolin. The white pigment preferably used is titanium dioxide. The same conditions apply with regard to the binder, concentration and particle size as for the black pigments. The thickness of the white pigment layer may be varied according to the desired degree of whiteness of the background. Thicknesses of between 5 and 20 μ are preferred.

Instead of containing a light impervious layer, the monosheet material according to the present invention may contain means for producing such a layer between the light-sensitive element and the image receiving layer, for example in the form of a container for a liquid containing a clouding agent (pigment) arranged at the side of the monosheet material so that it releases its contents between the above mentioned layers when exposed to mechanical forces to form such pigment layer between them.

The image receiving layer consists basically of a binder containing dye mordants for fixing the diffusible dyes.

The mordants used for acid dyes are preferably long chain quaternary ammonium or phosphonium compounds or ternary sulphonium compounds, e.g. those described in U.S. Patent Specifications Nos. 3,271,147 and 3,271,148. Certain metal salts and their hydroxides which react with acid dyes to form sparingly soluble compounds may also be used. The dye mordants are dispersed in the receiving layer in one of the usual hydrophilic binders, e.g. in gelatine, polyvinyl pyrrolidone or partially or completely hydrolysed cellulose esters. Some binders may, of course, themselves function as mordants, e.g. copolymers or polymer mixtures of vinyl alcohol and N-vinylpyrrolidone, for example as described in German Auslegeschrift No. 1,130,284, or binders which consist of polymers of quaternary nitrogen bases, e.g. polymers of N-methyl-2-vinylpyridine, for example, as described in U.S. Patent Specification No. 2,484,430. Guanyl hydrazone derivatives of acyl styrene polymers such as those described in German Offenlegungsschrift No. 2,009,498, for example, are also binders which function as mordants. However, the last mentioned mordanting binders would generally be used in combination with other binders, e.g. gelatine.

The usual transparent support materials used in photographic practice may be used as transparent substrates for the monosheet material according to the invention, e.g. films of cellulose esters, polyethylene terephthalate, polycarbonates or other film forming polymers. The alkaline processing substance adjusts the light sensitive material to a relatively high pH (about 11 to 14) which releases development and imagewise dye diffusion. It has been found that the dyes, and hence the images obtained, are not particularly stable at such high pH values. It is therefore necessary to adjust the material to almost neutral or slightly acid after development has been completed. This can be achieved in known manner by providing the material with an additional acid polymer layer which becomes accessible to the alkaline processing substance only gradually during development. By "acid polymer layer" is meant a layer of binder containing polymeric compounds which have acid groups, preferably sulpho or carboxyl groups. These acid groups react with the cations of the processing substance to form salts, thereby lowering the pH of the substance. The polymer compounds and hence the acid groups are, of course, incorporated in a diffusion resistant form in the said layer.

The acid polymers are in many cases derivatives of cellulose or derivatives of polyvinyl compounds, but other polymer compounds may also be used. The following are mentioned as examples of suitable acid polymers: Cellulose derivatives having a free carboxyl group, e.g. cellulose dicarboxylic acid semiesters with a free carboxyl group, such as cellulose acetate hydrogen phthalate, cellulose acetate hydrogen glutarate, ethyl cellulose acetate hydrogen succinate, cellulose acetate hydrogen succinate hydrogen phthalate, ethers and esters of cellulose which have been modified with other dicarboxylic acid anhydrides or with sulphonic acid anhydrides, for example with o-sulphobenzoic acid anhydride; carboxymethylcellulose; polystyrene sulphonic acid; polyvinylhydrogenphthalate, polyvinylacetatehydrogenphthalate; polyacrylic acid; acetals of polyvinyl alcohol with aldehydes which are substituted with carboxyl or sulpho groups, such as o-, m- or p-benzaldehyde sulphonic or carboxylic acid; partially esterified ethylene/maleic acid anhydride copolymers and partially esterified methyl vinyl ether/maleic acid anhydride copolymers.

The acid polymer layer must contain sufficient acid groups to lower the pH of the processing substance from an initial value of 11 to 14 so that the material will finally be almost neutral or slightly acid (pH 5 to 8).

The time delay in lowering of the pH is achieved in known manner by coating the acid polymer layer with a so-called retarding layer. This retarding layer is an alkali impermeable layer preferably consisting of a polymer which is inert to alkalies, for example a polyvinyl alcohol or a partially acetalised polyvinyl alcohol.

The amount of delay in lowering of the pH can be adjusted as desired by suitable choice of the thickness and composition of this retarding layer.

A barrier layer containing polymers having a new type of permeability behaviour has been described, for example, in German Offenlegungsschrift No. 2,455,762.

Neutralisation systems, that is to say, combinations of an acid polymer layer and a retarding layer, have been described, for example in German Patent Specification No. 1,285,310. Layer combinations of this type may be provided in the material according to the invention, for example in the light-sensitive part, between the transparent substrate and the image receiving layer.

Another possible arrangement consists of placing the neutralisation system of acid polymer layer and retarding layer on the cover sheet. The two layers must, of course, be arranged in a sequence such that the alkali of the processing substance must penetrate the retarding layer before it can reach the acid polymer layer.

The dye diffusion transfer process according to the invention may advantageously be carried out in or with a suitable self-developer camera. This camera may be provided for example, with devices which make it possible for a solution to be distributed between the light-sensitive element and the cover sheet after exposure of the light-sensitive element, this solution serving to shield the light-sensitive material against light from the top. A camera of this kind is preferably equipped with a pair of squeezing rollers between which the monosheet material is pulled out so that the containers arranged at the side of the monosheet material are split open in their passage between the rollers and release their contents between the layers of the monosheet material.

Since the light-sensitive element is protected against unwanted exposure on both sides by light impervious layers after it has passed between the squeezing rollers, the exposed material may be pulled out of the camera as soon as development has been started.

To process the monosheet material after it has been exposed imagewise, the light-sensitive element is brought into contact with the aqueous alkaline processing solution. The silver halide emulsion layers which have been exposed imagewise are thereby developed in the presence of the developer compound, and an imagewise distribution of oxidation products of the developer compound is obtained in correspondence with the silver image produced by development, the said oxidation products of the developer compound oxidizing the associated colour providing compound, whereupon the non-oxidized colour providing compound, which is also distributed imagewise, releases the diffusible dye under the action of the alkali of the activator or developer.

The aqueous alkaline processing solution may contain viscosity increasing additives, e.g. hydroxyethylcellulose. It may also contain the usual development accelerators, stabilizers, silver salt solvent, fogging agents or antioxidants and other additives.

The invention has been described above with reference to examples in which the photographically useful fragment is a diffusible dye or a diffusible dye precursor. Other arrangements are, however, also possible, for example one in which the photographically active group is an antifogging agent, a development inhibitor, a hardener, a developer or a substance which accelerates development. In all these cases, the photographically active group is released imagewise, i.e. in correspondence with the imagewise distribution of undeveloped silver halide if negative emulsions are used. This provides numerous possibilities of producing images.

Working Example 1

On a transparent support of cellulose triacetate a mordanting layer, a light reflecting layer and a light-sensitive silver halide emulsion layer are applied in that order. The layers are cast as follows:

Mordanting Layer

3.75 g of a copolymer of 1 part of styrene and 1 part of maleic acid imide of N,N - dimethyl - N - hexadecyl - N - ω - aminopropylammonium bromide were dissolved in 15 ml of ethanol and this solution was homogeneously dispersed in 75 ml of 5% aqueous gelatin solution. After addition of 2.6 ml of 5% aqueous saponin solution and 1 ml of 2% aqueous solution of mucochloric acid the casting viscosity (about 11 cps) was adjusted and the solution was dip-coated onto the transparent cellulose triacetate foil at 40°C with a velocity of 5 m/min.

Light-Reflecting Layer

A slurry made from 42 g of TiO_2 in 20 ml of water was dispersed in 150 ml of a 8% aqueous gelatin solution with the addition of 5 ml of 5% aqueous solution of sodium dodecylbenzenesulfonate and 5 ml of 5% aqueous saponin solution.

After the addition of 1 ml of a 2% aqueous solution of mucochloric acid the dispersion was adjusted to a viscosity of about 13 cps at 40°C and dip-coated onto the dried mordanting layer with a casting velocity of about 5 m/min.

Silver Halide Emulsion Layer

1 mmol of each of the oxidizable compounds mentioned in the following table were dissolved in 5 ml of ethyl acetate and homogeneously dispersed in 25 ml of a 5% aqueous gelatin solution with the addition of 5 ml of 5% aqueous solution of sodium dodecylbenzenesulfonate. After further addition of 50 ml of 5% gelatin solution and 1 ml of 2% aqueous solution of mucochloric acid the dispersion obtained was mixed with 18 g of a ready-to-cast silver halide emulsion. The silver halide emulsion had been prepared from 74 g of $AgNO_3$ per kg of emulsion; the ratio of gelatin to silver was 1.1:1 and the halide was bromide with 0.67 mol % of iodide. The resulting mixture was dip-coated at 40°C with a velocity of 5 m/min onto the dried light reflecting layer.

The several samples were exposed to light behind a gray step wedge on the side of the light sensitive layer, then developed for 4 minutes at 18°C in a developer composition described hereinafter, rinsed and dried.

Developed Composition

1.5 g of ethylene diaminotetraacetic acid-sodium salt,
11.5 g of borax,
1.0 g of sodium hexametaphosphate,
2.0 g of 1-phenyl-3-pyrazolidinone,
3.0 g of KBr,
made up to 1000 ml with water and adjusted with 1 N NaOH to pH 12.5.

Fully developed step wedges were obtained from each of the samples providing a coloured positive which can be viewed through the transparent support. The colour densities (D_{min} and D_{max}) have been measured behind coloured filters in a reflection densitometer and are shown in the following table.

TABLE 1

Compound No.	Colour Density					
	cyan		magenta		yellow	
	D_{min}	D_{max}	D_{min}	D_{max}	D_{min}	D_{max}
1	—	—	—	—	0.18	0.47
3	—	—	0.52	1.17	0.52	1.29
4	—	—	0.57	1.45	—	—
5	0.7	1.8	—	—	—	—
6					0.23	0.74

Working Example 2

A light-sensitive silver halide emulsion layer as described in Example 1 was cast on a transparent cellulose triacetate support layer.

In a first sample the light sensitive layer contained (instead of the compounds indicated in Example 1) 1 mmol of the carbinol compound 3 *b*.

In a second sample the light-sensitive layer contained additionally to said carbinol compound 3 *b* 0.2 mmol of compound No. 9.

After processing as described in Example 1 the following densities (D_{min} and D_{max}) were obtained.

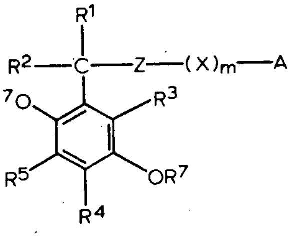
TABLE 2

	D_{min}	D_{max}
sample 1	0.55	1.38
sample 2	0.33	1.36

It is seen that compound 3 *b* produces a heavy fog which is considerably decreased by compound No. 9 in the region of low exposure (D_{min}) whereas in the region of high exposure (D_{max}) the density was not reduced by the presence of compound No. 9. This shows that development inhibitor is released from compound No. 9 substantially only from its non-oxidized form.

WHAT WE CLAIM IS:—

1. A photographic process in which a photographic material having at least one light-sensitive silver halide emulsion layer, and, in association therewith, a non-diffusible oxidizable compound of formula



in which

A either alone or together with the connecting members X (when present) and Z represents the residue of a photographically useful fragment;

X represents a bivalent linking member having the formula —R—$(L)_p$—$(R)_q$— in which R represents an alkylene group or a substituted or unsubstituted arylene or aralkylene group, and the two groups R may be the same or different;

L represents —O—, —CO—, —CONR^6—, —NR^{6}CO—, —SO$_2$—NR^6—, —NR^6—SO$_2$—, —O—CO—NR^6—, —NR^6—CO—O—, —S—, —SO—, or —SO$_2$— in which R^6 represents hydrogen or an alkyl group;

p=0 or 1;

q=0 or 1, provided that q=1 when p=1;

Z represents a bivalent connecting group which is electronegative with respect to the carbon atom shown;

R^1 and R^2 which may be the same or different represent hydrogen or a substituted or unsubstituted hydrocarbon group;

R^3, R^4 and R^5 which may be the same or different represent hydrogen, halogen, alkyl, alkoxy or acylamino in which the acyl group is derived from an aliphatic or aromatic carboxylic or sulphonic acid, or R^5, together with R^4, may represent the residue required to complete a condensed, substituted or unsubstituted benzene ring;

R^7 represents hydrogen or a photographically inert group which is capable of being hydrolysed under alkaline development conditions;

$m=0$ or 1;

at least one of the substituents R^1, R^2, R^3, R^4 and R^5 containing a residue which confers diffusion resistance, which compound, in its non-oxidized form, is subject to a splitting reaction under the conditions of alkaline development to release the photographically useful fragment including the connecting member $—Z—(X)_m—$ and which, in its oxidized form, is not subject to the said splitting reaction or only to a much less extent than in the non-oxidized form, is exposed imagewise and developed with a silver halide developer, which silver halide developer, in its oxidized form, oxidizes the non-diffusable oxidizable compound, thereby converting it into a form in which it cannot be split by alkali, or only to a slight extent, while a diffusible photographically useful fragment is released from the imagewise distribution of non-oxidized oxidizable compound as a result of being split by alkali.

2. A process as claimed in Claim 1 in which the photographically useful fragment is the residue of a diffusible dye or dye precursor and the diffusible dye or dye precursor released from the non-oxidised oxidizable compound is transferred to an image receiving layer.

3. A process as claimed in Claim 1 or Claim 2 in which R represents an alkylene group having from 1 to 6 carbon atoms.

4. A process as claimed in Claim 1 or Claim 2 in which R represents a phenylene group which may be substituted by alkyl, alkoxy, halogen, acylamino, acyl or alkoxy carbonyl.

5. A process as claimed in any one of Claims 1 to 4 in which Z represents an $—SO_2—$; —S—; —O— or $—NH—SO_2—$ group.

6. A process as claimed in any of Claims 1 to 5 in which R^1 and/or R^2 represents a substituted or unsubstituted alkyl group which has from 1 to 18 carbon atoms.

7. A process as claimed in Claim 6 in which R^1 and/or R^2 represents a methyl, ethyl, n-hexyl, n-octyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl or n-heptadecyl group.

8. A process as claimed in any of Claims 1 to 7 in which R^1 and/or R^2 represents a benzyl group.

9. A process as claimed in any of Claims 1 to 8 in which R^3, R^4 and/or R^5 represents chlorine or bromine.

10. A process as claimed in any of Claims 1 to 8 in which R^3, R^4 and/or R^5 represents an alkyl or alkoxy group having up to 18 carbon atoms.

11. A process as claimed in any of Claims 1 to 10 in which Z represents $—SO_2—$, R^1 represents hydrogen and R^2 represents hydrogen, alkyl or benzyl.

12. A process as claimed in any of Claims 1 to 11 in which the non-diffusible oxidizable compound is a compound of any of the formulae 1 to 16 as hereinbefore defined.

13. A process as claimed in any of Claims 2 to 12 in which a colour providing compound is incorporated in the casting solution for the layer at a concentration of from 5 to 80 g per litre of casting solution.

14. A process as claimed in Claim 13 in which the colour providing compound is incorporated at a concentration of from 20 to 40 g per litre of casting solution.

15. A process as claimed in Claim 1 substantially as herein described.

16. A coloured image which has been produced by a process as claimed in any of Claims 2 to 15.

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