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(54) A silver halide photographic colour material comprising a specific intermediate layer

(57) This invention provides a silver halide colour photographic material comprising at least three emulsion layers and at least one intermediate layer situated between two of the emulsion layers, wherein this intermediate layer comprises both a colourless coupling compound, containing a pyrazole ring in its chemical structure and a scavenger for oxidized developer, being a diffusion-resistant hydroxybenzene derivative. A method for producing a multi-colour filter for use in LCDs, using a colour photographic material according to this invention, is also provided.

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Description

1. Field of the Invention

This invention relates to a silver halide colour photographic material. In particular this invention relates to such a material suitable for use in the production of a multicolour filter array element that can be used in LCD's (Liquid Crystal Displays). A method for producing such a filter array element is also disclosed.

2. Background of the Invention

The production of multicolour masks for LCD's on the basis of a silver halide colour photographic print material has been described in several documents.

In JP-A 62-063901 it is disclosed that a multicolour mask (a colour filter) for LCD's, being water resistant and with light stable colours could be formed in a silver halide colour material comprising additional layers comprising UV absorbers and comprising a water repellent protective layer.

In JP-A 63/261361 it is disclosed to use a photographic material comprising two different colour couplers, forming dyes with different hues, in one emulsion layer. By doing so the fidelity of colour rendition can better be controlled.

EP-A 396 824 relates to a process for the production of a multicolour liquid crystal display device comprising a liquid crystal layer essentially consisting of nematic crystals in twisted or supertwisted configuration or smectic C (chiral smectic) ferroelectric liquid crystals wherein the liquid crystal molecules are aligned in such a way that said layer shows an electrically controllable rotation of the polarization plane of the light incident on the display. Said liquid crystal layer together with a multicolour filter element is arranged between front and rear transparent electrodes for altering pixelwise the electric field over the liquid crystal layer and said electrodes are associated respectively with a front and rear light polarizer element. Said process comprises in consecutive order the steps of :

(1) providing a photographic print material that contains on a glass support a plurality of differently spectrally sensitive silver halide emulsion layers,
(2) subjecting said print material to a single step multicolour pixelwise exposure,
(3) colour processing said exposed print material producing thereby in each silver halide emulsion layer a differently coloured pixel pattern,
(4) coating said colour processed print material at its silver halide emulsion layer assemblage side with a hydrophobic water-impermeable organic resin layer, and
(5) depositing by vacuum-coating one of said electrodes on said organic resin layer serving as a covering layer for said silver halide emulsion layer assemblage.

So, before introducing said multicolour filter in the liquid crystal device the uppermost emulsion layer of the thus processed photographic print material is coated with a hydrophobic water-impermeable organic resin to form a covering layer of said resin thereon, and by vacuum-deposition on top of the thus-applied resin coating a transparent electrically conducting (electrode) layer is formed. Said resin layer on top of the colour filter array provides a good planarity and prevents the release of volatile substances from the emulsion layer during vacuum-deposition, e.g. by sputtering, of the transparent conducting layer. Usually a bake at temperatures of 150 °C to 220 °C is needed to impart by curing a good impermeability to the resin layer. Therefore it is necessary that the processed photographic material can withstand these temperatures, without yellowing, discolouration etc.

In the disclosures above, the silver halide emulsion layers that are exemplified comprise gelatin and colour coupler in a weight ratio between 0.90 and 2.15, depending on the disclosure and the type of colour coupler present.

In EP-A 615 161 it is disclosed that the heat stability of a processed print material, as exemplified in EP-A 396 824, was not sufficient. It was shown that the heat stability of, especially, the cyan colour could largely be increased by coating the cyan forming layer (the red sensitive layer) most remote from the support. It was also shown in EP-A 615 161 that the heat stability could still further be increased when not only the cyan forming (red sensitive) layer was coated most remote from the support, but when the gelatin to coupler ratio of all three the layers was largely increased. Exemplified values of said ratio range from 3.30 to 5.28, depending on the type of colour coupler.

The high gelatin/coupler ratio however gives rise to problems in sharpness, in diminishing of maximal density for a given amount of colour coupler, etc. In the production of multicolour filter array elements for use in flat LCD's (Liquid Crystal Displays) the need for thinner layers is very stringent, not only because of the possibility to overcome the problems cited above with thicker layers, but also because it is easier to apply high quality flawless additional layers, e.g., passivation layers, conducting layers, etc, on a thinner multicolour filter array. Therefore the need for silver halide colour print materials, useful in the production of colour masks for LCD's, with low gelatin/coupler ratio and high thermal stability are still needed.

In print materials for the production of colour masks for LCD's it is also of utmost importance that the colour deterioration is avoided. Colour deterioration means that the colour separation between the layers carrying a yellow, magenta and cyan image respectively is bad. When, e.g., the exposure to light was such that only in the magenta forming layer an image should been formed, some development can also take place in the cyan and yellow forming layer, in such a way that the magenta image tends to become dull.

It is known to avoid this problem by coating intermediate layers between the colour forming layers that prevent the colour deterioration or by introducing colourless coupling compounds in the emulsion layers.

Mostly in such intermediate layers, a scavenger for oxidized developer is present. A material comprising such an intermediate layer has been described in, e.g., EP-A 396 824 and European Application 95200306.9 filed on february 8, 1995.

In JP-A 03/039902 it is disclosed to introduce a colourless coupling compound, being a pyrazolinone, in at least one emulsion layer in order to diminish colour deterioration.

In JP-A 04/004291 it is disclosed to introduce a colourless coupling compound, being a pyrazoloazole precursor compound, in at least one emulsion layer in order to diminish colour deterioration.

When applying the teachings of the disclosures, referred to above, the colour deterioration is indeed lowered; but when the gelatin/coupler ratio becomes low (lower than e.g. 5, often lower than 3), the colour deterioration is not brought to the level of materials wherein the gelatin to coupler ratio is larger than 5.

There is thus still need for a silver halide colour photographic material with low gelatin content (i.e. with thin layers) where the colour deterioration is minimized and even avoided.

3. Object and summary of the Invention

It is an object of the present invention to provide a silver halide colour photographic material with thin layers while keeping the correct colour rendering and wherein the colour deterioration is minimized.

It is a further object of the invention to provide a colour photographic material with thin layers that, when colour processed, develops very heat stable colours and that can withstand the treatment at high temperatures.

It is an other object of the invention to provide a photographic material suited for a simplified production of a multicolour filter useful in the manufacture of a multicolour liquid crystal display device (multicolour LCD) which manufacture includes high temperature treatment steps and wherein said heat treatment does not substantially affect the colour quality of said multicolour filter.

It is a further object of the present invention to provide a multicolour filter array element firmly associated with a transparent electrode layer in a multicolour liquid crystal display device, e.g. a multicolour active matrix LCD.

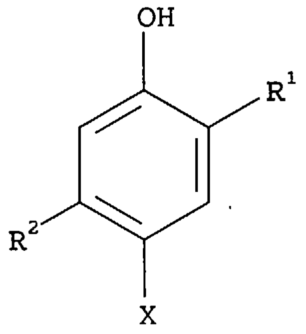
It is still an other object of the present invention to provide a process for the manufacture of a multicolour liquid crystal display device comprising a multicolour filter array element firmly associated with a transparent electrode layer.

Other objects and advantages will become clear from the detailed description and examples which are not limitative to the scope of the present invention.

The objects of the present invention are realized by providing a silver halide photographic material comprising

(i) a support,
(ii) at least three differently spectrally sensitized silver halide emulsion layers, each comprising gelatin and a colour coupler in a weight ratio ≤ 5.00, one of said at least three emulsion layers being sensitive to blue light and forming after image-wise exposure and development a yellow image (yellow layer), an other one of said at least three emulsion layers being sensitive to green light and forming after image-wise exposure and development a magenta image (magenta layer), and an other one of said at least three emulsion layers being sensitive to red light and forming after image-wise exposure and development a cyan image (cyan layer), and
(iii) at least one intermediate layer situated between two of said at least three emulsion layers, characterized in that said intermediate layer comprises both a colourless coupling compound, containing pyrazole ring in its chemical structure and a scavenger for oxidized developer being a diffusion-resistant hydroxybenzene derivative.

In a preferred embodiment said colourless coupling compound is of the group of methylpyrazolone couplers and said scavenger corresponds to the following general formula SD :


SD

wherein X is either an OH group or a leaving group, e.g. Cl and wherein R^1 and R^2 may be the same or different, and represent an unsubstituted or substituted alkyl group, an unsubstituted or substituted aryl group, an unsubstituted or substituted heterocyclic group, an substituted or unsubstituted amino group or an amidegroup.

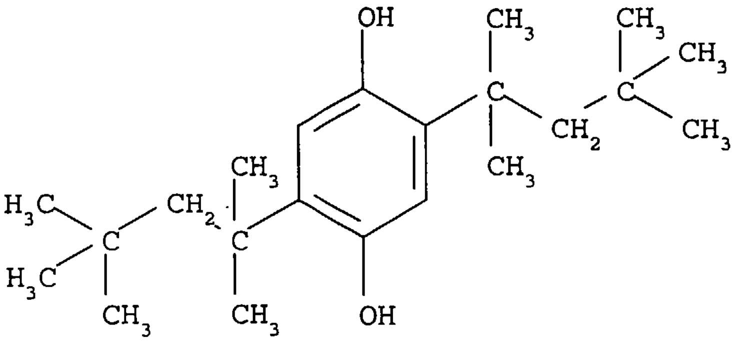
In a further preferred embodiment, in said scavenger, R^1 and R^2 are the same and each individually represents an alkyl group having between 6 and 20 carbon atoms.

In a further preferred embodiment said cyan layer is farthest from said support, said yellow layer is closest to said support, said magenta layer is in between said yellow and cyan layer and said at least one intermediate layer is present between said cyan layer and said magenta layer.

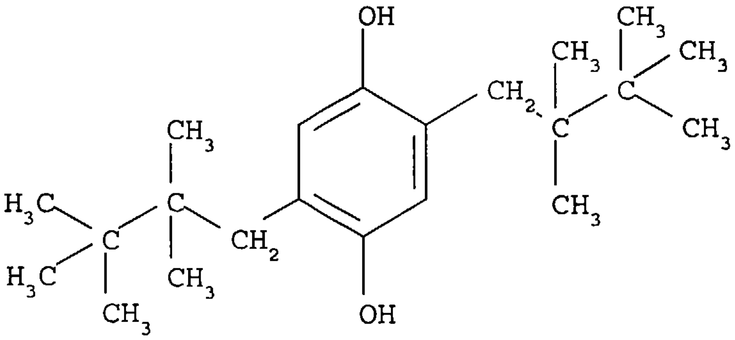
4. Detailed Description of the Invention.

It was found that the weight ratio of gelatine to colour coupler (GEL/COUP) in the various layers of a colour photographic material could be decreased to a factor of 5 and lower, even to a factor 3 or lower, when between at least the colour forming silver halide layers with low gelatin/coupler ratio, an intermediate layer was present and said intermediate layer comprised a combination of a scavenger for oxidized colour developer and a coupling compound giving no colour, i.e. a colourless coupling compound. The lower gelatin/coupler ratio did in that case not deteriorate the correct colour rendering nor did it enhance the colour deterioration.

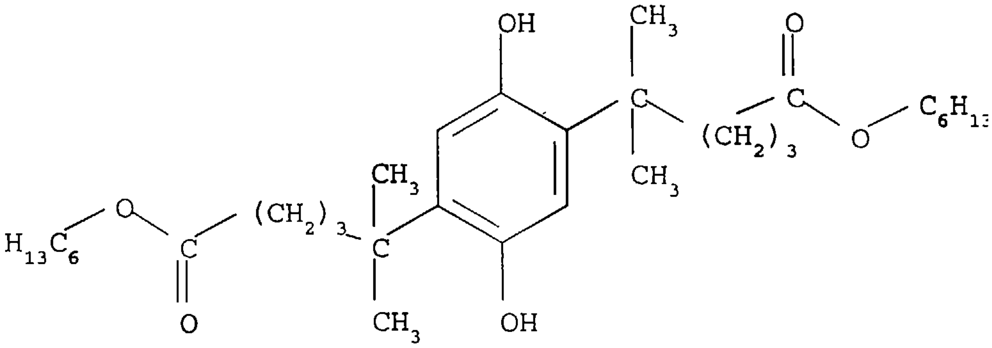
Typical examples of scavenger compounds are, e.g., SD1, SD2 and SD3.



SD1

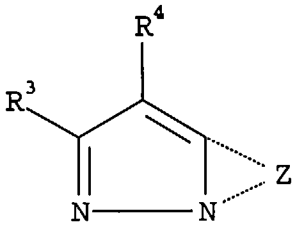


SD2



SD3

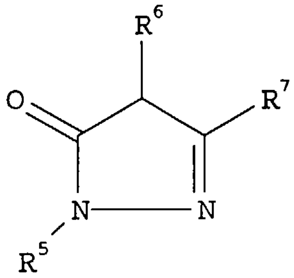
The colourless coupling compound is preferably a coupling compound comprising a pyrazole ring with general formula WK1 :



WK1

wherein R^3 and R^4 are equal or different and each individually represents an alkyl group, an aryl group or hydrogen, and Z represents the non-metallic atoms required to form a 5 or 6 membered ring structure.

More preferably the colourless coupling compound is a pyrazolone coupling compound with general formula WK2 :



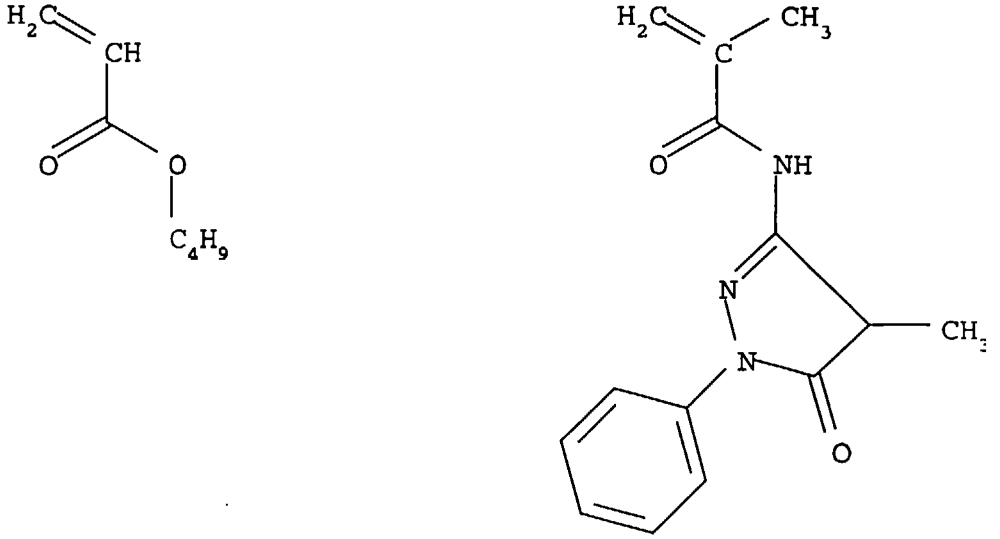
WK2

wherein R^5 represents hydrogen, an alkyl group or an aryl group, R^6 represents a C1 to C5 alkylgroup or an aryl group and R^7 represents hydrogen, an alkyl group, an aryl group, an heterocyclic group, a substituted or unsubstituted amino group, an amino group and an ether group.

In the most preferred embodiment R^6 is a methyl group.

The colourless coupling pyrazolone compound can be in a polymeric latex form, wherein, in the polymer forming said polymeric latex, pyrazolone comprising moieties are present. Very useful examples of colourless coupling compounds for use in the present invention are described in e.g. US 3,912,513.

A typical example of a very useful colourless coupling compound for use in a silver halide material according to this invention is



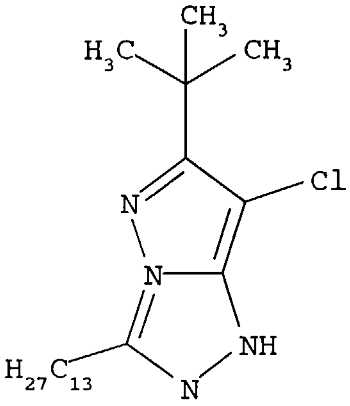
WK3

This is an example of a polymeric colourless coupling compound comprising moieties with pyrazolone groups and moieties of an acrylic acid ester.

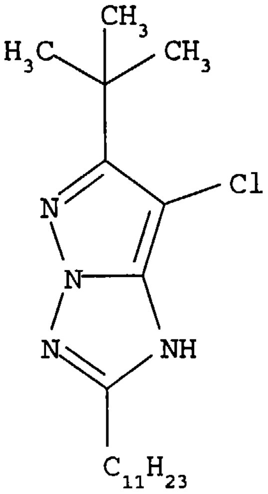
Surprisingly the presence of both this colourless coupling compound and this scavenger in an intermediate layer that is present between to emulsion layers having a low gelatin to coupler weight ratio, not only prevented largely the colour deterioration but enhanced also the maximal density that was obtained in one of the layers. This proved especially so when the intermediate layer was present between the cyan and the magenta forming layers, where both the colour deterioration (forming cyan in magenta) was diminished and the maximum density of the cyan layer was enhanced. In a preferred embodiment of this invention said intermediate layer, comprising both a colourless coupling compound, comprising pyrazole ring, and a diffusion-resistant hydroxybenzene derivative is present between the cyan layer and the magenta layer and the cyan layer comprises gelatin and colour coupling compound in a weight ratio equal to or smaller than 3. This unexpected beneficial effect greatly enhances the degrees of freedom in designing a cyan layer in a silver halide colour photographic material. It makes it, e.g., possible to lower the amount of cyan coupling compound in the cyan layer giving less yellowing of the processed material upon heating. Or it becomes possible to diminish the silver content of the cyan layer, or it makes it possible to keep the silver content, but to use other cyan colour coupling compounds.

An important advantage of the higher degree of freedom created by the use of an intermediate layer according to the present invention is that it brings the opportunity to use in the magenta layer 2-equivalent coupling compounds, instead of 4-equivalent coupling compounds. Most of the 2-equivalent magenta coupling compounds are slow reacting and give rather low maximum density. It was found that in a material comprising an intermediate layer according to the present invention, a very acceptable maximum density could be achieved by using a 2-equivalent coupling compound instead of a 4-equivalent one, while the thermal stability of the magenta colour formed remained the same, but the light stability was greatly enhanced.

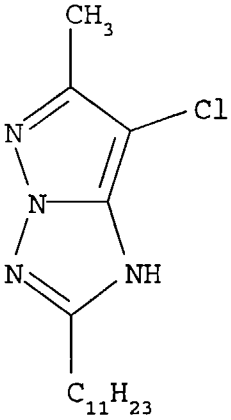
Preferred 2-equivalent magenta coupling compounds are :



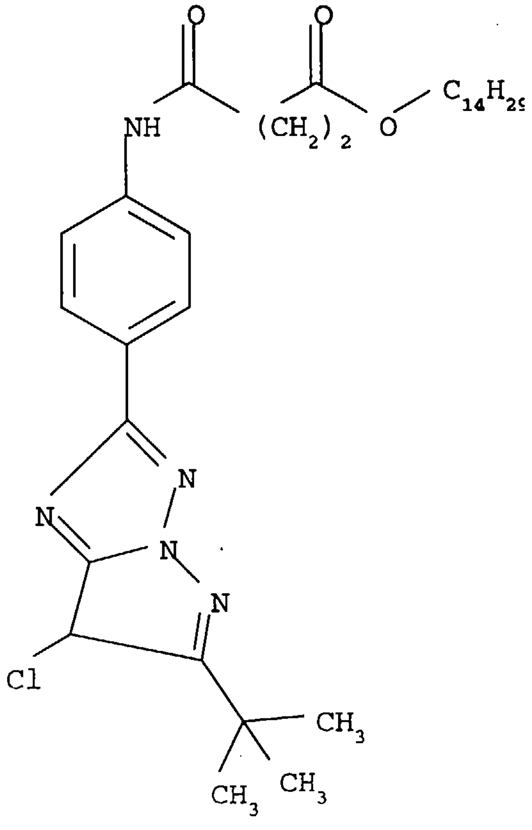
M21



M22



M23



M24

The silver halide emulsion layer may contain any type of light-sensitive silver halide emulsion, e.g. an emulsion that forms a latent image primarily on the surfaces of the silver halide grains, or that forms an internal latent image predominantly in the interior of the silver halide grains. The emulsions can be negative-working emulsions, e.g. surface-sensitive emulsions or unfogged internal latent image-forming emulsions, or positive-working emulsions e.g. direct-positive emulsions of the unfogged, internal latent image-forming type, the development of which is conducted with uniform light exposure or in the presence of a nucleating agent. Further are mentioned direct-positive emulsions of the pre-fogged type wherein during image-wise exposure chlorine, bromine and/or iodine is liberated which image-wise destroys the developable centres created during overall prefogging. Direct-positive emulsions need only one development (as do negative emulsions).

Reversal silver halide emulsions are not prefogged. Their processing includes 2 development steps and a fogging step. The first development is carried out with a black-and-white developer whereby a negative black-and-white silver image is formed. The remaining silver halide is made developable by fogging, either physically (by exposure to light) or chemically. Upon subsequent colour development, bleaching and fixing a positive colour image is obtained.

By negative-working is meant that the density observed after processing is proportional to the exposure. By positive-working is meant that the silver halide emulsions yield upon exposure and development positive images, i.e. the density is inversely proportional to the exposure.

The applied silver halide can be of the silver chloride, the silver chloride-bromide, the silver bromide, the silver bromide-iodide or the silver chloride-bromide-iodide type.

The silver halide can be surface sensitized. Noble metal (e.g. gold), middle chalcogen (e.g. sulfur, selenium or tellurium), and reduction sensitizers, employed individually or in combination, are specifically contemplated. Typical chemical sensitizers are listed in Research Disclosure December 1989, item 308119, section III.

The silver halide can be spectrally sensitized with dyes from a variety of classes, including the polymethine dye class, which includes the cyanines, merocyanines, complex cyanines and merocyanines (i.e. tri-, tetra-, and polynuclear cyanines and merocyanines) oxonols, hemioxonols, styryls, merostyryls, and streptocyanines; see said Research Disclosure, section IV.

Suitable vehicles for the emulsion layers and other layers of the print material are described in section IX of said Research Disclosure and brighteners and antifoggants are described respectively in sections V and VI, and hardeners for gelatin in section X.

The photographic material according to the present invention, can comprise any support known in the art, e.g. transparent or dyed plastic (polymeric) films. The plastic films may be, e.g. cellulosic esters, polyesters as e.g. polyethyleneterephthalate, polyethylenenaphthalate etc. Also opaque supports may be used, e.g. paper, polyethylene coated paper, opacified polymeric films, etc.

When the photographic material is intended for use in the production of multicolour filter array elements that can be used in LCD's (Liquid Crystal Displays), it is preferred to use glass as a support. The glass used as support is e.g. borax glass, borosilicate glass, lime glass, potash glass, soda glass, crown glass, flint glass, silica-flint glass, chromium glass, zinc-crown glass or quartz glass. The glass support has e.g. a thickness in the range of 0.3 to 1.5 mm.

The so-called subbing layers currently used in colour print film on a resin support cannot be used due to the very different nature of the glass substrates.

A strong adhesion of the hydrophillic colloid multilayer arrangement to the glass support can be realized by means of a very thin subbing layer containing gelatin, a water-soluble inorganic silicon compound like e.g. sodium silicate (water glass) and a gelatin hardening agent.

An equally strong adhesion can be obtained without a subbing layer by the addition to the first layer, which in a preferred embodiment is a gelatin-containing light-absorbing anti-halation layer, of an organic silicon compound such as an epoxysilane and a hardening agent for gelatin. Particularly suitable subbing layers on the basis of organic silicon compounds are described in US-P 3,661,584 and GB-P 1,286,467.

The reflections of light from the support back into the multilayer arrangement are eliminated by the presence of a light-absorbing (anti-halation) layer between the glass substrate and the first photographic silver halide emulsion layer. Therefore one or more dyes are present in said layer which dyes should be destroyed chemically in one or more processing liquids or simply be soluble in one or more of the processing liquids or in the rinse water and be washed out. Filter or anti-halation dyes may be present in one or more layers of the multilayer arrangement to decrease unwanted interlayer reflections and/or to improve the optical characteristics of individual layers. This practice is well known to those skilled in the art.

The silver halide photographic material according to the present invention is especially well suited for use in the production of colour filters for liquid crystal displays. Therefore this invention comprises also a method for manufacturing a multicolour filter array element, firmly associated with a transparent electrode layer in a multicolour liquid crystal display device, comprising the steps of :

(i) exposing a silver halide colour photographic print material comprising a plurality of differently spectrally sensitive silver halide emulsion layers on a glass support, by a single step multicolour pixelwise exposure,
(ii) colour processing said exposed print material producing thereby in each silver halide emulsion layer a differently coloured pixel pattern,
(iii) coating said colour processed print material at its silver halide emulsion layer side with a hydrophobic water-impermeable organic resin layer
(iv) curing said organic resin layer by heating said layer at temperatures between 100 °C and 250 °C
(v) depositing an transparent electrode layer on said organic resin layer, wherein

(1) said silver halide colour photographic material comprises

(a) a support,
(b) at least three differently spectrally sensitized silver halide emulsion layers, each comprising gelatin and a colour coupler in a weight ratio ≤ 5.00, one of said at least three emulsion layers being sensitive to blue light and forming after image-wise exposure and development a yellow image (yellow layer), an other one of said at least three emulsion layers being sensitive to green light and forming after image-wise exposure and development a magenta image (magenta layer), and an other one of said at least three emulsion layers being sensitive to red light and forming after image-wise exposure and development a cyan image (cyan layer), and
(c) at least one intermediate layer situated between two of said at least three emulsion layers, and

(2) said intermediate layer comprises both a colourless coupling compound, containing pyrazole ring in its chemical structure and a scavenger for oxidized developer being a diffusion-resistant hydroxybenzene derivative.

The pixelwise exposure of the multicolour print material according to the present invention can be performed in several ways.

For example, the exposure may proceed in a single step through a multicolour master, in a plurality of steps with light of different colour (blue, green and red) through a pitchwise shiftable black-and-white mask or simultaneously or subsequently by means of pixelwise modulated laser beams of different colour, blue, green and red.

A convenient method for manufacturing the colour filters for use according to the present invention, especially in mass-production when a great number of them is needed, is to carry out the exposure in a single step through a multicolour master.

When used in conjunction with a negative type multilayer silver halide colour material the master must be a coloured negative master, whereas a coloured positive master is needed when a direct positive or reversal type multilayer silver halide colour material is involved.

A coloured negative master has predominantly yellow-, magenta- and cyan coloured pixels at the places corresponding respectively with the blue, green and red pixels on the colour filter array element.

After processing the silver halide colour filter is covered with a protective resin, impermeable, layer which in the production of a multicolour filter associated with an electrode layer has to be present. In the manufacture of a liquid crystal display according to the present invention heat-curable resins are used for producing said impermeable layer.

Examples of heat-curable organic resins and curing agents therefor are described by Ernest W. Flick in "Handbook of Adhesive Raw materials" - Noyens Publications - Park Ridge, New Jersey, USA (1982). Polyimide resins that can be heat-cured are e.g. the photo-curable polyimide resins disclosed in US-P 4,698,295. Further are mentioned epoxy resins that can be heat-cured with amines thermally set free from an amine precursor e.g. ketimine which on reacting with water yields an amine [ref. The Chemistry of Organic Film Formers by D. H. Solomon, John Wiley & Sons, Inc. (1967), p.190].

The water-impermeable hydrophobic organic resin layer may be coated from a liquid composition containing (an) evaporatable solvent(s) or may be applied onto the processed multicolour material by lamination using e.g. a heat-curable layer sandwiched originally between a polyethylene film and a protective cover sheet analogously to the type of material described in J. photogr. Sci., <u>18</u>, 150 (1970).

The wet strength of the colour processed gelatin containing silver halide emulsion layer assemblage before coating with the organic resin layer in step (iv) of the present invention statement can be greatly improved as described in published EP-A 0 396 824.

A transparent conductive layer forming the electrode layer is applied to the impermeable resin layer by known techniques, e.g. a transparent indium tinoxyde (ITO) layer is applied by vacuum-deposition.

Although the multicolour filter array elements prepared according to the present invention are very well suited for the production of active matrix liquid crystal displays there use is not restricted to that type of displays. They can be incorporated likewise in passive matrix liquid crystal displays, especially in supertwisted nematic (STN), double supertwisted nematic (DSTN), retardation film supertwisted nematic (RFSTN), in ferroelectric (FLC), guest host (GH), polymerdispersed (PF), polymer network (PN) liquid crystal displays, and so on. They can further be incorporated in emissive displays like electroluminescent displays, CRT devices and in charge coupled device (CCD) cameras.

The following examples illustrates the present invention without however limiting it thereto.

EXAMPLES

All chemical formulas are given after the description of the various layers comprised in the material, except for SD1 and WK3, that were already given herein above.

COMPARATIVE EXAMPLE (CE1)

Following layers were coated in the order given on sodalime glass with a thickness of 1.5 mm to form a colour photographic material.

<u>Anti-halation layer</u>

A non-diffusing yellow dye of formula YD, was dispersed in gelatin.
To this dispersion epoxysilane E (structure defined hereinafter) acting as an adhesion promoter was added.
The coverages of yellow dye YD, gelatin and epoxysilane E were 0.5, 1.5 and 0.1 g/m^2 respectively.

<u>Blue sensitive layer</u>

A 100 % silver chloride emulsion with an average grain size of 0.4 µm was sensitized to blue light with a spectral sensitizing agent of formula SB. A yellow dye forming coupler of formula Y1 was added to this emulsion.
The amounts of silver halide, gelatine and colour coupler Y1 were 0.57, 3.30 and 1.0 g/m^2 respectively.

First intermediate layer

A substance of formula SD1, capable of scavenging oxidized colour developing agent was dispersed in gelatin and coated at a coverage of 0.08 g SD1/m^2 and of 0.77 g gelatine/m^2.

Green sensitive layer

A silver chloride-bromide (90/10 molar ratio) emulsion with an average grain size of 0.12 μm was sensitized to green light with a spectral sensitizing agent of formula SG. A magenta dye forming coupler of formula M1 was added to this emulsion.
The amounts of silver halide, gelatin and colour coupler M1 were 0.71, 2.8 and 0.53 g/m^2 respectively.

Second intermediate layer

This layer has the same composition as the first intermediate layer.

Red sensitive layer

A silver chloride-bromide (90/10 molar ratio) emulsion with an average grain size of 0.12 μm was sensitized to red light with a spectral sensitizing agent of formula SR. A cyan dye forming coupler of formula C1 was added to this emulsion.
The amounts of silver halide, gelatin and colour coupler C1 were 0.49, 6 and 0.95 g/m^2 respectively.
Yellow, magenta and cyan water-soluble dyes, acting as accutance dyes were present at an appropriate coverage in the blue, green en red sensitive layer respectively and hydroxytrichlorotriazine acting as hardening agent was present in the red sensitive layer at a coverage of 0.035 g/m^2.

EXAMPLE 1 (E1)

The comparative example was repeated, except for the gelatin/coupler ratio in the blue, green en red sensitive layers and for the composition of the second intermediate layer.
In the blue sensitive layer 1.15 g/m^2 of gelatine and 1.0 g/m^2 of coupler were present, in the green sensitive layer these amounts were 1.4 and 0.53 g/m^2 respectively and in the red sensitive layer these amounts were 3 and 0.95 g/m^2 respectively. The second intermediate layers comprised NO compound SD1.

EXAMPLE 2 (E2)

Example 1 was repeated, except for the composition of the second intermediate layer. Instead of NO compound SD1, 0.04 g compound SD1 per m^2 were present.

EXAMPLE 3 (E3)

Example 2 was repeated, except for the composition of the second intermediate layer. Instead of 0.04 g of compound SD1 per m^2, 0.08 g were present.

EXAMPLE 4 (E4)

Example 3 was repeated, except for the composition of the second intermediate layer. Instead of 0.08 g of compound SD1 per m^2, 0.16 g were present.

EXAMPLE 5 (E5)

Example 3 was repeated, except for the composition of the second intermediate layer. Instead of 0.08 g of compound SD1 per m^2, no compound SD1 was present, but 0.174 g/m^2 of compound WK3 was present.

EXAMPLE 6 (E6)

Example 5 was repeated, except for the composition of the second intermediate layer. Instead of 0.174 g/m^2 of compound WK3, 0.347 g/m^2 of compound WK3 was present.

EXAMPLE 7 (E7)

Example 5 was repeated, except for the composition of the second intermediate layer. Instead of 0.174 g/m^2 of compound WK3, 0.521 g/m^2 of compound WK3 was present.

EXAMPLE 8 (E8)

Example 3 was repeated, except for the composition of the second intermediate layer. Instead of 0.08 g of compound SD1 per m^2, 0.04 g/m^2 of compound SD1 and 0.174 g/m^2 of compound WK3 were present.

EXAMPLE 9 (E9)

Example 8 was repeated, except for the composition of the first and the second intermediate layer. Instead 0.174 g/m^2 of compound WK3, 0.347 g of compound WK3 were present.

EXAMPLE 10 (E10)

Example 8 was repeated, except for the composition of the first and the second intermediate layer. Instead of 0.04 g/m^2 of compound SD1 and 0.174 g/m^2 of compound WK3, 0.08 g/m^2 of compound SD1 and 0.174 g/m^2 of compound WK3 were present.

EXAMPLE 11 (E11)

Example 8 was repeated, except for the composition of the first and the second intermediate layer. Instead of 0.04 g/m^2 of compound SD1 and 0.174 g/m^2 of compound WK3, 0.16 g/m^2 of compound SD1 and 0.174 g/m^2 of compound WK3 were present.
In table 1, the composition of the second intermediate layer of the various examples, regarding the amounts of SD1 and WK3, is summarized.

TABLE 1

Ex #	Amounts SD1 and WK3 in the second intermediate layer	
	SD1 in g/m^2	WK3 in g/m^2
CE1	0.080	0
E1	0	0
E2	0.040	0
E3	0.080	0
E4	0.160	0
E5	0	0.174
E6	0	0.347
E7	0	0.521
E8	0.040	0.174
E9	0.040	0.347
E10	0.080	0.174
E11	0.160	0.174

COMPARATIVE EXAMPLE 2 (CE2)

Comparative example 1 was repeated except for the magenta coupler in the green sensitive layer, which now was

2-equivalent coupler M21 and for the cyan coupler which was coupler C2.

EXAMPLE 12 (E12)

Comparative example 2 was repeated, except for the gelatin/coupler ratio in the blue, green en red sensitive layers and for the composition of the second intermediate layer. In the blue sensitive layer 1.15 g/m^2 of gelatine and 1.0 g/m^2 of coupler were present, in the green sensitive layer these amounts were 1.4 and 0.53 g/m^2 respectively and in the red sensitive layer these amounts were 3 and 0.95 g/m^2 respectively. In the second intermediate layer 0.04 g/m^2 of compound SD1 was present.

EXAMPLE 13 (E13)

Example 12 was repeated, except for the composition of the second intermediate layer. Instead of 0.04 g of compound SD1 per m^2, 0.08 g were present.

EXAMPLE 14 (E14)

Example 12 was repeated, except for the composition of the second intermediate layer. In that layer 0.04 g of compound SD1 per m^2 and 0.174 g/m^2 of compound WK3 were present.

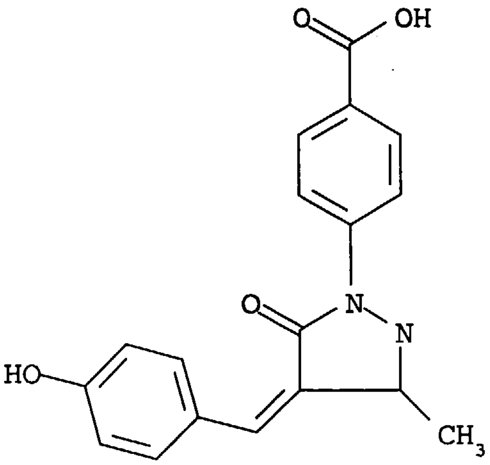
EXAMPLE 15 (E15)

Example 14 was repeated, except for the composition of the second intermediate layer. Instead of 0.04 g/m^2 of compound SD1, 0.08 g/m^2 were present.
In table 2, the composition of the second intermediate layer of the various examples, regarding the amounts of SD1 and WK3, is summarized.

TABLE 2

Ex #	Amounts SD1 and WK3 in the second intermediate layer	
	SD1 in g/m^2	WK3 in g/m^2
CE2	0.080	0
E12	0.040	0
E13	0.080	0
E14	0.040	0.174
E15	0.080	0.174

CHEMICAL FORMULAS



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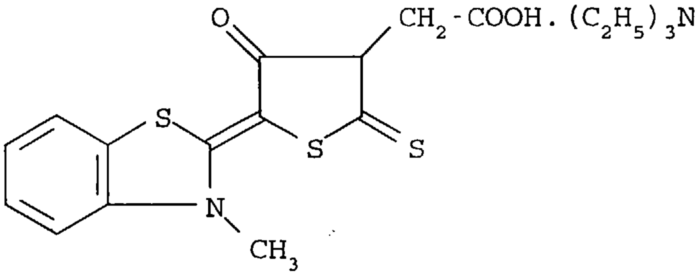

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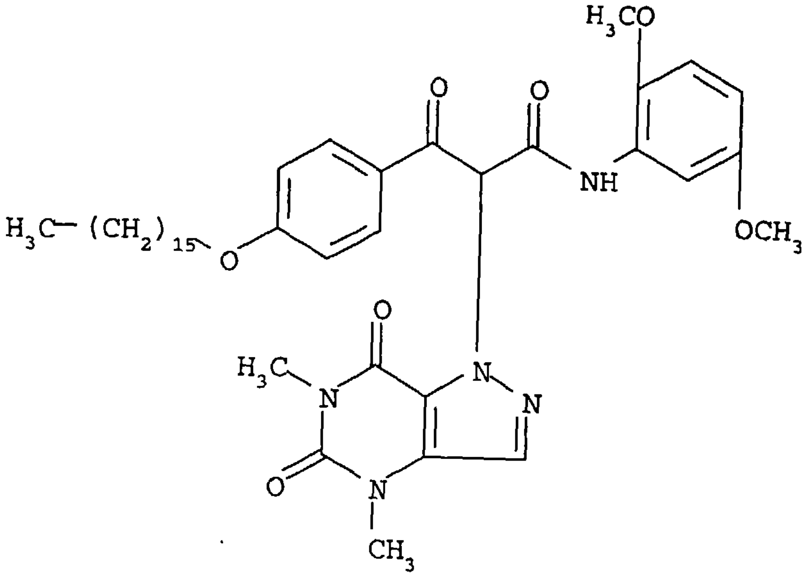

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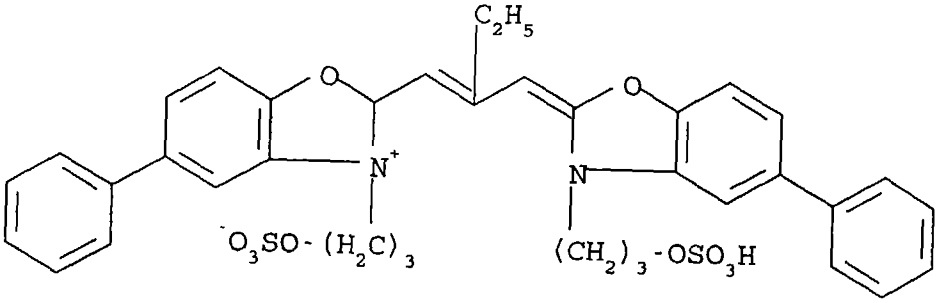
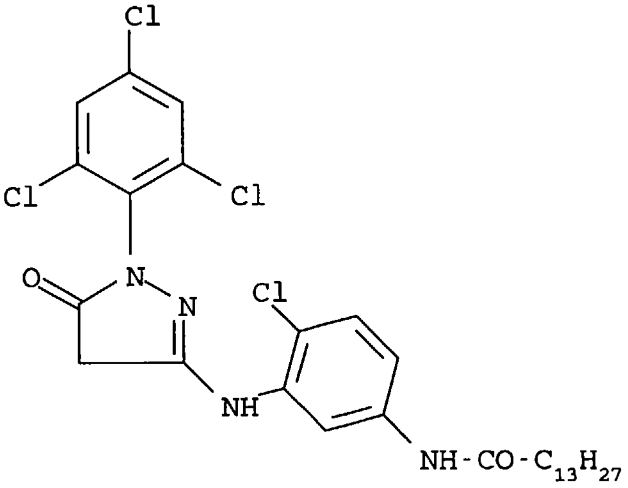
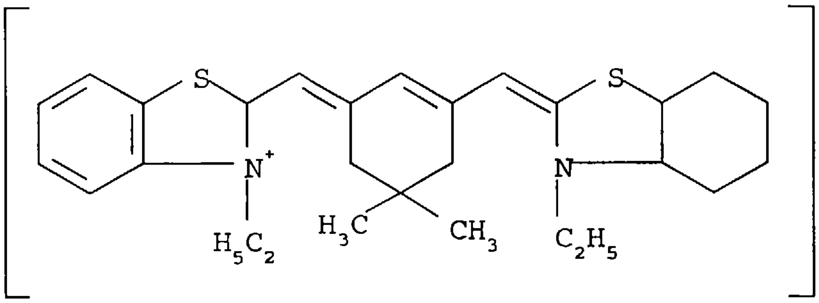


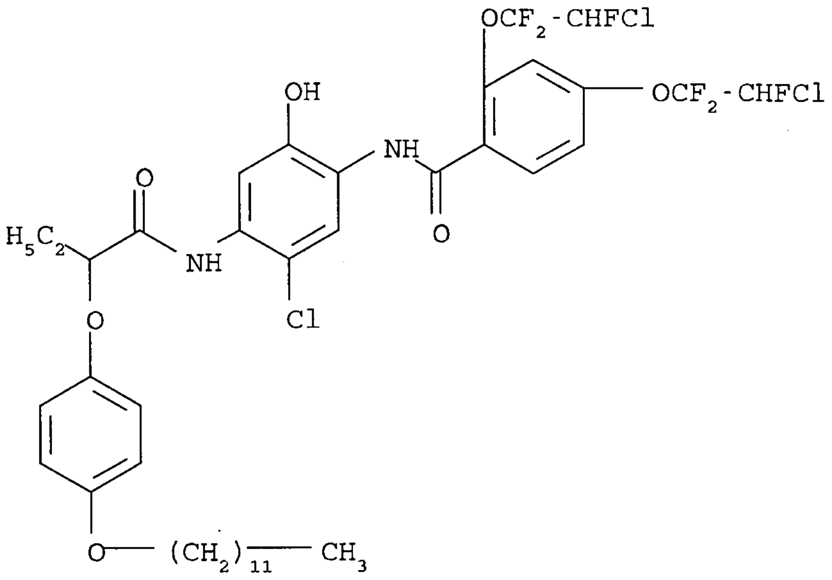
SG



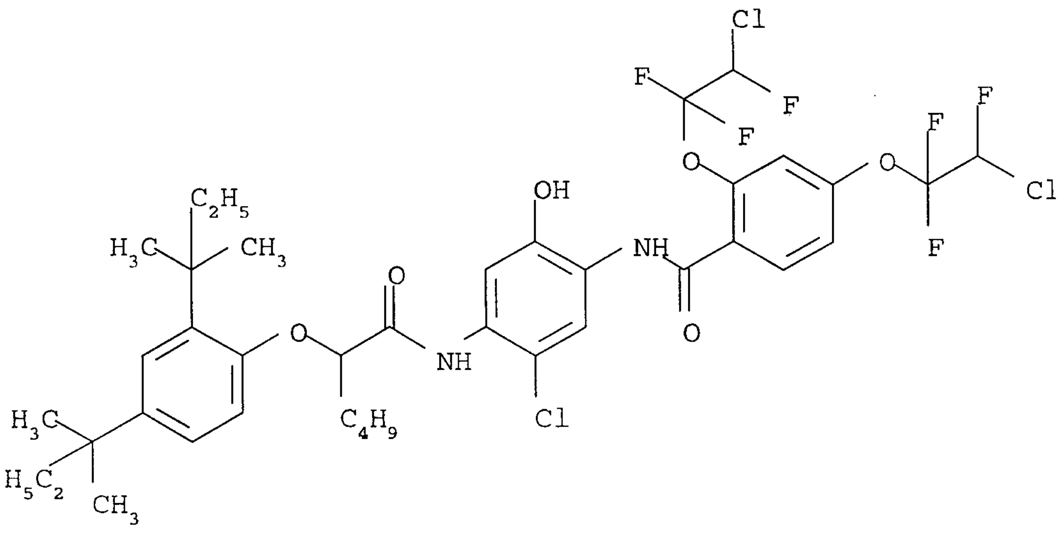
M1



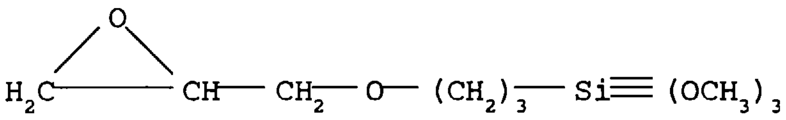
SR



C1



C2



E

Exposure

All materials were exposed so has to have, after processing in solutions with composition given immediately below, 3 images a yellow image, a magenta image and a cyan image each giving maximum density.

Processing

Developer

Sodium sulphite (anhydrous)	4 g
4-amino-3-methyl-N,N-diethylaniline hydrochloride	3 g
sodium carbonate (anhydrous)	17 g
sodium bromide	1.7 g
sulphuric acid 7 N	0.62 ml
water up to	1000 ml

After development each sheet was treated in an acid stop bath prepared by adding water up to 1 l to 50 ml of sulphuric acid 7 N. The treatment with stop bath was followed by 2 minutes rinsing in plain water followed by a 2 minutes fixing in an aqueous solution having the following composition :

58 % aqueous solution of $(NH_4)_2S_2O_3$	100 ml
sodium sulphite (anhydrous)	2.5 g
sodium-hydrogen sulphite (anhydrous)	10.3 g
water up to	1000 ml

The treatment with fixing liquid was followed by a 2 minutes rinsing in plain water followed by a 3 minutes bleaching in an aqueous solution having the following composition :

potassium hexacyanoferrate (III) (anhydrous)	30 g
sodium bromide (anhydrous)	17 g
water up to	1000 ml

Thereupon each sheet was treated with the fixing liquid again and rinsed for 3 minutes with plain water.
Finally each sheet was treated with an aqueous solution having a pH of 9 and containing per litre 20 ml of a 40 % aqueous solution of formaldehyde serving as hardening agent.

Measurement

The density of the yellow, magenta and cyan images were measured behind a blue, green and red filter. The densities measured in the yellow layer after green and red filter are a measure of the colour deterioration in the yellow image, the density measured behind the blue filter is maximum density. The densities measured in the magenta layer behind the blue and red filter are a measure of the colour deterioration in the magenta image, the density measured behind the green filter is maximum density. The densities measured in the cyan layer behind the blue and green filter are a measure of the colour deterioration in the cyan image, the density measured behind the red filter is maximum density. The results for comparative example 1 and examples 1 through 11 are given in table 3 and the results for comparative example 2 and examples 12 through 15 are given in table 4.

TABLE 3

Ex #	Yellow layer			Magenta layer			Cyan layer		
	BF*	GF**	RF†	BF	GF	RF	BF	GF	RF
CE	2.07	0.03	0.01	0.05	2.11	0.04	0.04	0.02	2.23
E1	2.01	0.03	0.02	0.06	2.23	0.19	0.04	0.12	2.36
E2	2.04	0.03	0.01	0.06	2.25	0.12	0.04	0.03	2.36
E3	1.98	0.03	0.01	0.06	2.23	0.08	0.04	0.04	2.35
E4	2.03	0.03	0.01	0.06	2.23	0.06	0.04	0.02	2.34
E5	2.05	0.03	0.01	0.06	2.16	0.10	0.04	0.03	2.36
E6	2.04	0.03	0.01	0.05	2.02	0.08	0.03	0.02	2.30
E7	2.04	0.03	0.01	0.05	2.06	0.07	0.04	0.03	2.27
E8	2.04	0.03	0.01	0.06	2.15	0.05	0.05	0.01	2.48
E9	2.05	0.03	0.01	0.06	2.19	0.04	0.05	0.02	2.46
E10	2.03	0.04	0.01	0.06	2.24	0.05	0.04	0.02	2.58
E11	2.00	0.03	0.01	0.06	2.12	0.06	0.04	0.02	2.55

* BF density of the layer behind blue filter
** GF density of the layer behind green filter
† RF density of the layer behind red filter

It is clear from the table above that in comparison with the comparative example with high gelatine content, the invention examples 1 to 4, where increasing amounts of scavenger SD1 are present have a higher maximum density in the cyan layer than the comparative material (CE), but that the cyan contamination of the magenta layer (measurement of the magenta layer behind a red filter) remains somewhat higher. Higher amounts of compound SD1 seem not to influence the maximum density in the cyan layer.

The invention examples 5 to 7, with increasing amount of colourless coupling compound WK3, it is seen that the cyan contamination of the magenta layer (measurement of the magenta layer behind a red filter) is not brought to the level of the comparison example and that increasing amounts of compound WK3 result in a decrease of the maximum density of the cyan layer.

The combination of compound SD1 and WK3 (examples 8 to 11) in the intermediate layers brings both the cyan contamination of the magenta layer (measurement of the magenta layer behind a red filter) to the level of the comparison example and do given a further increase in maximum density in the cyan layer. The optimum seems to be a combination of between 40 and 80 mg/m^2 of compound SD1 with around 174 mg/m^2 of compound WK3.

TABLE 4

Ex #	Yellow layer			Magenta layer			Cyan layer		
	BF*	GF**	RF†	BF	GF	RF	BF	GF	RF
CE2	2.06	0.03	0.01	0.05	1.84	0.06	0.04	0.02	1.88
E12	2.02	0.03	0.02	0.05	1.90	0.09	0.04	0.02	1.90
E13	2.05	0.03	0.01	0.05	1.92	0.08	0.04	0.02	1.93
E14	1.98	0.03	0.01	0.05	1.96	0.07	0.04	0.02	1.95
E15	2.06	0.03	0.01	0.06	1.93	0.06	0.04	0.02	1.99

* BF density of the layer behind blue filter
** GF density of the layer behind green filter
† RF density of the layer behind red filter

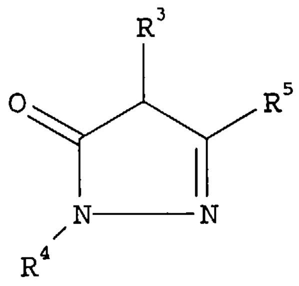
It is again seen that the lowering of the gelatine content brings about a higher magenta density and a higher cyan density. Although less pronounced it is only the simultaneous presence of SD1 and WK3 that bring the colour deterioration of the magenta and increases the cyan density.

Claims

1. A silver halide colour photographic material comprising

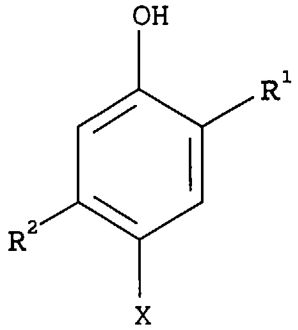
   (i) a support,
   (ii) at least three differently spectrally sensitized silver halide emulsion layers, each comprising gelatin and a colour coupler in a weight ratio ≤ 5.00, one of said at least three emulsion layers being sensitive to blue light and forming after image-wise exposure and development a yellow image (yellow layer), an other one of said at least three emulsion layers being sensitive to green light and forming after image-wise exposure and development a magenta image (magenta layer), and an other one of said at least three emulsion layers being sensitive to red light and forming after image-wise exposure and development a cyan image (cyan layer), and
   (iii) at least one intermediate layer situated between two of said at least three emulsion layers, characterised in that said intermediate layer comprises both a colourless coupling compound, containing pyrazole ring in its chemical structure and a scavenger for oxidized developer being a diffusion-resistant hydroxybenzene derivative.

2. A photographic material according to claim 1, wherein said colourless coupling compound is a pyrazolone coupling compound with general formula WK2 :



WK2

wherein R^5 represents hydrogen, an alkyl group or an aryl group, R^6 represents a C1 to C5 alkylgroup or an aryl group and R^7 represents hydrogen, an alkyl group, an aryl group, an heterocyclic group, a substituted or unsubstituted amino group, an amino group and an ether group and said scavenger corresponds to the following general formula SD



SD

wherein X is either an OH group or a leaving group and wherein R^1 and R^2 may be the same or different, and represent an unsubstituted or substituted alkyl group, an unsubstituted or substituted aryl group, an unsubstituted or substituted heterocyclic group, an substituted or unsubstituted amino group or an amidegroup.

3. A photographic material according to claim 2, wherein R^1 and R^2 are the same and each individually represents an substituted or unsubstituted alkyl group having between 6 and 20 C-atoms.

4. A photographic material according to claim 2 or 3, wherein R^6 is a methyl group.

5. A photographic material according to any of claims 1 to 4, wherein said cyan layer is farthest from said support, said yellow layer is closest to said support, said magenta layer is in between said yellow and cyan layer and said at least one intermediate layer is present between said cyan layer and said magenta layer.

6. A photographic material according to claim 5, wherein said cyan layer comprises gelatin and a colour coupling compound in a weight. ratio ≤ 3.00.

7. A method for manufacturing a multicolour filter array element, firmly associated with a transparent electrode layer in a multicolour liquid crystal display device, comprising the steps of :

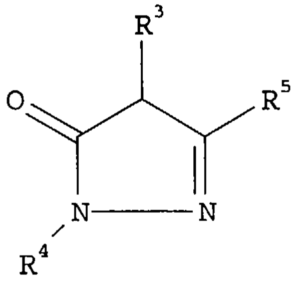
(i) exposing a silver halide colour photographic print material comprising a plurality of differently spectrally sensitive silver halide emulsion layers on a glass support, by a single step multicolour pixelwise exposure,
(ii) colour processing said exposed print material producing thereby in each silver halide emulsion layer a differently coloured pixel pattern,
(iii) coating said colour processed print material at its silver halide emulsion layer side with a hydrophobic water-impermeable organic resin layer
(iv) curing said organic resin layer by heating said layer at temperatures between 100 °C and 250 °C
(v) depositing an transparent electrode layer on said organic resin layer, wherein

(1) said silver halide colour photographic material comprises

(a) a support,
(b) at least three differently spectrally sensitized silver halide emulsion layers, each comprising gelatin and a colour coupler in a weight ratio ≤ 5.00, one of said at least three emulsion layers being sensitive to blue light and forming after image-wise exposure and development a yellow image (yellow layer), an other one of said at least three emulsion layers being sensitive to green light and forming after image-wise exposure and development a magenta image (magenta layer), and an other one of said at least three emulsion layers being sensitive to red light and forming after image-wise exposure and development a cyan image (cyan layer), and
(c) at least one intermediate layer situated between two of said at least three emulsion layers, and

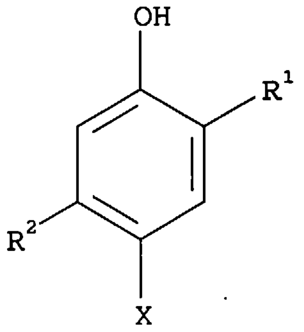
(2) said intermediate layer comprises both a colourless coupling compound, containing pyrazole ring in its chemical structure and a scavenger for oxidized developer being a diffusion-resistant hydroxybenzene derivative.

8. A method according to claim 7, wherein said colourless coupling compound is a pyrazolone coupling compound corresponding to general formula WK2



WK2

wherein R^5 and R^6 are the same or different and each independently represents hydrogen, an alkyl group or an aryl group and R^7 represents hydrogen, an alkyl group, an aryl group, an heterocyclic group, a substituted or unsubstituted amino group, an amino group and an ether group and said scavenger corresponds to the following general formula SD



SD

wherein X is either an OH group or a leaving group and wherein R^1 and R^2 may be the same or different, and represent an unsubstituted or substituted alkyl group, an unsubstituted or substituted aryl group, an unsubstituted or substituted heterocyclic group, an substituted or unsubstituted amino group or an amidegroup.

9. A method according to claim 8, wherein R^1 and R^2 are the same and each individually represents an substituted or unsubstituted alkyl group having between 6 and 20 C-atoms.

10. A method according to claim 8 or 9, wherein R^6 is a methyl group.

11. A method according to any of claim 7 to 10, wherein in said silver halide photographic material said cyan layer is farthest from said support, said yellow layer is closest to said support, said magenta layer is in between said yellow and cyan layer and said at least one intermediate layer is present between said cyan layer and said magenta layer

12. A method according to claim 11, wherein said cyan layer comprises gelatin and a colour coupling compound in a weight ratio ≤ 3.00.

European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 96 20 1046

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP-A-0 546 416 (AGFA GEVAERT AG) 16 June 1993 * page 16, line 11 - line 16; example 1 * * example 7; table 1 * * claims * ---	1-6	G03C7/12 G03C7/30
D,A	EP-A-0 615 161 (AGFA GEVAERT NV) 14 September 1994 ---	7-12	
D,A	PATENT ABSTRACTS OF JAPAN vol. 015, no. 180 (P-1199), 9 May 1991 & JP-A-03 039902 (KONICA CORP), 20 February 1991, * abstract * -----	7-12	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	11 September 1996	Philosoph, L

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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