

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: 83107210.3

(51) Int. Cl.²: **G 03 C 1/42**
G 03 C 5/36

(22) Date of filing: 22.07.83

(30) Priority: 27.08.82 IT 6521082

(43) Date of publication of application:
04.04.84 Bulletin 84/14

(84) Designated Contracting States:
BE DE FR GB

(71) Applicant: **MINNESOTA MINING AND
MANUFACTURING COMPANY**
3M Center, P.O. Box 33427
St. Paul, MN 55133(US)

(72) Inventor: **Luzzi, Antonio**
3M ITALIA RICERCHE S.p.A.
I-17.016 Ferrania/Savona(IT)

(72) Inventor: **Beruto, Marco**
3M ITALIA RICERCHE S.p.A.
I-17.016 Ferrania/Savona(IT)

(72) Inventor: **Ramello, Piero**
3M ITALIA RICERCHE S.p.A.
I-17.016 Ferrania/Savona(IT)

(74) Representative: **Giannesi, Pier Giovanni et al,**
c/o 3M ITALIA S.p.A. Industrial Property Dept.
I-17016 Ferrania (Savona)(IT)

(54) **Gelatin silver halide photographic elements for tanning development.**

(57) A photographic element for tanning development to be used with short exposures to high-intensity light can be obtained if a high-sensitivity emulsion is associated with a 3-pyrazolidinone type compound and then coated with gelatin at a low silver coverage and a low silver/gelatin ratio.

Gelatin Silver Halide Photographic ElementsFor Tanning DevelopmentField Of The Invention

5

The present invention refers to photographic elements for tanning development suitable for obtaining colored relief colloidal images upon short exposure to high-intensity light.

10

Background Of The Art

It is known that photographic elements which contain unhardened gelatin layers containing silver halide emulsions can be made image-wise insoluble upon exposure to a light source and processing in the presence of tanning developers. In fact, the oxidation products of the tanning developer, formed during development of the exposed regions of the image, are capable of producing image-wise hardened gelatin. The unexposed regions of the image, being unhardened, can be washed away with warm water or can be totally or partially transferred onto an image-receiving material. Photographic elements for tanning development are described in US patent 3,364,024. They normally consist of a base having coated thereon a gelatin silver halide emulsion layer and having an unsensitive unhardened gelatin pigmented layer in adjacent position thereto. Upon development of the exposed layer in the presence of a tanning developer of the hydroquinone type, the oxidation products of the hydroquinone harden the exposed regions of the sensitive layer and the adjacent ones of the pigmented layer.

Improved photographic elements for tanning development are described in Italian patent application S.N. 49,360 A/80 filed by the Applicant. In these elements, particular values of the silver coverage, silver/gelatin ratio of the sensitive layer and gelatin/tanning developer ratio allow to obtain a better image quality and a higher

exposure latitude.

The photographic elements for tanning development are generally useful in graphic art applications for the reproduction of originals wherein an image is formed by dots or lines with a process which is cheaper and quicker than the processes which make use of conventional photographic elements. In these applications, the photographic elements are exposed to normal light sources, such as quartz and tungsten lamps, for relatively long times ranging generally from 5 to 10 seconds, thus obtaining after development a tanned gelatin relief image. These elements cannot be used to form an image in applications such as "phototypesetting" (for type printing), which require short exposures to high intensity light (short herein meaning no more than about 10 microseconds).

15

Summary Of The Invention

A photographic element for tanning development to be used with short exposures to high-intensity light can be obtained if a high-sensitivity emulsion is associated with a compound of the 3-pyrazolidinone type and then coated with gelatin with a low silver coverage and a low silver/gelatin ratio.

20

Detailed Description Of The Invention

25

It was found that 3-pyrazolidinone compounds do not improve the conventional elements to be used in graphic art applications, while they give very good results when associated with high-sensitivity emulsions to be used in conventional photography, when such emulsions are processed in an alkaline activating bath after short exposure to high-intensity light.

30

It is essential to the purposes of the present invention that the emulsion is coated with low silver coverages and low

silver/gelatin ratio. It is also important that such emulsions are highly sensitive and have sufficiently coarse grains.

High-sensitivity emulsions herein means a (chemically digested and ripened) emulsion which, associated with a magenta coupler like 1-(2,4,6-trichlorophenyl)-3-[3-(2,4-ditert.amylphenoxyacetamido)-benzamido]-5-pyrazolone and with a sensitizer (e.g. anhydrous 5-chloro-5'-phenyl-3,3'-di-(3-sulfopropyl)-oxacarbocyanine hydroxide), gives a sensitivity of at least 20 ASA when exposed to white light through a step wedge and then developed with a p-phenylene diamine developer (e.g. 4-amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)-aniline sulfate).

Such emulsions are of the type normally used in traditional color photography, for example in the elements for color prints. The same high-sensitivity emulsions, exposed in a phototypesetter and processed with a tanning developer as said above, in absence of 1-phenyl-3-pyrazolidinone (or a compound equivalent thereto), do not give rise to image formation. In the presence of 1-phenyl-3-pyrazolidinone compounds in the same conditions (phototypesetting exposure and tanning development), emulsions known in the art of photographic elements for tanning development do not give rise to image formation. Other auxiliary developers, normally equivalent thereto, such as methol, did not prove to be effective as 1-phenyl-3-pyrazolidinone. Any 1-phenyl-3-pyrazolidinone compound known in the art, which has the same effects as 1-phenyl-3-pyrazolidinone, is deemed to be useful in the present invention. Some derivatives thereof are for instance described in GB patents 542,502; 761,300; 1,093,281; in IT patent 498,462 and in US patent 2,772,282. Examples of such derivatives are 1-phenyl-4,4-dimethyl-, 1-phenyl-5-methyl-, 1-chlorophenyl-, 1-phenyl-5,5-dimethyl-, 1,5-diphenyl-, 1-phenyl-4-ethyl-, 1-phenyl-4,4-dihydroxymethyl-, 1-p-tolyl-4,4-dihydroxymethyl- and 1-phenyl-4-hydroxy-methyl-4-methyl-3-pyrazolidinone compounds.

Such emulsions are characterized by a high iodide content (i.e. greater than 2.5 or 3% mole ratio) and by relatively large grain

size. Preferably, such iodide percentage is at least 4%, more preferably is comprised between 4 and 20% and most preferably between 5 and 15%. Bromide is the main component and is preferably present in a quantity of at least 65%, more preferably of at least 75%. Chloride can
5 be either present or not. It is preferred that the presence thereof be limited at a maximum of 30%, more preferably of 15% and most preferably of 7%.

The grain sizes appear also to be significant to the purposes of the present invention. It is preferred that the grains have
10 mean sizes of at least 0.30 micron. It is more preferred that the distribution curve thereof shows at least 30%, more preferably 50% and most preferably 70% of the grains with a diameter higher than 0.30 micron. It is surprising that such coarse grain and high-iodide content emulsions, per se having low developability characteristics, could be
15 developed within short times, as required by the above described conditions.

It is deemed to be essential to the purposes of the present invention that the emulsion is coated with a silver coverage lower than 0.6 grams per square meter, preferably lower than 0.5 grams per
20 square meter, more preferably lower than 0.4. It is also deemed essential that the silver/gelatin weight ratio be lower than 0.4, preferably lower than 0.3 and more preferably lower than 0.2. It is preferred that the gelatin/tanning developer weight ratio be comprised between 3 and 25, more preferably between 5 and 20 and most preferably
25 between 6 and 18.

A system of the above described type was in fact found, as indicated, to react in an unexpected way with the considered variables, such as the emulsion type and the presence of a 3-pyrazolidinone compound.

30 It was also found that catechol, as tanning agent, shows a particularly desirable behavior.

The present invention refers to a photographic element for

tanning development to be used for short exposures to high-intensity light having at least one substantially unhardened gelatin layer associated with a light-sensitive silver halide emulsion, a colored pigment and a tanning developer, characterized in that such emulsion is
5 a high-sensitivity emulsion reactively associated with a 3-pyrazolidinone compound.

The present invention preferably refers to a photographic element as per above including emulsions which, associated with a coupler and a sensitizer as described, give a sensitivity in a standard
10 color negative processing of at least 20 ASA, when processed in a C41 type process (see Photo Lab Index, Lifetime Ed., Morgan and Morgan Publishers).

The present invention in particular refers to the above described elements which contain emulsions having a silver iodide mole
15 percentage of at least 4, more preferably comprised between 4 and 20 and most preferably between 5 and 15.

The present invention in particular refers to a photographic element as described above, wherein the silver halide emulsions have a mean grain size of at least 0.30 micron. More in particular, it
20 refers to emulsions in which 30%, preferably 50% and more preferably 70% of the silver halide grains has a diameter higher than 0.30 micron.

Still in particular, the present invention refers to a photographic element as described above, wherein the tanning developer is a hydroquinone tanning developer.

25 Still in particular, the present invention refers to a photographic element as described above, wherein the tanning developer is pyrocatechol.

More in particular, the present invention refers to a photographic element as described above, wherein a single substantially
30 unhardened gelatin layer includes the silver halide emulsion, the photographically inert water insoluble colored pigment, the tanning developer and the 3-pyrazolidinone compound.

Still more in particular, the present invention refers to a photographic element as described above which comprises a base having coated thereon two superimposed substantially unhardened gelatin layers, one of which includes the silver halide emulsion and the tanning developer and the other the photographically inert water-insoluble colored pigment and the 3-pyrazolidinone compound.

Preferably, the present invention refers to a photographic element as described above, wherein the quantity of the 3-pyrazolidinone compound is in the range of 0.005 to 0.15 grams per square meter, more preferably of 0.01 to 0.1 grams per square meter and most preferably of 0.02 to 0.06 grams per square meter.

The conditions under which the elements of the present invention give surprising results are those based on an exposure to a 800 to 1200 volt flash for times ranging from 3 to 8 microseconds and then processing in an activating alkaline water bath. This normally includes an alkalizing agent (such as alkaline phosphates or carbonates, alkaline hydroxides, e.g. Na_2CO_3 at concentrations ranging from 0.4 to 15% by weight, preferably from 0.8 to 6% by weight and more preferably from 1 to 4% by weight) and, preferably, an agent retarding gelatin swelling (e.g. Na_2SO_4 at concentrations between 6 and 26% by weight, preferably between 10 and 20% and more preferably between 12 and 16% by weight). The activation normally takes place at temperatures ranging from 28 to 38°C, preferably from 30 to 36°C and more preferably from 32 to 34°C, in a time less than 60 seconds, preferably less than 40 seconds and more preferably less than 30 seconds.

In a particular aspect, the present invention refers to a process for the formation of a relief image with photographic elements for tanning development which consists of a short exposure thereof to high-intensity light and of a development under the above described conditions, characterized in that the exposure is performed with the above described emulsions and the development is carried out in the presence of a 3-pyrazolidinone compound associated therewith in said

photographic elements.

Emulsions particularly effective to the purposes of the present invention, as already indicated, are those normally used in conventional color photography, for instance bromo-iodide emulsions for color print negative photographic materials, such as for instance 3M Color Print ASA 100. Bromo-iodide emulsions used in radiography could also be used. In the choice, it is necessary to pay attention to the grain sizes, as already described. Of course, excessive grain sizes lead to quality decrease as regards definition and graininess. It is preferred than no more than 15% of the grains have sizes higher than 1 or 2 micron. The highest grain sizes of the emulsions of the present invention, anyhow, depend from the specific application of the invention itself and any man skilled in the art can find them with experiments depending upon his specific needs.

The emulsion type used is preferably a silver bromo-iodide or silver chloro-bromo-iodide emulsion as described hereinbefore, chemically and/or optically sensitized as known in the art.

The photographic elements for tanning development of the present invention comprise substantially unhardened gelatin, wherein substantially unhardened gelatin means gelatin which is not harder than that containing 0.3 grams of anhydrous formaline per each kilogram of fresh-coated gelatin as described in US patent 3,364,024. The base is one of the various bases known and used in photography, such as paper, resin-coated paper, cellulose triacetate and polyester bases.

Any dye material or pigment used in photography, which does not diffuse into the gelatin layer and is not reactive with the photographic emulsion to give negative phenomena such as fog or desensitization, can be used in the practice of the present invention. Carbon black, reduced colloidal silver, organic and inorganic pigments are examples of such dye materials, the most preferred being organic pigments which provide photographic elements for tanning development with a better stability over time. Particularly useful proved to be

some organic pigments sold in water dispersion, such as for instance Flexonil Blau of Hoechst, Rosso Sintosol NFRG, Arancio Velesta NPG, as well as Turchese Sintosol of ACNA. Such water dispersions are obtained by suspending the water-insoluble pigments in water containing a water-soluble solvent or polymer which acts as a support for the pigments themselves, as known in the art. Some dye mixtures, chosen so as to absorb red, green and blue light, as known in the art, to form a black colored layer, proved to particularly suitable to obtain black-colored images.

Among the tanning developers, whose oxidation products formed while developing the exposed element are capable of tanning the gelatin, the most preferred is hydroquinone (and the derivatives thereof such as chlorohydroquinone, bromohydroquinone, methylhydroquinone, morpholinohydroquinone) because of its wider action range due to a better stability of its oxidation product, but also other tanning developers such as pyrocatechol, pyrogallol and gallic acid can find an application in the photographic elements for tanning development of the present invention alone or in combination with hydroquinone. In particular, pyrocatechol gave very good results as regards sensitivity, image quality, definition and exposure latitude. Elements containing pyrocatechol proved also to have a longer shelf life.

A single gelatin layer coated on the base can at the same time contain the silver halide emulsion, the colored pigment, the tanning developer and the auxiliary developer, or such components of the photographic element can be distributed in separate gelatin layers coated on the base, for instance a gelatin layer containing the pigment and the auxiliary developer and a gelatin layer containing the silver halide emulsion and the tanning developer, or finally the said components can be contained in gelatin layers coated onto different bases to be put into contact during development.

Particularly useful to the purposes of the present invention proved to be the presence of a protective gelatin layer coated on

the photographic element in order to obtain a better coating quality and a better image quality of the developed element.

5 The auxiliary developers can be introduced during coating into the protective layer of the photographic element, into the gelatin layer containing the silver halide emulsion, into the gelatin layer containing the colored pigment or into the gelatin layer containing both the silver halide emulsion and the colored pigment. Of course immediately after coating, a given quantity of the auxiliary developer will diffuse into the adjacent gelatin layers, if present.

10 The photographic elements for tanning development of the present invention are developed by dipping them into an activating bath, followed by a stop bath and finally by washing them with water sprays. The activating bath contains an alkalizing agent such as sodium or potassium carbonate, sodium or potassium hydroxide. Particularly
15 useful was an activating bath including significant quantities of a water-miscible organic solvent, chosen in the class including dihydric alcohols, polyhydric alcohols and polyoxyethyleneglycols or mixtures thereof, and more particularly useful an activating bath including significant quantities of sodium sulfate in order to improve the
20 quality and repeatability of the obtained photographic results, especially when processing is performed with automatic processors provided with transporting rollers in contact with the air.

25 The stop bath can be a fixing bath, preferably a bleach-fixing bath (containing ferric-ammonium EDTA and thiosulfate), or an acid bath containing diluted acetic acid, or simply water.

30 The examples which follow to illustrate the present invention report experiments which make use of two emulsions (A and B) of the present invention in comparison with an emulsion (C) outside the scope of the present invention.

 In particular, emulsion A is a high-sensitivity silver bromo-iodide emulsion having 7% iodide moles, a mean silver halide grain size of 0.75 micron and at least 90% of the grains with a size

comprised between 0.35 and 1.6 micron. It is an emulsion which is used in color photographic materials (negative and reversal) which can be found on the market (such as 3M Color Print 100 ASA) and which, in the presence of a coupler, exposed for 1/20" at 5500°K and developed in the conventional (C41 type such as CNP₄) color processings, shows a sensitivity of about 100 ASA.

Emulsion B is a middle-sensitivity silver bromo-chloro-iodide emulsion having 5% chloride moles and 7% iodide moles, a silver halide grain size of about 0.35 micron and at least 60% of the grains with a size between 0.35 and 0.9 micron. It is an emulsion which is used in color photographic materials (negative and reversal) which can be found on the market (such as 3M Color Print 100 ASA) and which, in the presence of a coupler, exposed for 1/20" at 5500°K and developed in the conventional color processings, shows a sensitivity of about 40 ASA.

Emulsion C is a low-sensitivity silver bromo-chloride emulsion having 66% chloride moles, a mean silver halide grain size of 0.29 micron and only 13% of the grains with a size higher than 0.35 micron. It is an emulsion which is used in the materials for graphic arts which can be found on the market and which, exposed for 10" at 5200°K and developed in the conventional black-and-white processings, shows a sensitivity of about 0.4 ASA.

Example 1

25

A photographic element (Film A) for tanning development was prepared by coating a 10/100 resin-coated paper base with the following layers in the indicated order:

- 1) a light-insensitive unhardened gelatin pigmented layer containing gelatin at the coverage of 3 g/m² and a pigment dispersion (consisting of 4% gelatin, 11% Sintosomal Rosso and 9% Flexonil Blau) at a pigment total coverage of 2.2 g/m²;

- 2) a light-sensitive unhardened gelatin layer containing the high-sensitivity silver bromo-iodide emulsion (Emulsion A, having 93% bromide moles and 7% iodide moles), chemically and optically sensitized, at the coverage of 0.5 g/m^2 , gelatin in a quantity as to obtain a silver/gelatin weight ratio of 0.3 and hydroquinone in a quantity as to obtain a gelatin/hydroquinone weight ratio of 5.7;
- 3) an unhardened gelatin protective layer containing gelatin at the coverage of 1 g/m^2 and 2,5-diisooctylhydroquinone, dispersed with tricresylphosphate, at a coverage of 0.96 g/m^2 .

A second element (Film B) was prepared like the first one, but having coated on the base the following layers in the indicated order:

- 1) the same light-insensitive layer of Film A, but containing 0.02 g/m^2 of phenidone;
- 2) the same light-sensitive layer of Film A;
- 3) the same protective layer of Film A.

A third element (Film C) was prepared like the first one, having coated on the base the following layers in the indicated order:

- 1) the same light-insensitive layer of Film A;
- 2) the same light-sensitive layer of Film A, but having the low-sensitivity silver chloro-bromide emulsion (Emulsion C, having 66% chloride moles and 34% bromide moles) instead of Emulsion A;
- 3) the same protective layer of Film A.

A fourth element (Film D) was finally prepared like the first one, having coated on the base the following layers in the indicated order:

- 1) the same light-insensitive layer of Film C, but having 0.02 g/m^2 of phenidone;
- 2) the same light-sensitive layer of Film C;
- 3) the same protective layer of Film C.

Samples of the four elements were exposed in a 7700 Compu-graphic Editwriter Phototypesetter at 1000 volts for 3 microseconds and

processed in a roller automatic processor (Eskofot 965 Processor) in an activating bath (consisting of 700 ml. of 18% Na_2CO_3 and 300 ml. of ethyleneglycol) at 28°C, then in a stop bath (consisting of 0.2% acetic acid) at 40°C and finally washed with water sprays at room temperature.

5 In the case of Film A, C and D no tanning was obtained in the exposed regions, therefore no image was obtained, even with activating times longer than 1'30", while in the case of Film B a 40" activation was sufficient to obtain a tanned gelatin relief image of very good quality.

10

Example 2

A photographic element (Film A) for tanning development was prepared by coating a 10/100 resin-coated paper base with the following layers in the indicated order:

- 15 1) a light-insensitive unhardened gelatin layer containing gelatin at the coverage of 5 g/m^2 , the pigment dispersion of example 1 at a pigment total coverage of 2.2 g/m^2 and phenidone at a coverage of 0.005 g/m^2 ;
- 20 2) the same light-sensitive layer of Film A of example 1;
- 3) the same protective layer of Film A of example 1.

A second, third and fourth element (Film B, C and D) were prepared by coating a 10/100 resin-coated paper base with the following layers in the indicated order:

- 25 1) the same light-insensitive pigmented layer of Film A, but containing phenidone at the coverage of 0.01 (Film B), 0.02 (Film C) and 0.04 (Film D) g/m^2 , respectively;
- 2) the same light-sensitive layer of Film A of example 1;
- 3) the same protective layer of Film A of example 1.

30

Samples of the four films were exposed in a stroboscope under the same conditions as those reported in example 1 and processed in a roller automatic processor in an activating bath with water sprays

as described in example 1.

Samples of Film A were completely non-tanned and therefore no image was formed; samples of Film B were non-tanned only on the image edges; samples of Films C and D were tanned in a satisfactory manner. The image quality became better as the amount of phenidone increased in the insensitive pigmented layer.

Example 3

A photographic element (Film A) for tanning development was prepared by coating a 10/100 resin-coated paper base with the following layers in the indicated order:

- 1) a light-insensitive unhardened gelatin layer containing gelatin at the coverage of 3 g/m^2 , the pigment dispersion of example 1 at a pigment total coverage of 2.2 g/m^2 and phenidone at the coverage of 0.015 g/m^2 ;
- 2) a light-sensitive unhardened gelatin layer containing emulsion A of example 1 at the silver coverage of 0.4 g/m^2 , gelatin in a quantity as to obtain a silver/gelatin weight ratio of 0.3 and hydroquinone in a quantity as to obtain a gelatin/hydroquinone weight ratio of 5.7;
- 3) the same unhardened gelatin protective layer of Film A of example 1.

A second and a third elements (Films B and C) were prepared like the first one, having coated on the base the following layers in the indicated order:

- 1) the same light-insensitive layer of Film A, but containing phenidone at the coverage of 0.02 (Film B) and 0.025 g/m^2 (Film C), respectively;
- 2) the same light-sensitive layer of Film A;
- 3) the same protective layer of Film A.

Samples of the three films were exposed and processed in the same way as that described in example 2.

In the samples of Film A, tanning resulted poor, while it was good in the samples of both Film B and C; the image quality improved as the quantity of phenidone in the element increased.

5

Example 4

Six photographic elements (Films from A to F) for tanning development were prepared by coating a 10/100 resin-coated paper base with the following layers in the indicated order:

- 10 1) a light-insensitive unhardened gelatin layer containing gelatin at the coverage of 3 g/m^2 , the pigment dispersion of example 1 at a pigment total coverage of 2.2 g/m^2 and phenidone at the coverage of 0.02 (Films A, C and E) and 0.03 (Films B, D and F) g/m^2 , respectively;
- 15 2) a light-sensitive unhardened gelatin layer containing the medium sensitivity silver iodo-chloro-bromide emulsion (Emulsion B, having 88% bromide moles and 7% iodide moles), chemically and optically sensitized, at the silver coverage of 0.4 g/m^2 , gelatin in a quantity as to give a silver/gelatin weight ratio of 0.3 (Films A and B),
20 0.4 (Films C and D) and 0.5 (Films E and F), respectively and hydroquinone in a quantity as to give a gelatin/hydroquinone weight ratio of 5.7;
- 3) the same gelatin protective layer of Example 1.

25 Samples of the six elements were exposed in a stroboscope for 3 microseconds under lighting conditions equal to those described in example 1 and processed for 40" in an activating bath, then in a stop bath and finally washed with water sprays as described in the preceding examples.

30 All the samples of the six elements resulted to be well tanned; the image quality was better in Films A and B and best in Film B.

Example 5

Three photographic elements (Films A, B and C) for tanning development were prepared by coating a 10/100 resin-coated paper base with the following layers in the indicated order:

1) a light-sensitive unhardened gelatin layer containing the emulsion of example 4 at the coverage of 0.4 g/m^2 , gelatin in a quantity as to obtain a silver/gelatin weight ratio of 0.4, hydroquinone in a quantity as to obtain a gelatin/hydroquinone weight ratio of 8, 2,5-diisooctylhydroquinone, dispersed with tricresylphosphate, at the coverage of 0.05 g/m^2 , the pigment dispersion of example 1 at a pigment total coverage of 0.8 g/m^2 and phenidone at the coverage of 0 (Film A), 0.025 (Film B) and 0.05 g/m^2 (Film C);

2) an unhardened gelatin protective layer containing gelatin at the coverage of 1 g/m^2 .

Samples of the three elements were exposed in a 7700 Compugraphic Editwriter Phototypesetter for 3 microseconds with a 1000 volt flash and developed in a roller automatic processor (Eskofot 965) in an activating bath consisting of 2% Na_2CO_3 and 13% Na_2SO_4 for 20" at 33°C, then in a stop bath consisting of water at 40°C for 25" and finally washed with water sprays at room temperature. In the case of Film A, no tanning was obtained in the exposed regions (no image was obtained), while in the case of Films B and C a good tanning was obtained with image formation having better quality as the phenidone content increased.

Example 6

Nine photographic elements (Films from A to I) for tanning development were prepared by coating a 10/100 resin-coated paper base with the following layers in the indicated order:

1) a light-insensitive unhardened gelatin pigmented layer containing

gelatin at a coverage of 1.5 g/m^2 , a black colloidal silver dispersion at a silver coverage of 0.13 g/m^2 and phenidone at the coverage reported in the following table;

- 2) a light-sensitive unhardened gelatin layer containing the emulsion of example 5 at the silver coverage reported in the following table, gelatin in a quantity as to obtain a silver/gelatin weight ratio of 0.3 and hydroquinone in a quantity as to obtain a gelatin/hydroquinone weight ratio reported in the following table:

	Film	Phenidone g/m^2	Silver g/m^2	Gelatin/Hydroquinone
10	A	0.018	0.43	5.74
	B	0.0337	0.43	5.74
	C	0.018	0.58	5.74
	D	0.0337	0.58	5.74
15	E	0.018	0.43	10.66
	F	0.0337	0.43	10.66
	G	0.018	0.58	10.66
	H	0.0337	0.58	10.66
	I	0.026	0.51	8.20

- 20 Samples of the elements were exposed in a 7700 Compugraphic Editwriter Phototypesetter and processed in a roller automatic processor at the speed of 50 cm/min. in an activating bath of the following composition:

25 Na_2SO_4 : 130 g/liter
 Na_2CO_3 : 20 g/liter
 pH: 12.4,

- then in a stop bath consisting of water at 47°C and finally washed with water sprays at room temperature. The best results, as regards tanning and image quality, were obtained with the samples of Film F and H; slightly inferior, yet acceptable results were on the contrary obtained with the samples of Films B, D and I, while with the samples of Films A, C, E and G no tanning or a bad tanning was obtained.

Example 7

Nine photographic elements (Films from A to I) for tanning development were prepared by coating a 10/100 resin-coated paper base with the following layers in the indicated order:

- 1) a light-sensitive unhardened gelatin layer containing emulsion A of example 1 at the silver coverage of 0.45 g/m^2 , gelatin so as to obtain the silver/gelatin ratios reported in the following table, pyrocatechol in a quantity as to obtain the gelatin/catechol weight ratios reported in the following table, phenidone at the coverage reported in the following table and a gelatin dispersion of the pigments Flexonil Blau and Colanil Red in a weight ratio of 1:1 at a pigment total coverage of 0.8 g/m^2 ;
- 2) an unhardened gelatin protective layer containing gelatin at the coverage of 1 g/m^2 and 2,5-diisooctylhydroquinone, dispersed with tricresylphosphate, at the coverage of 0.14 g/m^2 .

<u>Film</u>	<u>Silver/Gelatin</u>	<u>Gelatin/Pyrocatechol</u>	<u>Phenidone</u>
			(g/m^2)
A	0.25	6	0.003
B	0.45	6	0.003
C	0.25	12	0.003
D	0.45	12	0.003
E	0.25	6	0.009
F	0.45	6	0.009
G	0.25	12	0.009
H	0.45	12	0.009
I	0.35	6	0.006

Samples of the elements were exposed in a 7700 Compugraphic Editwriter Phototypesetter and developed in a roller automatic processor (Eskofot 842 Processor) in an activating bath of the following composition:

Na_2SO_4 : from 12.2 to 15%

Na_2CO_3 : from 2.5 to 3%

pH: from 10.3 to 10.8

for times ranging from 20 to 30 seconds at a temperature from 32 to
 5 35°C, then in stop bath consisting of water at 40°C and finally washed
 with water sprays at room temperature.

Good results as regards sensitivity, edge quality and
 image quality were obtained with Film F and still better results with
 the films having a silver/gelatin weight ratio of 0.25 and 0.35, a
 10 gelatin/catechol weight ratio of 6 and 9 and a phenidone coverage of
 0.009 g/m^2 .

C l a i m s :

1. Photographic element for tanning development to be used with short exposures to high-intensity light having at least one unhardened gelatin layer associated with a light-sensitive silver halide emulsion, a colored pigment and a tanning developer, characterized in that such emulsion is a high-sensitivity emulsion associated with a 3-pyrazolidinone compound coated at a coverage lower than 0.6 grams per square meter and with a silver/gelatin weight ratio lower than 0.4.

2. Photographic element according to claim 1, wherein the silver halide emulsions contains at least 4% of silver iodide.

3. Photographic element according to claim 1, wherein the silver halide emulsion contains from 4 to 20% of silver iodide.

4. Photographic element according to claim 1, wherein the silver halide emulsion contains from 5 to 15% of silver iodide.

5. Photographic element according to claim 1, wherein the silver halide emulsion has a mean grain size of at least 0.30 micron.

6. Photographic element according to claim 1, wherein at least 30% of the silver halide grains has a size higher than 0.30 micron.

7. Photographic element according to claim 1, wherein at least 50% of the silver halide grains has a size higher than 0.30 micron.

8. Photographic element according to claim 1, wherein at

least 70% of the silver halide grains has a size higher than 0.30 micron.

9. Photographic element according to claim 1, wherein the
5 tanning developer is hydroquinone.

10. Photographic element according to claim 1, wherein the
tanning developer is pyrocatechol.

11. Photographic element according to claim 1, wherein the
10 3-pyrazolidinone compound is 1-phenyl-3-pyrazolidinone.

12. Photographic element according to claim 1, wherein a
single substantially unhardened gelatin layer includes the silver
15 halide emulsion, the tanning developer, the water-insoluble photogra-
phically inert colored pigment and the 3-pyrazolidinone compound.

13. Photographic element according to claim 1, which
comprises a base having coated thereon two superimposed unhardened
20 gelatin layers, one of which includes the silver halide emulsion and
the tanning developer and the other includes the water-insoluble photo-
graphically inert pigment and the 3-pyrazolidinone compound.

14. Photographic element according to claims from 1 to 13,
25 wherein the quantity of the 3-pyrazolidinone compound is in the range
from 0.005 to 0.15 grams per square meter.



European Patent
Office

EUROPEAN SEARCH REPORT

0104351

Application number

EP 83 10 7210

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. 3)
X,Y	US-A-3 240 599 (E.C. YACKEL et al.) * Whole document *	1-14	G 03 C 1/42 G 03 C 5/36
Y	GB-A-2 020 834 (3M) * Page 2, lines 4-15, 22-31 *	1-14	
Y	DE-C- 358 093 (G. KOPPMANN) * Whole document *	1	
Y	US-A-3 300 307 (A.C. SMITH) * Whole document *	1-14	
A	US-A-2 500 052 (E.C. YACKEL) * Figure 2 *	1	
P,X D	US-A-4 369 245 (M. BERUTO et al.) * Whole document *	1-14	TECHNICAL FIELDS SEARCHED (Int. Cl. 3) G 03 C 1/00 G 03 C 5/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19-01-1984	Examiner RASSCHAERT A.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			