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(54) Ultra rapid processed, photographic element.

(57) It is desirable from an economic standpoint to be able to more rapidly develop silver halide photographic elements. It has been found in the practice of the present invention that by a combination of particular grain sizes, ratio of gelatin to silver halide, and coating weights, the drying time of emulsions can be reduced without adversely affecting sensitometry.

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ULTRA RAPID PROCESSED, PHOTOGRAPHIC ELEMENT

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to photographic film capable of ultra rapid processing in automatic processors, and particularly to rapid processable black-and-white electronic imaging films or roomlight handleable graphic arts films.

2. Background of the Invention

A consistent goal in photography has been the reduction in time required to process a photographic film to obtain a high quality image. Many improvements had to be implemented both in the photographic film and processing chemistry before medical imaging moved from hand processing to automatic processors producing high quality images in 90 seconds. The improvements had to be made in four critical functions which are development, fixing, washing and drying. The reason why improvements had to be made in the functions themselves is that as the processing cycle is shortened, one or more of these are not completed. This can lend to images having low density, dye stain, film dampness or other deficiencies. Although the goal of more rapid processing is desirable, the shortened development, fixing, washing and drying cycles place more stringent requirements on the photographic film.

A major advance occurred with the advent of automatic processors with dry-to-dry cycle times of 90 seconds. An example of the automatic processors is described in Russell et al., U.S. Patent No. 3,025,779 and the film is presented in Barnes et al., U.S. Patent No. 3,545,971. Additional research has gone into additives to reduce swelling and improve drying as outlined in Allen et al., U.S. Patent No. 3,232,761 and G.B. Patent No. 1,336,113. Also receiving attention were improvements in development as described in Habu et al., U.S. Patent No. 4,145,218, Jacobson, U.S. Patent No. 3,832,178 and Pollet et al., U.S. Patent No. 4,132,551 and advances in fog stability as described in Machida et al., E.P. 89,231 and Sakamoto et al., E.P. 237,256. Finally, ultra rapid processing systems have been described in Suzuki et al., E.P. 239,363, Suzuki et al., E.P. 238,271, Suzuki et al., E.P. 248,390 and Schwienbacher, U.S. Patent No. 3,694,209.

Our invention is aimed at laser scanners, particularly those using a Helium/Neon laser or laser diodes. Any other laser source may also be used, of course. The diode has the benefit of potentially huge power increases over other laser sources. A commercially available 3M Laser Imager uses a 15 mW diode. However, literature has already appeared on 100 mW diodes.

Ultra Rapid Processing is defined in the content of the present invention as 10 to 60 seconds dry-to-dry time in an automatic processor.

The present invention is aimed particularly at electronic imaging due to the potential for more powerful exposing devices. The introduction of more powerful imaging devices will lead to finer grain silver halide films requiring thinner layers or less gelatin. The reduced gelatin and fine grain emulsion are extremely advantageous for rapid processing. Also critical is a high hardness to reduce swelling and water retention which reduces the demands of drying.

A good example of increased power from a recording device is a laser diode. The present laser diode scanners (3M Laser Imager) use a 15 mwatt diode emitting in the near infrared, commonly from 770 to 830 nm. Literature has already appeared on experimental laser diodes capable of producing 100 mwatts of output power. This would mean a 6 to 7 fold power increase over the present 15 mwatt diode. The increased power will permit the use of a much smaller silver halide grain leading to a much easier transition to an ultra rapid processing system.

The driving forces to ultra rapid processing are quite basic. The first would be an increase in productivity. More films could be processed in a given time period. The second is faster throughput for an individual film so as to reduce the waiting time from 90 to 30 seconds. This would be useful in medical applications such as in an emergency room or in determining whether additional images are required to complete a patient examination.

It would also be very advantageous to have thin layers and fast throughput in various areas of the pre-press, graphic arts film usage. The thinner layers with less gelatin per area offer advantages for reducing

film dimension changes due to the effects of preconditioning, processing and drying. Also, faster turn-around times would help increase productivity by almost instantly permitting evaluation of a particular exposure. This would be especially beneficial in stripping operations where many contact and duplicating films are made as part of the preparation of composites for the generation of printing plates. The fast throughput would be equally advantageous when making masks or producing color modifioations as in dry etching.

SUMMARY OF THE INVENTION

The present invention describes an ultra rapid processing system for silver halide photographic films. The invention is directed towards electronic imaging in the medical markets such as CRT or laser imaging and to roomlight handleable graphic arts films. However, this is not meant to limit the invention to the medical market or electronic imaging. The invention is demonstrated with fine grain, silver halide films exposed with a laser scanning device.

Any of the various types of photographic silver halide emulsions may be used in the practice of the present invention. Silver chloride, silver bromide, silver iodo bromide, silver chlorobromide, silver chlorobromoiodide and mixtures thereof may be used for example. Any configuration of grains, cubic orthorhombic, hexagonal, epitaxial, lamellar, tabular or mixtures thereof may be used. These emulsions are prepared by any of the well known procedures, e.g., single or double jet emulsions as described by Nietz et al., U.S. Patent 2,222,264, Illingsworth, U.S. Patent 3,320,069, McBride, U.S. Patent 3,271,157 and U.S. Patents 4,425,425 and 4,425,426.

The silver halide emulsions of this invention can be unwashed or washed to remove soluble salts. In the latter case the soluble salts can be removed by chill-setting and leaching or the emulsion can be coagulation washed e.g., by the procedures described in Hewitson et al., U.S. Patent 2,618,556; Yutzy et al., U.S. Patent 2,614,928; Yackel, U.S. Patent 2,565,418; Hart et al., U.S. Patent 3,241,969; and Waller et al., U.S. Patent 2,489,341.

Photographic emulsions in accordance with this invention can be sensitized with chemical sensitizers, such as with reducing agents; sulfur, selenium or tellurium compounds; gold, platinum or palladium compounds; or combinations of these. Suitable chemical sensitization procedures are described in Shepard, U.S. Patent 1,623,499; Waller, U.S. Patent 2,399,083; McVeigh, U.S. Patent 3,297,447; and Dunn, U.S. Patent 3,297,446.

The silver halide emulsions of this invention can contain speed increasing compounds such as polyalkylene glycols, cationic surface active agents and thioethers or combinations of these as described in Piper, U.S. Patent 2,886,437; Chechak, U.S. patent 3,046,134; Carroll et al., U.S. Patent 2,944,900; and Goffe, U.S. Patent 3,294,540.

Silver halide emulsions of this invention can be protected against the production of fog and can be stabilized against loss of sensitivity during keeping. Suitable antifoggants and stabilizers which can be used alone or in combination, include the thiazolium salts described in Staud, U.S. Patent 2,131,038 and Allen U.S. Patent 2,694,716; the azaindenes described in Piper, U.S. Patent 2,886,437 and Heimbach, U.S. Patent 2,444,605; the mercury salts described in Allen, U.S. Patent 2,728,663; the urazoles described in Anderson, U.S. Patent 3,287,135; the sulfocatechols described in Kennard, U.S. Patent 3,235,652; the oximes described in Carrol et al., British Patent 623,448; nitron; nitroindazoles; the polyvalent metal salts described in Jones, U.S. Patent 2,839,405; the thiuronium salts described in Herz, U.5. Patent 3,220,839; and the palladium, platinum and gold salts described in Trivelli, U.S. Patent 2,566,263 and Damschroder, U.S. Patent 2,597,915.

Silver halide grains in accordance with the invention can be dispersed in colloids that can be hardened by various organic or inorganic hardeners, alone or in combination, such as the aldehydes, and blocked aldehydes, ketones, carboxylic and carbonic acid derivatives, sulfonate esters, sulfonyl halides and vinyl sulfones, active halogen compounds, epoxy compounds, aziridines, active olefins, isocyanates, carbodiimides, mixed function hardeners and polymeric hardeners such as oxidized polysaccharides, e.g., dialdehyde starch, oxyguargum, etc.

Photographic emulsions according to the present invention can contain various colloids alone or in combination as vehicles or binding agents. Suitable hydrophilic materials include both naturally-occurring substances such as proteins, for example, gelatin, gelatin derivatives (e.g., phthalated gelatin), cellulose derivatives, polysaccharides such as dextran, gum arabic and the like; and synthetic polymeric substances such as water soluble polyvinyl compounds, e.g., poly(vinylpyrrolidone) acrylamide polymers or other

synthetic polymeric compounds such as dispersed vinyl compounds in latex form, and particularly those which increase the dimensional stability of the photographic materials. Suitable synthetic polymers include those described, for example, in U.S. Patents 3,142,568 of Nottorf; 3,193,386 of White; 3,062,674 of Houck, Smith and Yudelson; 3,220,844 of Houck, Smith and Yudelson; Ream and Fowler, 3,287,289; and Dykstra, U.S. Patent 3,411,911; particularly effective are those water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates, those which have cross linking sites which facilitate hardening or curing and those having recurring sulfobetaine units as described in Canadian Patent 774,054.

Emulsions in accordance with this invention can be used in photographic elements which contain antistatic or conducting layers, such as layers that comprise soluble salts, e.g., chlorides, nitrates, etc., evaporated metal layers, ionic polymers such as those described in Minsk, U.S. Patents 2,861,056 and 3,206,312 or insoluble inorganic salts such as those described in Trevoy, U.S. Patent 3,428,451.

Photographic emulsions of the invention can be coated on a wide variety of supports. Typical supports include polyester film, subbed polyester film, poly(ethylene terephthalate) film, cellulose nitrate film, cellulose ester film, poly(vinyl acetal) film, polycarbonate film and related or resinous materials, as well as glass, paper, metal and the like. Typically, a flexible support is employed, especially a paper support, which can be partially acetylated or coated with baryta and/or an alpha-olefin polymer, particularly a polymer of an alpha-olefin containing 2 to 10 carbon atoms such as polyethylene, polypropylene, ethylenebutene copolymers and the like.

Emulsions of the invention can contain plasticizers and lubricants such as polyalcohols, e.g., glycerin and diols of the type described in Milton, U.S. Patent 2,960,404; fatty acids or esters such as those described in Robijns, U.S. Patent 2,588,765 and Duane, U.S. Patent 3,121,060; and silicone resins such as those described in DuPont British Patent 955,061.

The photographic emulsions as described herein can contain surfactants such as saponin, anionic compounds such as the alkylarylsulfonates described in Baldsiefen, U.S. Patent 2,600,831 fluorinated surfactants, and amphoteric compounds such as those described in Ben-Ezra, U.S. Patent 3,133,816.

Photographic elements containing emulsion layers as described herein can contain matting agents such as starch, titanium dioxide, zinc oxide, silica, polymeric beads including beads of the type described in Jelley et al., U.S. Patent 2,992,101 and Lynn, U.S. Patent 2,701,245.

Emulsions of the invention can be utilized in photographic elements which contain brightening agents including stilbene, triazine, oxazole and coumarin brightening agents. Water soluble brightening agents can be used such as those described in Albers et al., German Patent 972,067 and McFall et al., U.S. Patent 2,933,390 or dispersions of brighteners can be used such as those described in Jansen, German Patent 1,150,274 and Oetiker et al., U.S. Patent 3,406,070.

Photographic elements containing emulsion layers according to the present invention can be used in photographic elements which contain light absorbing materials and filter dyes such as those described in Sawdey, U.S. Patent 3,253,921; Gaspar, U.S. Patent 2,274,782; Carroll et al., U.S. Patent 2,527,583 and Van Campen, U.S. Patent 2,956,879. If desired, the dyes can be mordanted, for example, as described in Milton and Jones, U.S. Patent 3,282,699.

Contrast enhancing additives such as hydrazines, rhodium, iridium and combinations thereof are also useful.

Photographic emulsions of this invention can be coated by various coating procedures including dip coating, air knife coating, curtain coating, or extrusion coating using hoppers of the type described in Beguin, U.S. Patent 2,681,294. If desired, two or more layers may be coated simultaneously by the procedures described in Russell, U.S. Patent 2,761,791 and Wynn, British Patent 837,095.

The silver halide photographic elements can be used to form dye images therein through the selective formation of dyes. The photographic elements described above for forming silver images can be used to form dye images by employing developers containing dye image formers, such as color couplers, as illustrated by U.K. Patent No. 478,984; Yager et al., U.S. Patent No, 3,113,864; Vittum et al., U.S. Patent Nos. 3,002,836, 2,271,238 and 2,362,598. Schwan et al. U.S. Patent No. 2,950,970; Carroll et al., U.S. Patent No. 2,592,243; Porter et al., U.S. Patent Nos. 2,343,703, 2,376,380 and 2,369,489; Spath U.K. Patent No. 886,723 and U.S. Patent No. 2,899,306; Tuite U.S. Patent No. 3,152,896 and Mannes et al., U.S. Patent Nos. 2,115,394, 2,252,718 and 2,108,602, and Pilato U.S. patent No. 3,547,650. In this form the developer contains a color-developing agent (e.g., a primary aromatic amine which in its oxidized form is capable of reacting with the coupler (coupling) to form the image dye. Also, instant self-developing diffusion transfer film can be used as well as photothermographic color film or paper using silver halide in catalytic proximity to reducable silver sources and leuco dyes.

The couplers may be present either directly bound by a hydrophilic colloid or carried in a high

temperature boiling organic solvent which is then dispersed within a hydrophilic colloids. The colloid may be partially hardened or fully hardened by any of the variously known photographic hardeners. Such hardeners are free aldehydes (U.S. Patent 3,232,764), aldehyde releasing compounds (U.S. Patent 2,870,013 and 3,819,608), s-triazines and diazines (U.S. Patent 3,325,287 and 3,992,366), aziridines (U.S. Patent 3,271,175), vinylsulfones (U.S. Patent 3,490,911), carbodiimides, and the like may be used.

The dye-forming couplers can be incorporated in the photographic elements, as illustrated by Schneider et al. Die Chemie, Vol. 57, 1944, p. 113, Mannes et al. U.S. Patent No. 2,304,940, Martinez U.S. Patent No. 2,269,158, Jelley et al. U.S. Patent No. 2,322,027, Frolich et al. U.S. Patent No. 2,376,679, Fierke et al. U.S. Patent No. 2,801,171, Smith U.S. Patent No. 3,748,141, Tong U.S. Patent No. 2,772,163, Thirtle et al. U.S. Patent No. 2,835,579, Sawdey et al. U.S. Patent No. 2,533,514, Peterson U.S. Patent No. 2,353,754, Seidel U.S. Patent No. 3,409,435 and Chen Research Disclosure, Vol. 159, July 1977, Item 15930. The dye-forming couplers can be incorporated in different amounts to achieve differing photographic effects. For example, U.K. Patent No. 923,045 and Kumai et al. U.S. Patent No. 3,843,369 teach limiting the concentration of coupler in relation to the silver coverage to less than normally employed amounts in faster and intermediate speed emulsion layers.

The dye-forming couplers are commonly chosen to form subtractive primary (i.e., yellow, magenta and cyan) image dyes and are non-diffusible, colorless couplers, such as two and four equivalent couplers of the open chain ketomethylene, pyrazolone, pyrazolone, pyrazolotriazole, pyrazolobenzimidazole, phenol and naphthol type hydrophobically ballasted for incorporation in high-boiling organic (coupler) solvents.

Other conventional photographic addenda such as coating aids, antistatic agents, acutance dyes, antihalation dyes and layers, antifoggants, latent image stabilizers, antikinking agents, and the like may also be present.

Although not essential in the practice of the present invention, one particularly important class of additives which finds particular advantage in the practice of the present invention is high intensity reciprocity failure (HIRF) reducers. Amongst the many types of stabilizers for this purpose are chloropalladites and chloroplatinates (U.S. Patent No. 2,566,263), iridium and/or rhodium salts (U.S. Patent No. 2,566,263; 3,901,713), cyanorhodates (Beck et al., J. Signalaufzeichnungsmaterialen, 1976, 4, 131), and cyanoiridates.

EXPERIMENTAL

The films were tested in a modified 3M XP-515, 90 second, automatic processor which (in the standard operating mode) can be adjusted to give dry-to-dry processing times of roughly 120 to 70 seconds. The standard production model was modified by switching the drive gears. This allowed dry-to-dry processing times of 90 to 22 seconds. The XP-515 processor uses a water spray system and has infrared drying. The processor contained Kodak RP X-Omat developer and fix. The fix temperature was 91 ° F throughout the study whereas the developer temperature was examined at 95 and 104 ° F.

A hardness test was run on many of the coatings. This test determines the melting time of the light sensitive material and was described previously on page 110 of Suzuki, E.P.A. 238,271. A 1 cm by 2 cm film strip is cut and immersed in a 1.5% aqueous, sodium hydroxide solution. The sodium hydroxide solution was held at 50 ° C without agitation. The melting time is the time required for the emulsion layer to dissolve into the sodium hydroxide solution.

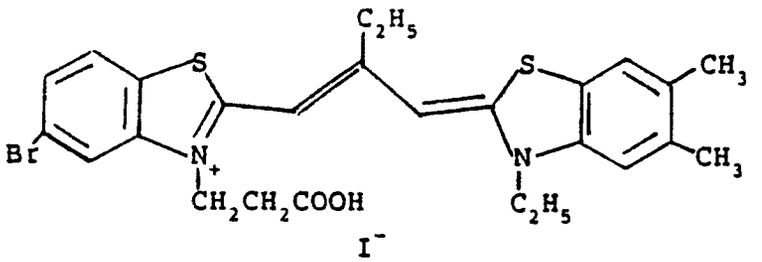
The drying property and water content of the films were evaluated by procedures described on page 117 and 108 respectively of Suzuki, E.P.A. 238,271. The drying property of a film was evaluated by the degree of sticking between processed films. The processing cycle time in each case was 30 seconds dry-to-dry and the rating scale was 1 (poor) to 5 (excellent). Ratings 3-5 were considered acceptable but rating 2 would be insufficient drying for practical applications. The water content of the photographic materials was measured in a fashion very similar to that described in E.P.A. 238,271. The films were run through a Kodak M6 processor containing Kodak RP X-Omat developer and fix at 95 ° F and 90 ° F respectively. The 20 by 20 cm test films were exposed to light and then partially processed. They were removed from the M6 processor after the water wash stage but before reaching the drying zone. The elapsed time was 60 seconds from when the film entered the processor to when it exited the water wash. The wet film was then measured within 60 seconds to give the wet weight Ww(g). The dry weight, Wd(g) was measured after drying the film and allowing at least one hour equilibration time at 72 ° F and 55% r.h. The water content of the film was then calculated from the following equation:

Water Content (g/m^2) = (Ww-Wd) x (10,000 cm^2/20cm x 20cm)

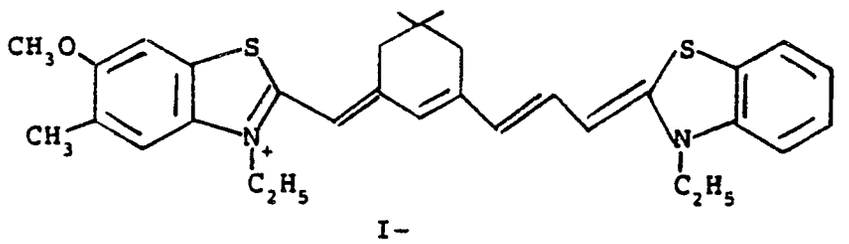
Four silver halide emulsions were used to demonstrate the invention. All were prepared by a double jet precipitation. Emulsion A was a 64% chloride and 36% bromide emulsion with an average size of 0.24 micrometers. Emulsion B was an ammoniacal iodobromide emulsion with all potassium iodide and ammonia in the kettle before precipitation. The resulting emulsion was 3% iodide and 97% bromide with an average grain size of 0.24 micrometers. Emulsion C was a 64% chloride and 36% bromide emulsion with an average grain size of 0.17μ. Emulsion D was a 90% chloride and 10% bromide emulsion with a 0.09 micrometer average grain size. Emulsions A, C and D were chemically digested with p-toluenesulfinic acid, sodium thiosulfate and sodium gold tetrachloride ($NaAuCl_4$). A sulfur and gold digest was used for emulsion B.

Final preparation of the emulsions comprised adjusting the pH to 6.5 to 7.0 and the pAg to 7.2. Sensitizing dyes (1-3 below), phenyl-5-mercaptotetrazole (PMT), ammonium salts and phosphonium salts were added as methanol solutions. Poly(ethylacrylate) (PEA) was added as a 20% aqueous dispersion. Formaldehyde hardener and leucophor BCF (LEUC, Sandoz) were added as aqueous solutions.

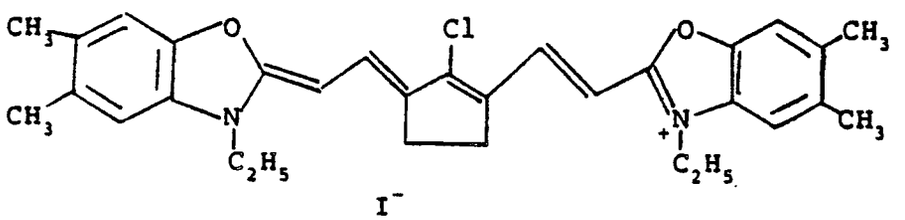
D1



D2



D3



The coated and dried films were aged one week before exposing on a sensitometer for 10^{-3} seconds through various narrow band filters to mimic the light output of the different laser devices. Sensitometric results include Dmin, Dmax, Speed (at 0.D. = 1.0), average contrast (CONT) and change in speed and contrast due to reducing the processing time from 90 to 30 seconds (Δ90 to 30).

EXAMPLES 1-5

An experiment was run to test the importance of gelatin level to ultra rapid processing. Emulsion A (0.24 microns, Cl/Br) was coated with different levels of gelatin and overcoated with varying thickness of topcoat (TC). The coating additives per mole of silver consisted of 30 mg of infrared dye, Dye 2, 115 mg of PMT, 20 g of PEA and 11 mg (per g of gelatin) of formaldehyde. The films were coated at 2.4 grams of silver per square meter on blue, 7 mil polyester base with an infrared absorbing, antihalation back coating. The AH formula was described in U.S. Patent Application 59,931, Example 2. The AH flows were reduced to 68% for this application which produced an AH layer with 2.80 g gelatin/m^2 and 3.65 mg of formaldehyde hardener per gram of gelatin. The materials were exposed with a 820 nm narrow band filter and developed

with processor cycle times of 90, 45 and 30 seconds at both 104° and 95° F developer temperature. The results are listed in Table 1.

It can be concluded form Table 1 that lower gelatin levels reduce the loss of speed and contrast for ultra rapid processing. Additional improvements are obtained by the higher developer temperature of 104° F which increases the initial speed and contrast of the films and also reduces the speed and contrast drops when processing dry-to-dry in 30 seconds.

TABLE 1

Ex.	Gel Content (g/m^2 per side) Emul Layer	TC Layer	Gel Total	Hardener (mg/g gel)	Drying Property (30 sec)	Melting Time (min)	Water Retention (g/m^2)
1	1.74	0.75	2.49	11.0	5	85	8.5
2	1.74	1.31	3.05	11.0	4	95	9.3
3	2.11	0.75	2.86	11.0	5	90	9.1
4	2.11	1.31	3.42	11.0	4	95	9.2
5	2.48	0.75	3.23	11.0	3	92	9.5
A	2.48	1.03	3.51	11.0	2	90	10.2
B	2.48	1.31	3.79	11.0	2	95	10.4

TABLE 1 (cont.)

Ex.	Dev. Temp (°F)	90 Second Processing				45 Second Processing				30 Second Processing				Δ 90 to 30	
		Dmin	Dmax	SPD	CONT	Dmin	Dmax	SPD	CONT	Dmin	Dmax	SPD	CONT	SPD	CONT
1	95	0.18	3.38	2.23	2.60	0.18	3.31	2.12	2.47	0.17	3.23	2.05	2.35	0.18	0.25
2	95	0.18	3.33	2.17	2.52	0.18	3.19	2.05	2.34	0.17	2.92	1.97	2.07	0.20	0.45
3	95	0.18	3.36	2.22	2.62	0.18	3.29	2.09	2.44	0.17	3.00	1.99	2.15	0.23	0.47
4	95	0.18	3.35	2.16	2.55	0.17	3.07	2.01	2.20	0.17	2.84	1.93	1.94	0.23	0.61
5	95	0.18	3.40	2.23	2.57	0.17	3.31	2.12	2.42	0.17	3.04	2.03	2.14	0.20	0.43
A	95	0.18	3.34	2.21	2.55	0.17	3.12	2.07	2.34	0.17	2.92	1.98	2.06	0.23	0.49
B	95	0.18	3.28	2.14	2.49	0.17	3.10	2.01	2.19	0.17	2.75	1.92	1.82	0.22	0.67

TABLE 1 (cont.)

Ex.	Dev. Temp (°F)	90 Second Processing				45 Second Processing				30 Second Processing				Δ 90 to 30	
		Dmin	Dmax	SPD	CONT	Dmin	Dmax	SPD	CONT	Dmin	Dmax	SPD	CONT	SPD	CONT
1	104	0.19	3.52	2.33	2.55	0.18	3.38	2.23	2.57	0.18	3.36	2.18	2.48	0.15	0.07
2	104	0.19	3.39	2.25	2.48	0.18	3.37	2.17	2.45	0.18	3.15	2.08	2.26	0.17	0.22
3	104	0.19	3.36	2.29	2.58	0.18	3.34	2.20	2.52	0.18	3.22	2.14	2.38	0.15	0.20
4	104	0.19	3.35	2.25	2.48	0.18	3.33	2.16	2.44	0.18	3.10	2.07	2.24	0.18	0.24
5	104	0.19	3.46	2.32	2.55	0.18	3.39	2.22	2.52	0.18	3.26	2.15	2.34	0.17	0.21
A	104	0.19	3.32	2.28	2.51	0.18	3.24	2.18	2.45	0.18	3.16	2.12	2.31	0.16	0.20
B	104	0.19	3.27	2.21	2.31	0.18	3.04	2.09	2.25	0.18	2.92	2.04	2.10	0.17	0.21

EXAMPLES 6-16

The effects of hardener level (formaldehyde) ammonium salts and phosphonium salts were evaluated using the same emulsion and procedure as described in Examples 1-5. The changes are listed in Table 2 and include the quantity of formaldehyde and the addition of the following ammonium and phosphonium salts.

PPh_4Cl : tetraphenylphosphonium chloride
PPh_4Br : tetraphenylphosphonium bromide
TPMP : triphenylmethyltriphenylphosphonium bromide
THAI : tetraheptylammonium iodide

The results are listed in Table 2 with all trials coated at 2.4 g Ag/m^2. The ammonium and phosphonium salts show little, if any, improvement in the loss of speed and contrast for 30 second processing at a developer temperature of 95° F. However, the ammonium and phosphonium salts greatly reduce the loss of speed and contrast for 30 second development at a developer temperature of 104° F. The favored salt would be the ammonium salt, THAI, which increases the initial speed and provides sensitometric values at 30 second processing in 104° F developer (see Example 14) equal to a system without any additives (Example 6) processed in 90 seconds with 95° F developer.

The hardness level is also critical for rapid processing. Lower hardener quantities (Examples C and D) reduce the loss of speed and contrast on rapid processing but lead to reduced drying properties and melting times. Therefore, the level of hardener is critical to ultra rapid processing and must be sufficient to ensure adequate drying.

TABLE 2

Ex.	Gel Content (g/m^2 per side) Emul Layer	TC Layer	Gel Total	Organic Salt	Hardener (mg/g gel)	Drying Property (30 sec)	Melting Time (min)	Water Retention (g/m^2)
6	1.74	0.75	2.49	none	11.0	5	90	8.5
7	1.74	0.75	2.49	100 mg PPh_4Cl	11.0	5	65	8.6
8	1.74	0.75	2.49	400 mg PPh_4Cl	11.0	5	85	8.7
9	1.74	0.75	2.49	100 mg PPh_4Br	11.0	5	60	8.9
10	1.74	0.75	2.49	400 mg PPh_4Br	11.0	5	75	8.4
11	1.74	0.75	2.49	100 mg TPMP	11.0	5	80	8.4
12	1.74	0.75	2.49	400 mg TPMP	11.0	5	60	7.6
13	1.74	0.75	2.49	100 mg THAI	11.0	5	85	8.5
14	1.74	0.75	2.49	400 mg THAI	11.0	5	85	8.6
15	1.74	0.75	2.49	none	22.0	5	120	7.0
16	1.74	0.75	2.49	none	7.33	5	70	9.2
C	1.74	0.75	2.49	none	3.67	3	35	9.1
D	1.74	0.75	2.49	none	1.83	2	20	9.8

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TABLE 2 (cont.)

Ex.	Dev. Temp (°F)	90 Second Processing				45 Second Processing				30 Second Processing				Δ 90 to 30	
		Dmin	Dmax	SPD	CONT	Dmin	Dmax	SPD	CONT	Dmin	Dmax	SPD	CONT	SPD	CONT
6	95	0.17	3.42	2.21	2.60	0.17	3.46	2.12	2.54	0.17	3.18	2.06	2.30	0.15	0.30
7	95	0.17	3.53	2.20	2.63	0.17	3.38	2.11	2.49	0.17	3.29	2.06	2.34	0.14	0.29
8	95	0.17	3.57	2.17	2.56	0.17	3.42	2.09	2.43	0.17	3.29	2.04	2.31	0.13	0.25
9	95	0.17	3.54	2.21	2.58	0.17	3.47	2.13	2.50	0.17	3.32	2.06	2.33	0.15	0.25
10	95	0.17	3.51	2.20	2.56	0.17	3.44	2.12	2.47	0.17	3.30	2.07	2.34	0.13	0.22
11	95	0.17	3.44	2.20	2.57	0.17	3.39	2.12	2.45	0.17	3.26	2.06	2.27	0.14	0.30
12	95	0.17	3.50	2.21	2.60	0.17	3.41	2.13	2.50	0.17	3.27	2.06	2.34	0.15	0.26
13	95	0.17	3.50	2.24	2.63	0.17	3.32	2.12	2.31	0.17	3.22	2.07	2.30	0.17	0.33
14	95	0.17	3.58	2.29	2.66	0.17	3.43	2.20	2.56	0.17	3.25	2.12	2.37	0.17	0.29
15	95	0.17	3.41	2.18	2.60	0.17	3.30	2.10	2.41	0.17	3.00	2.02	2.14	0.16	0.46
16	95	0.17	3.64	2.23	2.77	0.17	3.52	2.13	2.56	0.17	3.43	2.08	2.46	0.15	0.31
C	95	0.17	3.59	2.22	2.78	0.17	3.61	2.14	2.64	0.17	3.34	2.08	2.52	0.14	0.26
D	95	0.17	3.58	2.21	2.77	0.17	3.60	2.14	2.64	0.17	3.53	2.10	2.57	0.11	0.20

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TABLE 2 (cont.)

Ex.	Dev. Temp (°F)	90 Second Processing				45 Second Processing				30 Second Processing				Δ 90 to 30	
		Dmin	Dmax	SPD	CONT	Dmin	Dmax	SPD	CONT	Dmin	Dmax	SPD	CONT	SPD	CONT
6	104	0.18	3.55	2.30	2.70	0.17	3.40	2.20	2.62	0.17	3.20	2.08	2.38	0.22	0.32
7	104	0.18	3.56	2.31	2.63	0.17	3.36	2.20	2.58	0.17	3.23	2.11	2.40	0.20	0.23
8	104	0.18	3.51	2.25	2.57	0.17	3.33	2.17	2.50	0.17	3.39	2.11	2.47	0.14	0.10
9	104	0.18	3.54	2.30	2.66	0.17	3.27	2.19	2.53	0.17	3.34	2.13	2.47	0.17	0.19
10	104	0.18	3.46	2.28	2.52	0.17	3.46	2.21	2.53	0.17	3.37	2.14	2.45	0.14	0.07
11	104	0.18	3.48	2.31	2.61	0.17	3.53	2.25	2.64	0.17	3.42	2.17	2.57	0.14	0.04
12	104	0.18	3.49	2.32	2.61	0.17	3.43	2.24	2.58	0.17	3.40	2.16	2.51	0.16	0.10
13	104	0.18	3.61	2.37	2.71	0.17	3.52	2.27	2.66	0.17	3.49	2.20	2.56	0.17	0.15
14	104	0.18	3.49	2.37	2.64	0.17	3.53	2.31	2.60	0.17	3.47	2.23	2.57	0.14	0.07
15	104	0.18	3.29	2.27	2.59	0.17	3.16	2.16	2.44	0.17	3.08	2.08	2.21	0.19	0.38
16	104	0.18	3.51	2.30	2.76	0.17	3.59	2.23	2.72	0.17	3.35	2.15	2.58	0.15	0.18
C	104	0.18	3.63	2.30	2.83	0.17	3.75	2.26	2.78	0.17	3.60	2.18	2.76	0.12	0.07
D	104	0.18	3.61	2.28	2.87	0.17	3.80	2.25	2.85	0.17	3.59	2.16	2.77	0.12	0.10

EXAMPLE 17

Feasibility of ultra rapid processing in present exposing devices was demonstrated for Example 14. Example 14 was exposed on a 3M Laser Imager incorporating a 15 mwatt laser diode emitting at 820 nm. A step wedge was printed on the film of Example 14. A step wedge was also printed with the 3M Laser Imager at the same contrast and density settings (equal power) on a typical 90 second processable film, Example B. Example B was processed at 90 seconds dry-to-dry whereas Example 14 was processed at 30 seconds in the XP-515 processor. Both films were processed in 95°F developer. The density steps are plotted in Table 3 and verify that film 14 gives the same densities processed at 30 seconds as a standard film, Example B, processed at 90 seconds dry-to-dry. In addition, film 14 was dry after 30 second processing and passed the ANSI test for hypo retention demonstrating 30 year archival stability.

Table 4 contains a summary of data presented earlier for Example 14 and Example B. The sensitometric data in Table 4 was obtained from the 10^{-3} second flash sensitometer described at the beginning of the experimental section in combination with an 820 nm narrow band filter. The first two entries in Table 4 support the conclusion of the feasibility study shown above using the 3M Laser Imager which conclusion is that Example B processed for 90 seconds is roughly equivalent to Example 14 processed for 30 seconds. Entry 3 in Table 4 shows that greater densities can be obtained from Example 14 processed at 30 seconds by increasing the developer temperature from 95°F to 104°F, Therefore, ultra rapid processing (30 seconds dry-to-dry) has been demonstrated with experimental film 14 and a laser scanning device (3M Laser Imager).

TABLE 3

Step Wedge (Step #)	Density* (Ex. B)	Density** (Ex. 14)
1	0.20	0.19
2	0.57	0.56
3	0.98	0.97
4	1.33	1.29
5	1.60	1.55
6	1.82	1.75
7	2.02	1.99
8	2.12	2.13
9	2.30	2.25
10	2.42	2.37
11	2.53	2.49
12	2.61	2.58
13	2.65	2.63
14	2.70	2.68
15	2.74	2.72
16	2.77	2.75

* Processed 90 seconds dry-to-dry with 95°F developer

** Processed 30 seconds dry-to-dry with 95°F developer

TABLE 4

				Sensitometry			
Ex.	Entry	Dev. Temp. (°F)	Processing Time (sec)	Dmin	Dmax	SPD	CONT
B	1	95	90	0.18	3.28	2.14	2.49
14	2	95	30	0.17	3.25	2.12	2.37
14	3	104	30	0.17	3.47	2.23	2.57

EXAMPLES 18-24

Fine grain emulsions C and D were tested for ultra rapid processing. The coatings were prepared as described in Examples 1-16 but with dyes D-2 and D-3 and lower silver coatings weights of 1.7 and 1.4 g Ag/m^2 respectively. Formaldehyde was the hardening agent. Full details of the coating additives are given in Table 5. This set was coated on 7 mil (0.018 cm) clear polyester base and sensitometric results were evaluated With an 820 nm narrow band filter.

The data in Table 5 show that the 0.16μ emulsion can be used in the present laser exposing devices even with 30 second, dry-to-dry processing. The 0.16μ emulsion (Example 20) was optimized for speed with dye, D-3, and then processed with a 30 second cycle time with 104° F developer. The sensitometric data for Example 20 are identical to Example B processed in 90 seconds using 95° developer. Therefore, the 15 mwatt laser diode in 3M's Laser Imager would produce sufficient energy (see also Example 17) to image the 0.16μ emulsion (Example 20) when the developer temperature is set at 104° F and the processor has a 30 second cycle time.

Examples 21-24 do not have sufficient sensitivity to produce images off a laser device in present production when processed in 30 seconds. The films are roughly 1.0 log E slow which would require a 10 fold power increase in the laser scanning device. Although this appears to be a dramatic power increase, this may be obtained in the near future since papers and articles have appeared on 100 mwatt laser diodes.

TABLE 5

Ex.	Gel Content (g/m^2 per side) Emul Layer	TC Layer	Gel Total	Emul (μ)	Dye (mg)	PMT (mg)	LEUC (g)	THAI (mg)	PEA (g)	Ag Cwt (g/mole)	Hardener (mg/g gel)	Dying Property (30 sec)	Melting Time (min)	Water Retention (g/m^2)
18	1.23	0.75	1.98	0.16	30mg D2	115	0	0	20	1.7	3.67	5	51	6.2
19	1.23	0.75	1.98	0.16	30mg D2	115	0	400	20	1.7	3.67	5	49	6.9
20	1.23	0.75	1.98	0.16	15mg D3	J72	2	0	20	1.7	3.67	5	56	7.3
21	0.91	0.47	1.38	0.09	30mg D3	0	2	0	0	1.4	11.0	5	77	5.5
22	0.91	0.47	1.38	0.09	30mg D3	0	1	0	0	1.4	11.0	5	75	5.8
23	0.91	0.47	1.38	0.09	30mg D3	0	2	0	20	1.4	11.0	5	70	5.6
24	0.91	0.47	1.38	0.09	30mg D3	38	2	0	0	1.4	11.0	5	75	6.0

TABLE 5 (cont.)

Ex.	Dev. Temp (°F)	90 Second Processing				30 Second Processing				Δ 90 to 30	
		Dmin	Dmax	SPD	CONT	Dmin	Dmax	SPD	CONT	SPD	CONT
18	104	0.05	3.07	2.02	3.06	0.04	2.94	1.95	2.89	0.07	0.17
19	104	0.05	3.03	2.05	2.93	0.04	2.90	2.01	2.82	0.04	0.11
20	104	0.05	3.00	2.24	2.75	0.04	3.04	2.13	2.62	0.11	0.13
21	104	0.04	3.53	1.34	3.12	0.04	3.19	1.18	2.92	0.16	0.20
22	104	0.04	3.58	1.31	3.21	0.04	3.31	1.19	2.99	0.12	0.22
23	104	0.04	3.45	1.37	3.20	0.04	3.03	1.20	2.82	0.17	0.38
24	104	0.04	3.66	1.37	3.22	0.04	3.28	1.21	2.89	0.16	0.33

EXAMPLES 25-33

Fine grain emulsion D (0.09 microns, Cl/Br) was tested further for ultra rapid processing. The emulsion layer was coated with different levels of gelatin and overcoated with varying thickness of topcoat (TC). The coating additives were the same as example 21 in Table 5. The set was coated on 7 mil (0.018 cm) clear polyester base and sensitometric results were evaluated with an 820 nm narrow band filter. The AH formula coated on the reverse side of the base was described in U.S. Patent Application 59,931, Example 2. The AH flows were reduced to 30% for these examples which produced an AH layer with 1.24 g gelatin/m^2 and 7.3 mg of formaldehyde per gram of gelatin. The results are given in Table 6.

The results for examples 25-33 are basically the same as for examples 21-24. Examples 25-33 do not have sufficient sensitivity to produce images off a laser device in present production when processed in 30 seconds. The films are roughly 1.0 log E slow which would require a 10 fold power increase in the laser scanning devices. Although this appears to be a dramatic power increase, this may be obtained in the near future since papers and articles have appeared on 100 mwatt laser diodes.

TABLE 6

Ex.	Gel Content (g/m^2 per side) Emul Layer	TC Layer	Gel Total	Hardener (mg/g gel)	Drying Property (30 sec)	Melting Time (min)	Water Retention (g/m^2)
25	0.52	0.28	0.80	11.0	5	80	3.5
26	0.52	0.38	0.90	11.0	5	80	3.6
27	0.52	0.47	0.99	11.0	5	80	3.6
28	0.71	0.28	0.99	11.0	5	80	3.8
29	0.71	0.38	1.09	11.0	5	80	4.0
30	0.71	0.47	1.18	11.0	5	80	4.6
31	0.91	0.28	1.19	11.0	5	75	3.9
32	0.91	0.38	1.29	11.0	5	75	4.2
33	0.91	0.47	1.38	11.0	5	75	4.6

TABLE 6 (cont.)

Ex.	Dev. Temp (°F)	90 Second Processing				30 Second Processing				Δ 90 to 30	
		Dmin	Dmax	SPD	CONT	Dmin	Dmax	SPD	CONT	SPD	CONT
25	95	0.05	3.96	1.25	3.01	0.04	3.56	1.01	2.83	0.24	0.18
26	95	0.04	3.84	1.23	2.89	0.04	3.46	1.01	2.68	0.22	0.21
27	95	0.04	3.64	1.21	2.81	0.04	3.29	0.99	2.59	0.22	0.22
28	95	0.05	3.91	1.33	3.14	0.04	3.53	1.07	2.89	0.26	0.25
29	95	0.04	3.89	1.33	3.09	0.04	3.53	1.06	2.83	0.27	0.26
30	95	0.04	3.76	1.32	2.97	0.04	3.40	1.04	2.74	0.28	0.23
31	95	0.05	4.04	1.34	3.05	0.04	3.37	1.09	2.81	0.25	0.24
32	95	0.04	3.71	1.33	2.97	0.04	3.38	1.11	2.71	0.22	0.26
33	95	0.04	3.63	1.31	2.87	0.04	3.14	1.08	2.63	0.23	0.24

TABLE 6 (cont.)

Ex.	Dev. Temp (°F)	90 Second Processing				30 Second Processing				Δ 90 to 30	
		Dmin	Dmax	SPD	CONT	Dmin	Dmax	SPD	CONT	SPD	CONT
25	104	0.06	4.12	1.32	2.91	0.04	3.64	1.15	2.77	0.17	0.14
26	104	0.05	4.00	1.32	2.88	0.04	3.46	1.16	2.72	0.16	0.16
27	104	0.05	3.62	1.31	2.70	0.04	3.35	1.14	2.65	0.17	0.05
28	104	0.06	3.86	1.35	2.85	0.04	3.50	1.21	2.75	0.14	0.10
29	104	0.06	3.81	1.36	2.80	0.04	3.38	1.18	2.73	0.18	0.07
30	104	0.06	3.59	1.36	2.74	0.04	3.35	1.18	2.66	0.18	0.08
31	104	0.05	3.79	1.40	2.93	0.04	3.53	1.24	2.84	0.16	0.09
32	104	0.05	3.71	1.40	2.84	0.04	3.28	1.24	2.71	0.16	0.13
33	104	0.05	3.54	1.39	2.81	0.04	3.31	1.23	2.66	0.16	0.15

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EXAMPLE 34-38

An ultra rapid processed, helium-neon laser film was constructed to show the breadth of the invention. Emulsion B (0.24 micron, Br/I) was sensitized with 100 mg/mole Ag of dye, D-1. Also added was 20 g/mole Ag of PEA and formaldehyde. The trials were coated on 7 mil clear polyester base at 2.2 g Ag/m^2. The polyester base hd an antihalation backside coating containing an AH dye absorbing at 633 nm, 2.80 g of gelatin/m^2 and 7.38 mg of formaldehyde hardener per gram of gelatin. The films were exposed with a 633 nm narrow band filter with the results listed in Table 7.

The data in Table 7 again show the importance of reducing the gelatin to permit ultra rapid processing and also show that the invention is not limited to laser diodes but can work with other exposing devices.

TABLE 7

Ex.	Gel Content (g/m^2 per side) Emul Layer	TC Layer	Gel Total	Hardener (mg/g gel)	Drying Property (30 sec)	Melting Time (min)	Water Retention (g/m^2)
34	1.57	0.75	2.32	7.34	5	55	8.8
35	1.57	1.03	2.60	7.34	5	55	9.1
36	1.57	1.31	2.88	7.34	5	55	9.0
37	2.23	0.75	2.98	7.34	4	70	9.3
38	2.23	1.03	3.26	7.34	3	70	9.3
E	2.23	1.31	3.54	7.34	2	70	9.6

TABLE 7 (cont.)

Ex.	Dev. Temp (°F)	90 Second Processing				45 Second Processing				30 Second Processing				Δ 90 to 30	
		Dmin	Dmax	SPD	CONT	Dmin	Dmax	SPD	CONT	Dmin	Dmax	SPD	CONT	SPD	CONT
34	95	0.05	3.16	2.35	2.17	0.05	3.07	2.25	2.07	0.04	3.10	2.15	2.00	0.20	0.17
35	95	0.05	3.01	2.37	2.00	0.05	3.00	2.26	1.90	0.04	2.93	2.13	1.86	0.24	0.14
36	95	0.05	3.05	2.33	1.92	0.04	2.92	2.20	1.75	0.04	3.06	2.15	1.75	0.18	0.17
37	95	0.05	3.11	2.37	2.20	0.05	3.07	2.24	1.95	0.04	2.93	2.13	1.74	0.24	0.46
38	95	0.05	3.13	2.38	2.18	0.05	3.01	2.25	1.87	0.04	2.89	2.14	1.71	0.24	0.47
E	95	0.05	3.10	2.39	2.20	0.05	3.00	2.25	1.86	0.04	2.81	2.14	1.63	0.25	0.57

TABLE 7 (cont.)

Ex.	Dev. Temp (°F)	90 Second Processing				45 Second Processing				30 Second Processing				Δ 90 to 30	
		Dmin	Dmax	SPD	CONT	Dmin	Dmax	SPD	CONT	Dmin	Dmax	SPD	CONT	SPD	CONT
34	104	0.05	3.38	2.50	2.37	0.05	3.25	2.36	2.22	0.04	3.20	2.25	2.01	0.25	0.36
35	104	0.05	3.25	2.52	2.25	0.04	3.08	2.36	2.02	0.04	2.94	2.24	1.85	0.28	0.40
36	104	0.05	3.00	2.50	2.15	0.04	2.88	2.34	1.88	0.04	2.75	2.22	1.68	0.28	0.47
37	104	0.05	3.18	2.50	2.22	0.05	3.09	2.36	2.06	0.04	2.96	2.24	1.80	0.26	0.42
38	104	0.05	3.15	2.49	2.23	0.05	3.03	2.34	2.00	0.04	2.86	2.24	1.71	0.25	0.52
E	104	0.05	3.06	2.51	2.17	0.05	2.86	2.34	1.87	0.04	2.73	2.23	1.65	0.28	0.52

Claims

1. A silver halide photographic material comprising at least one hardened hydrophilic colloid silver halide emulsion layer on a support, said silver halide emulsion layer comprising silver halide grains at least 80% of which are less than 0.80 microns, and said photographic material, upon completion of the washing step during processing with a roller transport type automatic processor, having a water content of 3.5 to 9.5 g/m^2.

2. A silver halide photographic material comprising at least one hardened hydrophilic colloid silver halide emulsion layer on a support, said silver halide emulsion layer comprising silver halide grains of an average diameter of from 0.05 to 0.70 microns and at least 80% of which grains have diameters less than 0.80 microns and greater than 0.02 microns, said silver halide emulsion layer having less than 3.50 g gelatin per square meter, and said photographic material, upon completion of the washing step during processing with a roller transport type automatic processor, having a water content of 3.5 to 9.5 g/m^2.

3. The material of claims 1 or 2 having a protecting coating layer free of photographic silver halide over said silver halide emulsion layer.

4. The material of claim 3 wherein the total weight of gelatin in said emulsion layer and said protective layer is 0.8 to 3.5 g/m^2.

5. The material of claims 1 or 2 wherein the weight of silver in said silver halide emulsion layer is less than 3.0 g/m^2 and the average diameter of said silver halide particles is between 0.05 and 0.35 microns.

6. The material of claim 3 wherein the weight of silver in said silver halide emulsion layer is less than 3.0 g/m^2 and the average diameter of said silver halide particles is between 0.05 and 0.35 microns.

7. The material of claim 1 wherein the melting time of said silver halide emulsion layer is 1.5% by weight aqueous NaOH at 50 $^\circ$ C is greater than or equal to 45 minutes.

8. The material of claim 4 wherein the melting time of said silver halide emulsion layer is 1.5% by weight aqueous NaOH at 50 $^\circ$ C is greater than or equal to 45 minutes.

9. The material of claim 6 wherein the melting time of said silver halide emulsion layer is 1.5% by weight aqueous NaOH at 50 $^\circ$ C is greater than or equal to 45 minutes.

10. The material of claim 3 wherein the weight of silver on said silver halide emulsion layer is between 1.0 and 2.5 g/m^2 and the average diameter of said silver halide particles is between 0.05 and 0.25 microns.