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<p>(21) International Application Number: PCT/US79/00294 (22) International Filing Date: 1 May 1979 (01.05.79) (31) Priority Application Numbers: 901,995 2939,257 (32) Priority Dates: 2 May 1978 (02.05.78) 5 September 1978 (05.09.78) (33) Priority Country: US (71) Applicant: POLAROID CORPORATION [US/US]; 549 Technology Square, Cambridge, MA 02139, (US). (72) Inventor: KLIEM, Peter, O.; 158 Sherburn Circle, We- ston, MA 02193, (US).</p>	<p>(74) Agents: ISAACS, Alvin; 549 Technology Square, Cam- bridge, MA 02139, (US). (81) Designated States: DE (European patent), FR (Euro- pean patent), GB (European patent), JP. Published with: <i>International search report</i></p>	
<p>(54) Title: PHOTSENSITIVE ELEMENTS</p> <p>(57) Abstract</p> <p>Photosensitive elements particularly suitable for use in diffusion transfer photographic film units which include a plurality of essential layers including at least one photosensitive silver halide layer having associated therewith a dye image-forming material which is diffusible during processing as a function of the point-to-point degree of silver halide exposure to actinic radiation and a layer adapted to receive image-forming material diffusing thereto and means for applying an aqueous processing composition. The silver halide layer comprises gelatin and inert particles which are compatible with gelatin, non-swelling in alkali and substantially non-film forming, wherein said inert particles are equal to or less than the silver halide grains in average diameter and wherein the silver halide grains are 2.5 microns or less in average diameter. Preferably, the inert particles are derived from a polymeric latex. In a particularly preferred embodiment, the photosensitive silver halide layer comprises a first and second photosensitive silver halide layer in contiguous relationship.</p>		

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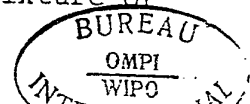
PHOTOSENSITIVE ELEMENTS 1

BACKGROUND OF THE INVENTION

Diffusion transfer photographic products and processes are known to the art and details relating thereto can be found in U. S. Patents Nos. 2,983,606; 3,415,644; 5 3,415,645; 3,415,646; 3,473,925; 3,482,972; 3,551,406; 3,573,042; 3,573,043; 3,573,044; 3,576,625; 3,576,626; 3,578,540; 3,569,333; 3,579,333; 3,594,164; 3,594,165; 10 3,597,200; 3,647,437; 3,672,486; 3,672,890; 3,705,184; 3,752,836; 3,857,865; all of which are incorporated here their entirety. Essentially, diffusion transfer photographic products and processes involve film units having a photo- 15 sensitive system including at least one silver halide layer, usually integrated with an image-providing material. After photoexposure, the photosensitive system is developed to establish an imagewise distribution of a diffusible image-providing material, at least a portion of which is trans- 20 ferred by diffusion to an image-receiving layer capable of mordanting or otherwise fixing the transferred image-providing material. In some diffusion transfer products the transfer image is viewed by reflection after separation 25 of the image-receiving element from the photosensitive system. In other products, however, such separation is not required and instead the transfer image-receiving layer is viewed against a reflecting background usually provided 30 by a dispersion of a white reflecting pigment, such as, for example, titanium dioxide. The latter type of film unit is generally referred to in the art as integral negative-positive film units and are described, for example, in the above-mentioned U. S. Patents Nos. 3,415,644 and 35 3,594,165.

It is known in the art to incorporate polymeric latices into gelatin silver halide emulsion layers to increase the flexibility of the silver halide layer, thus eliminating the occurrence of fog due to stresses set up in the film unit containing the aforementioned silver halide layer.

U. S. Patent No. 2,772,166 discloses gelatin silver halide emulsions which also contain a hydrosol resulting from the emulsion polymerization of a mixture of



styrene, acrylonitrile or a vinylidene chloride with an alkyl acrylate or alkyl methacrylate and acrylic acid. The described hydrosol is used in the range of 1 to 10% of the gelatin.

5 U. S. Patent No. 2,835,582 is directed to mixtures of gelatin and polymeric hydrosols in silver halide layers wherein the hydrosol is prepared by polymerizing at least one monoethylenically unsaturated monomer in the presence of an ampholytic surface active agent. Among the
10 suitable monomeric materials are mentioned methylmethacrylate and styrene. It is a requirement that the polymeric materials be film formers and the essence of the invention resides in the presence of the ampholytic surface active material to provide its enhanced compatibility
15 with gelatin.

U. S. Patent No. 3,157,510 is directed to gelatin silver halide emulsions which also include a dispersion of minute particles of a water insoluble soft acrylate polymer resin at a level of about 5 to 40% by weight of gelatin.

20 U. S. Patent No. 3,325,286 is directed to gelatin silver halide emulsions which include an aqueous dispersion of a polymeric vinyl compound and at least one anionic dispersing agent specified in the patent. The emulsion layer also requires a polyoxyethylene compound as defined
25 in the patent. One of the polymeric materials recited is a homopolymer of an α -hydrocarbon substituted acrylic acid ester.

U. S. Patent No. 3,547,650 is directed to gelatin-silver halide emulsions which include an aqueous dispersion
30 of a polymeric vinyl compound dispersed with a mixture of specified organic phosphates. One of the polymerized vinyl compounds recited comprises a homopolymer of an α -hydrocarbon substituted acrylic acid ester.

U. S. Patent No. 3,772,032 is directed to a
35 gelatin silver halide emulsion which includes a polymeric latex prepared by emulsion polymerization in the presence of at least 5% by weight of an emulsifying agent to reduce the stress sensitivity of the emulsion. This patent states



that employing the specified emulsifying agent at a level of at least 5% by weight, no fog is found in emulsions employing large amounts of methylmethacrylate in the latex whereas normally the presence of even 50% of
5 methylmethacrylate in the latex results in intolerable increases in fog.

U. S. Patent No. 3,773,517 is directed to gelatin-silver halide emulsion which include a polymer latex prepared by copolymerization of a monomer yielding a water
10 insoluble homopolymer and a monomer yielding a water soluble polymer. The patent requires the polymerization to occur in the presence of a specified alkylaryl polyether phosphate surface active agent. One of the monomers which would produce a water insoluble homopolymer is an
15 alkylmethacrylate.

U. S. Patent No. 3,418,132 is directed to a photographic film unit which, in one embodiment, is particularly suited for rapid access processing by virtue of the incorporation of inert particles into at least one layer
20 of the photographic element. The inert particles include starch, barium sulfate, calcium carbonate, synthetic resins etc. The inert particles are in the range of 7 to 15 microns.

Film units containing contiguous silver halide
25 emulsion layers sensitive to the same spectral region are known to the art as shown by the following representative patents.

U. S. Patent No. 3,505,068 is directed to a photographic element which contains overlying silver
30 halide emulsions wherein the first emulsion is a regular silver haloiodide emulsion and the second contains grains which have an iodide-free shell and a silver iodide core.

U. S. Patent No. 3,663,228 is directed to a photographic film unit having a plurality of silver halide
35 emulsion layers divided into sets with each set of a different speed while the layers in each set have the same speed but are responsive to different spectral regions. Color filters are disposed between the layers.



U. S. Patent No. 3,695,882, is directed to a photosensitive element comprising a support carrying two emulsions, each containing a non-diffusing color coupler. Each emulsion has a different speed and different silver halide-coupler molar ratio.

U. S. Patent No. 3,846,135 is directed to a synergistic increase in the sensitivity of two superposed silver halide layers when the lower layer is less sensitive than the upper layer and has a maximum density of at least 1.5 compared to a maximum density of at least 0.9 for the upper layer. The lower layer is about 5 to 15 μ thick.

U. S. Patents Nos. 3,960,558 and 4,003,744 disclose diffusion transfer film units which employ split silver halide emulsions having dye image-forming material associated therewith and which, in fact, contain dye image-forming material in one of said contiguous layers.

U. S. Patent No. 3,632,342 is directed to a photographic element comprising a support carrying at least one layer containing a high contrast silver halide emulsion layer containing an acrylic latex material and an additional silver halide layer containing a hydrophilic colloid which is free of latex micelles. It is stated that discrete micelles are preferred but that coalescing may occur. Copolymers of hydrophilic and hydrophobic monomers are disclosed.



SUMMARY OF THE INVENTION

The photographic film unit of the present invention comprises at least a first photosensitive silver halide emulsion layer having associated therewith a dye image-forming material, preferably a dye developer which is soluble and diffusible in alkali as a function of the exposure and development of the silver halide emulsion layer, and a polymeric layer dyeable by said dye image-providing material wherein said dyeable polymeric layer is at least in superposed relationship with said photosensitive element after exposure of said element and during processing of the exposed photosensitive silver halide emulsion, that is, during contact of said emulsion with the aqueous alkaline processing composition; and wherein said photosensitive silver halide emulsion layer comprises photosensitive silver halide grains disposed in a mixture of gelatin and inert particles which are substantially non-swelling in alkali, compatible with gelatin, and substantially non-film forming or non-coalescing; which particles are equal to or less than the silver halide grains in average diameter and wherein the silver halide grains are 2.5 microns or less in diameter.

Preferably the film units of the present invention are integral negative-positive film units of the types described, for example, in U. S. Patents Nos. 3,415,644 and 3,647,437, which patents are incorporated herein. Preferred inert particles are derived from polymeric latices which comprise homopolymers of methylmethacrylate or styrene.

The term "photosensitive silver halide emulsion layer" as used herein, is intended to include a first and second photosensitive silver halide layer sensitive to the same portion of the spectrum and in contiguous relationship i.e., so-called "split emulsions", which will be described below in greater detail.



DETAILED DESCRIPTION OF THE INVENTION

The present invention will be described with respect to dye developers as the dye image-forming materials although it will be understood that other dye
5 image-forming materials may be employed in the present invention.

Dye developers are well known in the art. A dye developer is a compound which contains a silver halide developing moiety and the chromophoric system of a dye.
10 In multicolor processes, a dye developer providing an image dye of appropriate color is associated with each silver halide emulsion layer; for example, a cyan dye developer with a red sensitive silver halide layer; a magenta dye developer with a green sensitive silver halide
15 emulsion layer; and a yellow dye developer with a blue sensitive silver halide emulsion layer. Unoxidized dye developer is insoluble in water but soluble and mobile in aqueous alkali. Oxidation of the dye developer as a result of development of exposed silver halide results in
20 its immobilization, while unoxidized dye developer can diffuse to the dyeable image-receiving layer producing a positive image therein.

To provide rapid transfer of the unoxidized dye developer and to avoid any unwanted interactions in the
25 negative, it is preferred that the unoxidized dye developer pass through the associated silver halide emulsion layer as rapidly as possible consistent with development thereof. Since gelatin swells to a considerable degree upon contact with the photographic processing composition and thus
30 would be a factor in slowing dye developer transfer, it is desirable to form the silver halide emulsion layer with a minimum of gelatin. The minimum quantity of gelatin employed, however, is controlled to a great degree by the size of the silver halide grains. Thus, it is desirable
35 to employ sufficient gelatin to retain the silver halide grains within the layer, that is, to prevent any projection of the grains or portion of the grains through the gelatin layer at the interface into contact with adjacent layers.



Thus, it will be seen that larger size grains, as commonly employed for high speed emulsions, would require more gelatin than smaller grains at the same unit weight coverage to form a continuous layer without any projection of the grains into contact with adjacent layers.

By means of the present invention it has now been found that the transfer of image-forming materials through gelatin-silver halide emulsion layers can be accelerated, while at the same time completely retaining the silver halide grains within the layer and without adversely affecting the photographic properties of the film unit. In fact, unexpected photographic advantages are achieved as evidenced by H & D curves showing a reduction in slope, increased toe extent and enhanced dynamic range.

As stated above, these advantages are achieved by disposing in the gelatin-silver halide layer inert particles which are substantially non-swelling in aqueous alkali; which are compatible with gelatin to avoid coagulation within the layer; which possess a refractive index sufficiently close to that of gelatin to avoid undue light scattering; which are substantially non-film forming (film forming would further inhibit dye transfer) and which are sufficiently hard to retain their physical identity as individual particles in the presence of aqueous alkali and thus provide a non-swelling, sizeable mass to bulk the gelatin layer.

Inert particles suitable for use in the present invention include starch, barium sulfate, calcium carbonate, cellulose esters such as cellulose acetate propionate, cellulose esters such as ethyl cellulose, gloss, synthetic resins such as polyvinyl acetate, polycarbonates, homo and copolymers of styrene, inorganic oxides such as zinc oxide, silica, titanium dioxide, magnesium oxide and aluminum oxide, as well as hardened gelatin grains, calcium sulfate, barium carbonate and the like.

As stated above, the preferred inert particles



for use in the present invention are polymethylmethacrylate and polystyrene and are provided for the film unit by disposing polymethylmethacrylate latex or polystyrene latex in the emulsion.

5 The film forming and hardness characteristics of polymers are properties associated with the glass transition temperature of the polymer. Thus, the Tg of the polymer should be above the temperature at which the polymer is dried. Preferably, the Tg is above 35°C, more
10 preferably, above 60°C. In a particularly preferred embodiment, the Tg is above 100°C.

It should be understood that the polymer latex may be a homopolymer or a copolymer provided that the comonomers do not modify the copolymer to the extent that
15 the required properties are not retained.

The inert particles should be no larger than the silver halide grains with which they are associated. In the present invention the maximum average diameter of the silver halide grains is 2.5 microns or less and preferably
20 less than 2.0 microns. Thus, the maximum average diameter of the inert particles is 2.5 microns. The lower limit of the particles is determined by the fact that one should avoid packing of the particles such as would impede dye transfer. Preferably, inert particles not less than 0.075
25 microns in diameter would be employed.

In a particularly preferred embodiment the inert particles leave an average diameter which is 10-15% of the average diameter of the silver halide grains associated therewith.

30 The quantity of polymer latex to be employed may be readily determined for any given silver halide emulsion. For a given silver halide grain size, as the quantity of gelatin decreases, the polymer gelatin ratio goes up to keep the layer dimensions the same. Sufficient gelatin
35 must be present to keep the layer intact and prevent dusting of the polymer particles. Preferably, a ratio (weight basis) of 0.5 to 1 to 10 to 1 polymer latex (solids) to gelatin is employed. Particularly preferred is a 1 to 1

ratio for fine grains (less than about 1μ) and 6 to 1 for coarse grains (greater than about 1.3μ). Thus, in a preferred embodiment, the average mean diameter of the fine grains is less than about 1μ and the large grains, greater than 1.3μ .

5 As stated above, the novel photosensitive silver halide layer of the present invention may comprise a first and second photosensitive silver halide layer in contiguous relationship and which are responsive to substantially the same spectral range. Thus, in an alternative embodiment,
10 the diffusion transfer photographic film unit of the present invention comprises a plurality of layers which include a first photosensitive silver halide emulsion layer comprising silver halide grains of a first mean particle size and a second photosensitive silver halide emulsion layer comprising
15 silver halide grains of a second mean particle size; said first and second silver halide emulsion layers being in contiguous relationship with the first silver halide layer being distal to the exposure surface of the film unit with respect to the second silver halide layer; said first
20 and second silver halide layers being free of dye image-forming material but having associated therewith a dye image-forming material which is diffusible as function of the point-to-point degree of silver halide exposure to actinic radiation, and a layer adapted to receive image-
25 forming material diffusing thereto and means for applying an aqueous processing composition therebetween; wherein at least one of said silver halide layers comprise gelatin and inert particles as defined above. If inert particles are employed in only one layer it is in the layer containing
30 the larger silver halide grains. The intrinsic speed of the second silver halide emulsion layer is greater than that of the first silver halide emulsion layer.

However, when the thickness of the gelatin associated with the layers falls to about 50% or less of
35 the mean volume diameter of the grains, the coated layers do not retain their integrity but rather combine, intermixing the grain sizes, so that the resulting combined



silver halide layer functions as if a single layer of blended grain sizes were coated, thus losing all the benefits achieved in a layered structure and introducing the drawbacks of the single layered, low gelatin system.

5 It is believed that the advantages of this invention result, at least in part, by maintaining better separation of the development process of the individual grains as well as separation of the by-products of development by virtue of incorporating the above-described inert particles.

10 By employing such inert particles in the layers, the layers retain their integrity with the differently sized silver halide particles retained in their own separate and distinct layer.

As stated above, the intrinsic speed of the

15 second silver halide layer, i.e., the layer closest to the exposure surface, possesses a higher intrinsic speed than the first silver halide layer. Preferably, the speed difference is at least about 2 stops and may range up to about 8 stops. In a particularly preferred embodiment, the

20 difference is about 5 stops.

The polymeric latices preferred for employment in the present invention may be prepared by known techniques. The following non-limiting example illustrates the preparation of a latex preferred for use in the present invention.

25

Example A

Water	118 l.
Methyl methacrylate	5l kg.
Potassium persulfate	0.15 kg.
30 Ascorbic acid	0.01 kg.
Dowfax 2A1 20% solution (dodecyldiphenyl oxide disulfonate sodium salt, sold by Dow Chemical Co., 35 Midland, Michigan)	1.275 kg.

A reactor was charged with 102 l. of demineralized water and the Dowfax 2A1 and heated under nitrogen to 83°C whereupon 7.65 kg. of methyl methacrylate was added



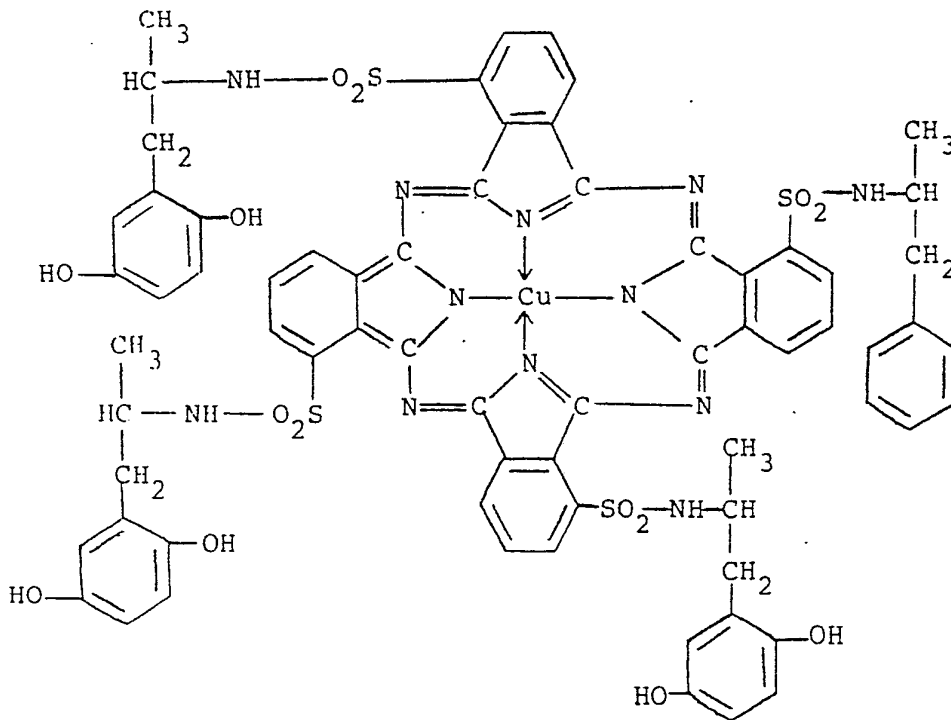
and mixed until the temperature returned to 83°C. After 5 min. at 83°C, 4.93 kg. of initiator solution (0.15 kg. of potassium persulfate and 14.79 kg. water) was added. After the exotherm, the temperature was reduced to 85 C and the remaining methyl methacrylate was added at a rate of about 361 g/min. and the remaining initiator solution at a rate of about 111 g/min. At the end of the monomer and initiator addition, the temperature was maintained at 85°C for 10 min. and then the ascorbic acid was added. The resulting latex had a 30% solids and the latex particles had an average diameter of about a 0.125μ.

The following non-limiting examples illustrate the present invention:

EXAMPLE 1 (Control)

A photosensitive element was prepared by coating, in succession, on a gelatin subbed, opaque polyethylene terephthalate film base, the following layers.

1. a layer comprising the cyan dye developer



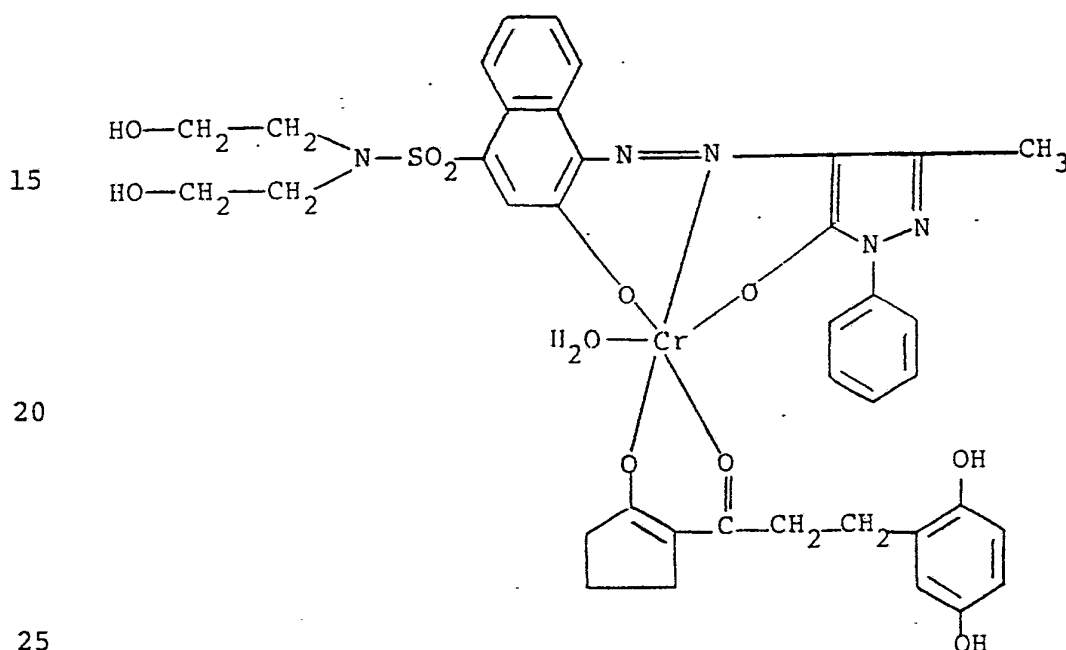
dispersed in gelatin and coated at a coverage of about 747 mgs/m² of dye, about 1554 mgs/m² of gelatin, about 270 mgs/m² of 4'-methylphenylhydroquinone, and about

270 mgs/m² of 2-phenyl benzimidazole;

2. a red-sensitive gelatino silver iodobromide emulsion layer comprising a 50/50 blend of 1.05 μ and 1.5 μ grains coated at a coverage of about 1280 mgs/m² of silver and about 768 mgs/m² of gelatin;

3. an interlayer coated at a coverage of about 2500 mgs/m² of a 60-30-4-6 tetrapolymer of butylacrylate, diacetone acrylamide, styrene and methacrylic acid, and about 77 mgs/m² of polyacrylamide;

4. a layer comprising the magenta dye developer

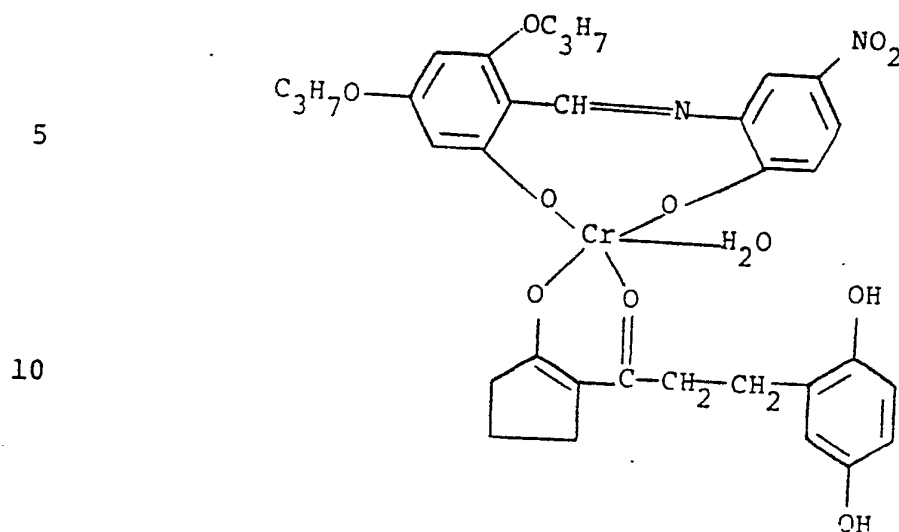


dispersed in gelatin and coated at a coverage of about 646 mgs/m² of dye and about 426 mgs/m² of gelatin and about 229 mgs/m² of 2-phenylbenzimidazole;

5. a green-sensitive gelatino silver iodobromide emulsion layer coated at a coverage of about 753 mgs/m² of silver and about 347 mgs/m² of gelatin;

6. an interlayer containing the tetrapolymer referred to above in layer 3 at a coverage of about 1369 mgs/m², about 24 mgs/m² of polyacrylamide, and about 75 mgs/m² succindialdehyde;

7. a layer comprising the yellow dye developer



dispersed in gelatin and coated at a coverage of about
 15 968 mgs/m² of dye and about 450 mgs/m² of gelatin and about
 208 mgs/m² of 2-phenyl benzimidazole;

8. a blue-sensitive gelatino silver iodobromide
 emulsion layer coated at a coverage of about 1280 mgs/m² of
 silver, about 743 mgs/m² of gelatin, and about 204 mgs/m²
 20 of 4'-methylphenylhydroquinone;

9. an overcoat layer coated at a coverage of
 about 484 mgs/m² gelatin and 43 mgs/m² of carbon black.

An image-receiving element was prepared by coat-
 ing the following layers in succession on a 4 mil polyethy-
 25 lene terephthalate film base, said layers respectively
 comprising:

1. as a polymeric acid layer, the partial butyl
 ester of polyethylene/maleic anhydride copolymer at a
 coverage of about 28,000 mgs/m²;

30 2. a timing layer containing about a 75:1 ratio
 of a 60-30-4-6 copolymer of butylacrylate, diacetone
 acrylamide, styrene and methacrylic acid and polyvinyl
 alcohol at a coverage of about 5600 mgs/m²; and

3. A polymeric image-receiving layer containing
 35 a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-
 vinylpyridine, at a coverage of about 3300 mgs/m².

An aqueous alkaline solution was prepared
 comprising

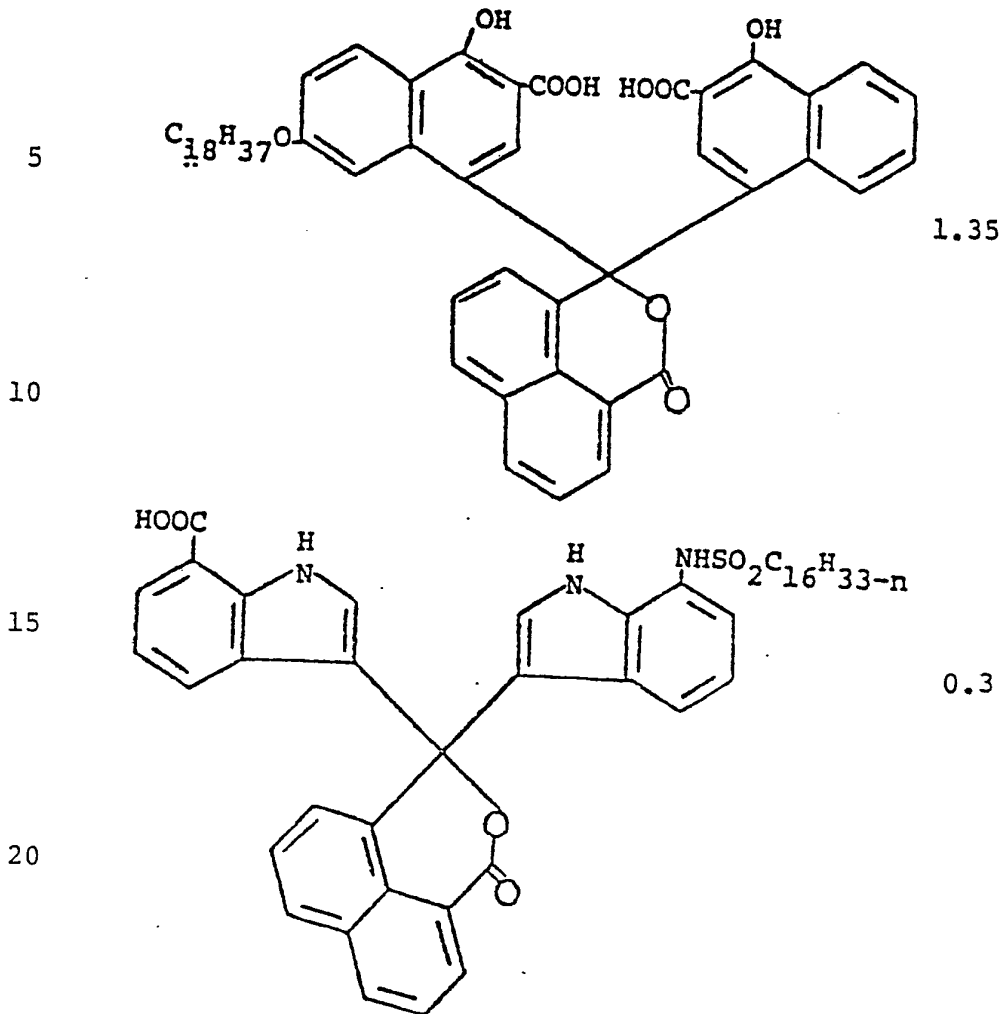
	<u>Weight %</u>
Potassium hydroxide	5.25
5 N-phenethyl- α -picolinium bromide (50% solution in water)	1.27
Sodium carboxymethyl hydroxethyl cellulose (Hercules Type 420H)	2.0
Titanium dioxide	37.4
10 6-methyl uracil	0.7
bis-(β -aminoethyl)-sulfide	0.022
Benzotriazole	5.48
15 Colloidal silica aqueous dispersion (30% SiO ₂)	0.55
N-2-hydroxyethyl-N,N',N'-tris- carboxymethyl-ethylene diamine	0.75
4-aminopyrazolo (3, 4d) pyrimidine	0.25
6-benzylamino-purine	0.41
20 Polyethylene glycol (molecular weight 4,000)	0.45
Water	44.26

25

30

35





25 EXAMPLE 2

A second film unit was prepared as described above except that layer 2, the green-sensitive silver halide emulsion layer additionally contained 120 mgs/ft² (1292 mgs/m²) (solids) of a polymethylmethacrylate latex having an average particle size of about 0.125 and layer 6 was reduced in coverage by 40%.

The film units were processed in the following manner:

The film unit was exposed with white light to a multicolor target and the processing composition was spread between the two elements in a layer approximately 0.0028" thick in the dark.

The following sensitometer data (green light reflection data in neutral column) was obtained in the resulting multicolor reflection prints:



TABLE 1

		<u>Control</u>	<u>Example 2</u>
5	D_{\max}	1.90	1.88
	Slope	1.61	1.31
	Toe Extent	34	48
	Dynamic Range	17	23
10	1.5 Speed	2.11	2.16
	0.45 Speed	1.46	1.34

From the foregoing it can be seen that a 30 unit reduction in slope is achieved; an increase in toe extent of about 14 units as well as an increase in dynamic range of more than 5 units. The loss indicated in the other properties is not considered significant; i.e., the advantages far outweigh the slight decrease recorded in D_{\max} and speed which, in fact, may be within experimental error. It should be understood that these enhanced photographic results are obtained at the same time the magenta dye transfer is accelerated.

EXAMPLE 3

To illustrate the rapid dye transfer achieved by the novel invention the following structures were prepared:

A. On a polyester base was coated 25 mgs/ft² (269 mgs/m²) of the cyan dye of Example 1; 50 mgs/ft² (538 mgs/m²) of gelatin and 2 mgs/ft² (21.5 mgs/m²) of succinaldehyde.

B. Structure A was overcoated with 180 mgs/ft² (1938 mgs/m²) of derivatized gelatin.

C. Structure A was overcoated with 180 mgs/ft² (1938 mgs/m²) of inert gelatin.

D. Structure A was overcoated with a mixture of gelatin (40 mgs/ft²) (431 mgs/m²) and polymethylmethacrylate latex (160 mgs/ft²) (1722 mgs/m²) (0.125 μ average diameter). The processing composition described above was spread between the above structures and the superposed dye-



image-receiving sheet described in Example 1 in a thickness of 28 mils. The density of dye deposited in the receiving sheet was measured as a function of time. The resulting data are set forth below:

5



TABLE 2

Overcoat	Coverage mgs/ft ²	Coverage mgs/m ²	30 sec.	Density			
				1 min.	1.5 min.	3 min. 5 min.	
A None	0		0.88	1.16	1.26	1.82	1.94
B Derivatized gelatin	180		0.29	0.65	0.84	1.06	1.27
C Inert gelatin	180		0.68	0.87	1.00	1.24	1.37
D Gelatin	40						
Polymethylmethacrylate	160		.81	1.10	1.25	1.46	1.55



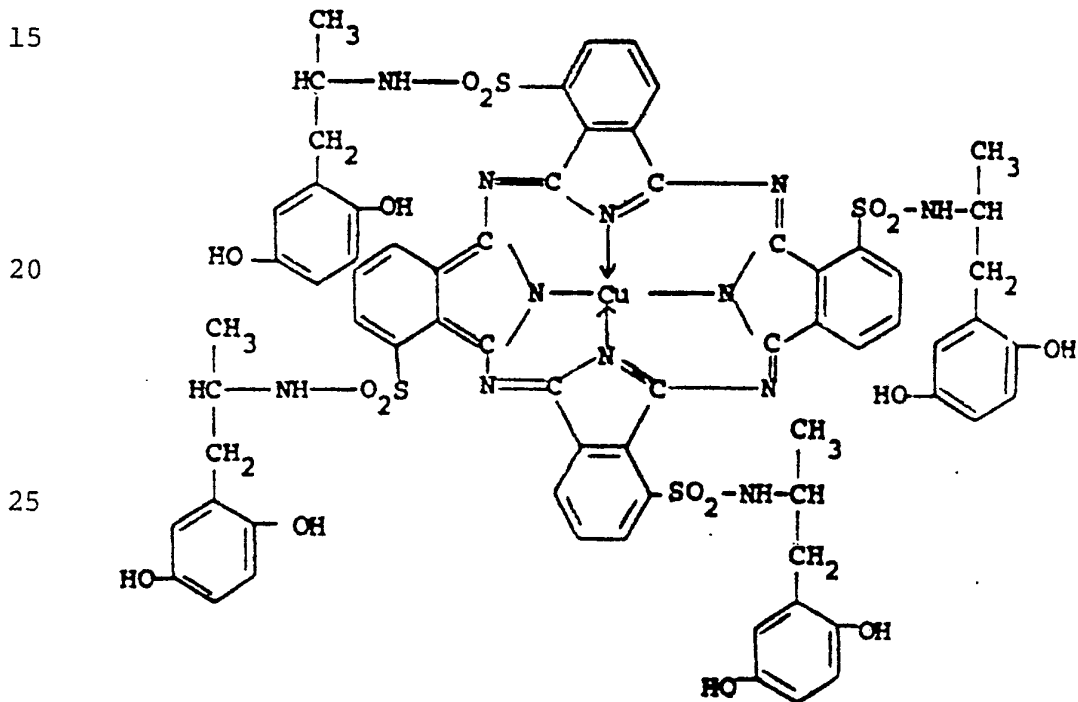
The above table illustrates the adverse effect gelatin has on dye transfer. The table also shows that a layer with a greater coverage than the gelatin layer but composed of gelatin and latex particles provides transfer rates approaching that obtained with no overcoat at all, especially in the initial time period.

The following non-limiting example illustrates a particularly preferred film unit of the present invention:

EXAMPLE 4 (Control)

A photosensitive element was prepared by coating, in succession, on a gelatin subbed, opaque polyethylene terephthalate film base, the following layers:

1. a layer comprising the cyan dye developer



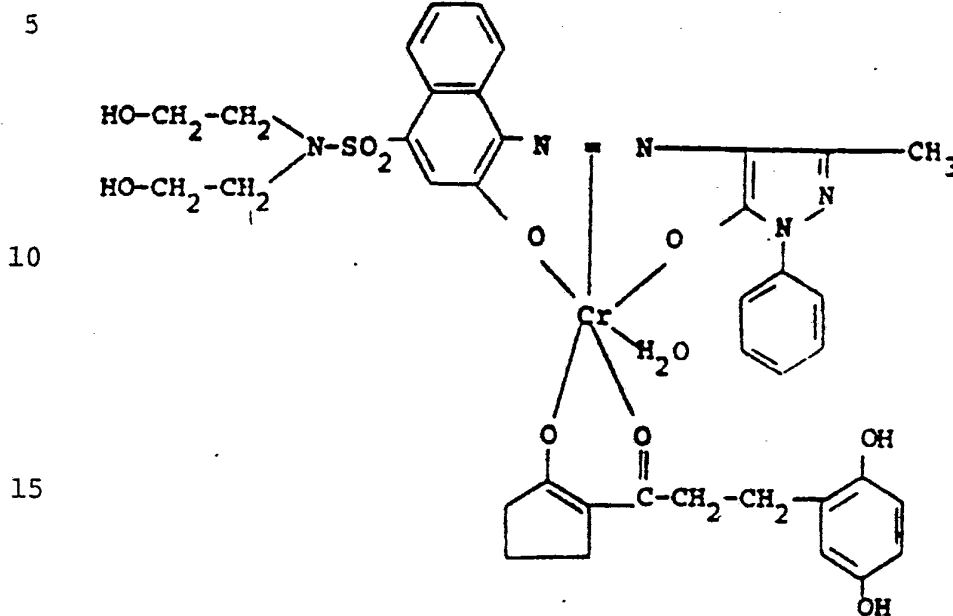
30 dispersed in gelatin and coated at a coverage of about 747 mgs/m² of dye, about 1554 mgs/m² of gelatin, about 270 mgs/m² of 4'-methylphenylhydroquinone, and about 270 mgs/m² of 2-phenyl benzimidazole;

35 2. a red-sensitive gelatino silver iodobromide emulsion layer coated at a coverage of about 1280 mgs/m² of silver and about 768 mgs/m² of gelatin;

3. an interlayer coated at a coverage of about 2500 mgs/m² of a 60-30-4-6 tetrapolymer of butylacrylate,

diacetone acrylamide, styrene and methacrylic acid, and about 77 mgs/m² of polyacrylamide;

4. a layer comprising the magenta dye developer



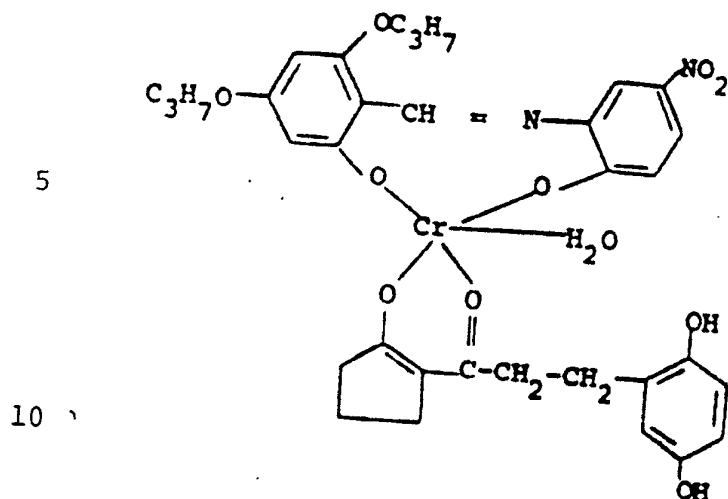
20 dispersed in gelatin and coated at a coverage of about 646 mgs/m² of dye and about 426 mgs/m² of gelatin and about 229 mgs/m² of 2-phenylbenzimidazole;

25 5. a green-sensitive silver halide emulsion unit consisting of a first layer of 0.6 μ average mean diameter grains coated at a level of about 366 mgs/m² of silver and about 161 mgs/m² of gelatin and a second layer of 1.42 μ average mean diameter grains coated at a level of about 387 mgs/m² silver and about 186 mgs/m² of gelatin with a speed difference between said first and second layer of about 5 stops;

30 6. an interlayer layer containing the tetrapolymer referred to above in layer 3 at a coverage of about 1369 mgs/m², about 24 mgs/m² of polyacrylamide, and about 75 mgs/m² succindialdehyde;

7. a layer comprising the yellow dye developer

35



dispersed in gelatin and coated at a coverage of about 968 mgs/m² of dye and about 450 mgs/m² of gelatin and about 208 mgs/m² of 2-phenyl benzimidazole;

15 8. a blue-sensitive gelatino silver iodobromide emulsion layer coated at a coverage of about 1280 mgs/m² of silver, about 743 mgs/m² of gelatin, and about 204 mgs/m² of 4'-methylphenylhydroquinone;

20 9. an overcoat layer coated at a coverage of about 484 mgs/m² of gelatin and 43 mgs/m² of carbon black.

EXAMPLE 5

A second film unit was prepared as described except that in layer 5 each green-sensitive silver halide emulsion layer additionally contained 4 times the coverage of gelatin of a polymethylmethacrylate latex having an average particle size of about 0.125 μ and layer 6 was reduced in coverage by 40%.

The film units of Examples 4 and 5 were processed in the following manner, using the image-receiving element and processing composition described in Example 1.

The film unit was exposed to white light and the processing composition was spread between the two elements in a layer approximately 0.0028" thick in the dark.

The following sensitometer data (green light reflection data in neutral column) was obtained in the resulting multicolor reflection prints:

TABLE 1

	<u>Example 3</u>	<u>Example 4</u>	
	<u>Control</u>		
5	D _{max}	1.83	1.90
	Slope	1.71	1.20
	Toe Extent	37	51
	Dynamic Range	17.150	28.990
10	1.5 Speed	2.21	2.14
	0.45 Speed	1.55	1.24

From the foregoing it can be seen that a slight increase in D_{max}, a 51 unit reduction in slope, an increase in toe extent of about 14 units as well as an increase in dynamic range of almost 12 units are achieved. The loss indicated in the other properties is not considered significant; i.e., the advantages far outweigh the slight decreases recorded in speed. It should be understood that these enhanced photographic results are obtained at the same time the dye transfer is accelerated and silver halide layer integrity maintained.

It should be noted that the interlayer (layer 6) adjacent the silver halide emulsion layer containing the inert particles was reduced in coverage by 40%. This is an additional and unexpected advantage of the present invention which further enhances dye transfer.

A film unit similar to Example 5 was prepared except that the polymer latex employed was a 90/10 methylmethacrylate/hydroxypropyl acrylate copolymer. Upon exposure and processing similar advantageous results were obtained.



1. A photosensitive element for use in a diffusion transfer film unit which comprises a support carrying at least one photosensitive silver halide layer having a dye image-forming material associated therewith, wherein said silver halide layer comprises gelatin and inert particles which are substantially non-swelling in aqueous alkali, compatible with gelatin and substantially non-film forming; said inert particles being less than or equal to the silver halide grains in average diameter; said silver halide grains being 2.5 microns or less in average diameter.

2. The element of claim 1 wherein said photosensitive silver halide layer comprises,

a) a first photosensitive silver halide layer distal to the exposure surface of said element and comprising silver halide grains possessing a first mean particle size;

b) a second photosensitive silver halide layer having a second mean particle size; said second photosensitive layer having a higher intrinsic speed than said first photosensitive silver halide layer; said first and second photosensitive silver halide layers being in contiguous relationship; said inert particles being disposed in at least said second silver halide layer;

3. The element of claims 1 or 2 wherein the inert particles are derived from a polymeric latex.

4. The element of claim 3 wherein said polymer is polymethylmethacrylate.

5. The element of claim 3 wherein said polymer is polystyrene.

6. The element of claims 1 and 2 wherein the inert particle to gelatin ratio (by weight) is about 0.5 to 1 to 10 to 1.

7. The element of claim 6 wherein said inert particle to gelatin ratio is about 1 to 1.

8. The element of claim 6 wherein said inert particle to gelatin ratio is about 6 to 1.



9. The element of claims 1 and 2 wherein said dye image-forming material is a dye developer.

10. The element of claim 2 wherein the average mean diameter of said silver halide grains is said first
5 photosensitive silver halide layer is less than about 1 micron and wherein the average mean diameter of said grains in said second photosensitive layer is greater than about 1.3 microns.

11. The element of claim 2 wherein the speed
10 difference between said first and second photosensitive silver halide layers ranges from about 2 to about 8 stops.

12. The element of claim 11 wherein said speed difference is about 5 stops.

13. A diffusion transfer film unit comprising a
15 support carrying at least one silver halide emulsion layer having a dye image-forming material associated therewith and a dyeable receiving layer adapted to receive a dye image diffusing thereto after photoexposure and processing of said silver halide emulsion layer; wherein said silver
20 halide emulsion comprises gelatin and inert particles which are substantially non-swelling in aqueous alkali, compatible with gelatin and substantially non-film forming; said inert particles being less than or equal to the silver halide grains in average diameter; said silver halide grains being
25 2.5 microns or less in average diameter.

14. The film unit of claim 13 which includes a first and second photosensitive silver halide layer, said first photosensitive silver halide layer being distal to the exposure surface of said element and comprising silver
30 halide grains possessing a first mean particle size; said second photosensitive silver halide layer having a second mean particle size; said second photosensitive layer having a higher intrinsic speed than said first photosensitive silver halide layer; said first and second photosensitive
35 silver halide layers being in contiguous relationship; said inert particles being disposed in at least said second silver halide layer.

15. The film unit of claims 13 or 14 wherein



said inert particles are derived from a polymer latex.

16. The film unit of claim 15 wherein said polymer is polymethylmethacrylate.

17. The film unit of claim 16 wherein said
5 polymer is a methylmethacrylate/hydroxypropylmethacrylate copolymer.

18. The film unit of claim 15 wherein said polymer is polystyrene.

19. The film unit of claim 15 wherein said
10 polymer to gelatin ratio is about 0.5 to 1 to 10 to 1.

20. The film unit of claim 19 wherein said polymer to gelatin ratio is about 1 to 1.

21. The film unit of claim 19 wherein said polymer to gelatin ratio is about 6 to 1.

15 22. The film unit of claim 13 wherein said dye image-forming material is a dye developer.

23. The film unit of claim 13 which includes a rupturable container of processing composition adapted to discharge its contents between a predetermined pair of
20 layers.

24. The film unit of claim 23 wherein said dye-able receiving layer is adapted to be superposed over the silver halide emulsion layer subsequent to photoexposure and adapted to be separated therefrom after processing.

25 25. The film unit of claim 18 which is a permanent laminate and wherein the image is viewable in said receiving layer without separation of said receiving layer from said film unit.

26. The film unit of claim 14 wherein the mean
30 particle size of said grains in said first photosensitive silver halide layer is less than about 1.0μ and the mean particle size of said grains in said second photosensitive silver halide layer is at least 1.3μ .

27. The film unit of claim 14 wherein the speed
35 difference between said first and second photosensitive silver halide layers is about 2 to 8 stops.

28. The film unit of claim 27 wherein said speed difference is about 5 stops.



29. A photographic film unit which comprises, in combination:

a photosensitive element having a diffusion transfer image-receiving element affixed at least one edge thereof, said photosensitive element comprising a support carrying:

- a) a red-sensitive silver halide unit having associated therewith a cyan dye developer;
- b) a green-sensitive silver halide unit having associated therewith a magenta dye developer;
- c) a blue-sensitive silver halide unit having associated therewith a yellow dye developer; wherein at least one of said silver halide units comprises gelatin and inert particles which are substantially non-swelling in aqueous alkali; compatible with gelatin and substantially non-film forming; wherein said photosensitive and said image-receiving elements are adapted to be superposed with the support layers outermost; said inert particles being less than or equal to the silver halide grains in average diameter; said silver halide grains being 2.5 microns or less average diameter.

30. The film unit of claim 28 wherein at least one of said silver halide units comprises,

1. a first photosensitive silver halide layer distal to the exposure surface of said film unit and comprising silver halide grains possessing a first mean particle size;
2. a second photosensitive silver halide layer having a second mean particle size; said second photosensitive layer having a higher intrinsic speed than said first photosensitive silver halide layer; said first and second photosensitive silver layers being in contiguous relationship; said inert particles being disposed in at least said second silver halide layer.

31. The film unit of claims 28 and 29 wherein said inert particles are derived from a polymer latex.

32. The film unit of claim 30 including a rupturable container retaining an aqueous alkaline processing



composition and adapted to discharge its contents intermediate said superposed photosensitive and image-receiving elements.

5 33. The film unit of claims 28 and 29 wherein the support layer of said image-receiving element is transparent.

34. The film unit of claim 33 in which said unit is a composite structure comprising said photosensitive element and said image-receiving element permanently
10 affixed to the other in superposed relationship, the support layers of each of said elements being outermost.

35. The film unit of claim 28 wherein said polymer latex is disposed in said green-sensitive silver halide unit.

15 36. The film unit of claim 30 wherein said polymer is polymethylmethacrylate.

37. The film unit of claim 30 wherein said polymer is polystyrene.

20 38. The film unit of claim 28 wherein said polymer to gelatin ratio (by weight) is about 0.5 to 1 to 10 to 1.

39. The film unit of claim 38 wherein said polymer to gelatin ratio is about 1 to 1.

25 40. The film unit of claim 38 wherein said polymer to gelatin ratio is about 6 to 1.

41. The film unit of claim 29 wherein the mean particle size of said grains in said first photosensitive silver halide layer is less than about 1.0μ and the mean particle size of said grains in said second photosensitive
30 silver halide layer is at least 1.3μ .

42. The film unit of claim 40 wherein the speed difference between said first and second photosensitive silver halide layers is about 2 to 8 stops.

35 43. The film unit of claim 41 wherein said speed difference is about 5 stops.

44. A photosensitive element for use in a diffusion transfer film unit which comprises a support carrying:



a) a first photosensitive silver halide layer distal to the exposure surface of said element and comprising silver halide grains possessing a first mean particle size;

5 b) a second photosensitive silver halide layer having a second mean particle size; said second photosensitive layer having a higher intrinsic speed than said first photosensitive silver halide layer; said first and second photosensitive silver halide layers being in contiguous
10 relationship and having associated therewith a dye image forming material which is diffusible during processing as a function of the point-to-point degree of silver halide exposure to actinic radiation; said first and second photosensitive silver halide layers comprising gelatin and inert
15 particles which are substantially non-swelling in aqueous alkali, compatible with gelatin, and substantially non-film forming; said inert particles being equal to or less than the silver halide grain in average diameter; said silver halide grains being 2.5 microns or less in average
20 diameter.

45. A photographic diffusion transfer film unit comprising a support carrying at least one photosensitive element comprising a first and second photosensitive silver halide layer and a dyeable receiving layer adapted to
25 receive a dye image diffusing thereto after photoexposure and processing of said photosensitive element, said first photosensitive silver halide layer being distal to the exposure surface of said element and comprising silver halide grains possessing a first mean particle size; said
30 second photosensitive silver halide layer having a second mean particle size; said second photosensitive layer having a higher intrinsic speed than said first photosensitive silver halide layer; said first and second photosensitive silver halide layers being in contiguous relationship and
35 having associated therewith a dye image forming material which is diffusible during processing as a function of the point-to-point degree of silver halide exposure to actinic radiation; said first and second photosensitive silver



halide layers comprising gelatin and inert particles which are substantially non-swelling in alkali, compatible with gelatin, and substantially non-film forming; said inert particles being less than or equal to the silver halide grains in average diameter; said silver halide grains being 2.5 microns or less in average diameter.

46. A photographic film unit which comprises, in combination:

a photosensitive element having a diffusion transfer image-receiving element affixed at least one edge thereof, said photosensitive element comprising a support carrying:

a) a red-sensitive silver halide unit having associated therewith a cyan dye developer;

b) a green-sensitive silver halide unit having associated therewith a cyan dye developer;

c) a blue-sensitive silver halide unit having associated therewith a yellow dye developer; wherein at least one of said silver halide units comprises:

1) a first photosensitive silver halide layer distal to the exposure surface of said film unit and comprising silver halide grains possessing a first mean particle size;

2) a second photosensitive silver halide layer having a second mean particle size; said second photosensitive layer having a higher intrinsic speed than said first photosensitive silver halide layer; said first and second photosensitive silver halide layers being in contiguous relationship and having associated therewith a dye image forming material which is diffusible during processing as a function of the point-to-point degree of silver halide exposure to actinic radiation; said first and second photosensitive silver halide layers comprising gelatin and inert particles which are substantially non-swelling in alkali, compatible with gelatin, and substantially non-film forming; said inert particles being less than or equal to the silver halide grains in average diameter; said silver halide grains being 2.5 microns or less in average diameter wherein said



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photosensitive and said image-receiving elements are adapted to be superposed with the support layers outermost.



INTERNATIONAL SEARCH REPORT

International Application No PCT/US 79/00294

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ¹				
According to International Patent Classification (IPC) or to both National Classification and IPC				
Int. CL. G03C 1/40, 1/76, 3/00, 1/10				
US CL. 96/73, 74, 77, 99, 100				
II. FIELDS SEARCHED				
Minimum Documentation Searched ⁴				
Classification System	Classification Symbols			
US	96/3, 29D, 73, 74, 77, 95, 99, 100, 113, 114, 114.7			
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵				
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴				
Category ⁶	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸		
A	US, A, 2,772,166, Published 27 NOVEMBER 1956, FOWLER	1-46		
X	US, A, 2,835,582, Published 20 MAY 1958, FOWLER ET AL.	1-46		
X	US, A, 3,142,568, Published 28 JULY 1964, NOTTORF	1-46		
A	US, A, 3,157,510, Published 17 NOVEMBER 1964, AMERING	1-46		
A	US, A, 3,287,289, Published 22 NOVEMBER 1966, REAM ET AL.	1-46		
A	US, A, 3,325,286, Published 13 JUNE 1967, NOTTORF	1-46		
X	US, A, 3,411,907, Published 19 NOVEMBER 1968, WHITMORE	1-46		
X	US, A, 3,411,911, Published 19 NOVEMBER 1968, DYKSTRA	1-46		
A	US, A, 3,505,068, Published 07 APRIL 1970, BECKETT ET AL.	2-12, 14-22, 25-28, 30-46		
A	US, A, 3,418,132, Published 24 DECEMBER 1968, Column 6, lines 36 to 68 KITZE	1-46		
X	US, A, 3,620,747, Published 16 NOVEMBER 1971, Column 7, lines 40 to 55, column 11, lines 15 to 25, MARCHANT ET AL.	1-46		
<p>¹⁵ Special categories of cited documents:</p> <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;"> <p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> </td> <td style="width: 50%; border: none;"> <p>"P" document published prior to the international filing date but on or after the priority date claimed</p> <p>"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance</p> </td> </tr> </table>			<p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p>	<p>"P" document published prior to the international filing date but on or after the priority date claimed</p> <p>"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance</p>
<p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p>	<p>"P" document published prior to the international filing date but on or after the priority date claimed</p> <p>"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance</p>			
IV. CERTIFICATION				
Date of the Actual Completion of the International Search ³	Date of Mailing of this International Search Report ²			
13 AUGUST 1979	29 AUG 1979			
International Searching Authority ¹	Signature of Authorized Officer ¹⁹			
ISA/US	<div style="display: flex; align-items: center;"> <div style="flex: 1;">RICHARD L. SCHILLING</div> <div style="flex: 1; text-align: right;"> </div> </div>			

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

X	US, A, 3,632,342, Published 04 JANUARY 1972, SALESIN ET AL.	1-46
A	US, A, 3,663,228, Published 16 MAY 1972, WYCKOFF	2-12, 14-22, 25-28, 30-46
A	US, A, 3,695,882, Published 03 OCTOBER 1972, KUMAI ET AL.	2-12, 14-22, 25-28, 30-46
X	US, A, 3,772,032, Published 13 NOVEMBER 1973, PEARSON ET AL.	1-46
X	US, A, 3,773,517, Published 20 NOVEMBER 1973, DODWELL	1-46
A	US, A, 3,775,129, Published 27 NOVEMBER 1973, DODWELL	1-46
A	US, A, 3,846,135, Published 05 NOVEMBER 1974, HELLMIG ET AL.	2-12, 14-22, 25-28, 30-46

V. OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹⁰

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. Claim numbers _____, because they relate to subject matter¹² not required to be searched by this Authority, namely:

2. Claim numbers _____, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out¹³, specifically:

VI. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ¹¹

This International Searching Authority found multiple inventions in this international application as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

Remark on Protest

The additional search fees were accompanied by applicant's protest.

No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

X	US, A, 3,880,658, Published 29 APRIL 1975, Column 26, lines 35-68 LESTINA ET AL.	1-46
X	US, A, 3,960,558, Published 01 JUNE 1976, Column 5, lines 25-53, column 7, lines 19-33, CARDONE	1-46
X	US, A, 4,003,744, Published 18 JANUARY 1977, Column 6, lines 26-58, column 8, line 58 to column 9, line 3, KLIEM	1-46
X, PUS,	A, 4,133,687, Published 09 JANUARY 1979, CHEN ET AL.	1-46

V. OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹⁰

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. Claim numbers _____, because they relate to subject matter ¹¹ not required to be searched by this Authority, namely:
2. Claim numbers _____, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹², specifically:

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2. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

Remark on Protest

- The additional search fees were accompanied by applicant's protest.
- No protest accompanied the payment of additional search fees.