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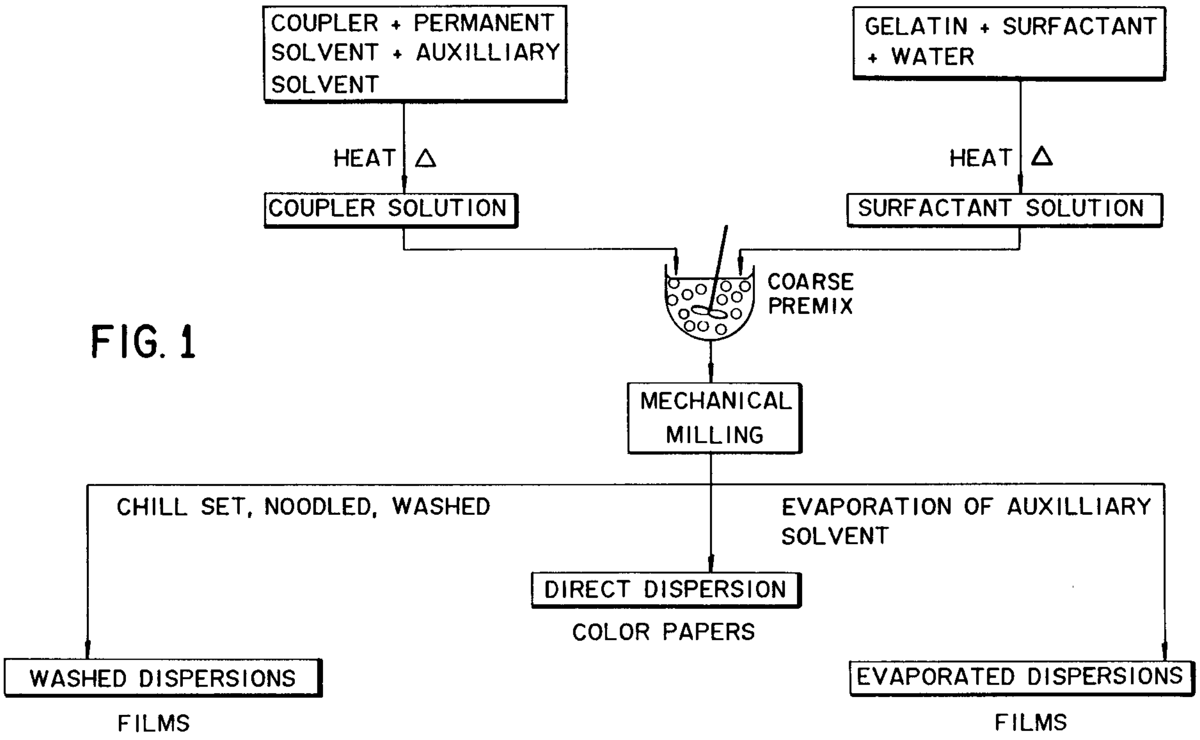
(54) Yellow layer for colour photographic paper.

(57) Polyalkylene oxide compounds or block polymeric or block oligomeric surface active compounds comprising at least a polyoxypropylene (POP) block and a polyoxyethylene (POE) block are added to conventional dispersions of pivalylacetanilide (PAA)-yellow couplers, such dispersions in a coated silver halide photographic element produce substantially higher dye yield compared to the conventional dispersion without any additive. Further, the yellow dye formed from such dispersions containing the addenda of this invention are substantially more light stable compared to dispersions that does not contain such addenda.

The required amounts of the said polyoxyethylene (POE) - polyoxypropylene (POP) compound may be added to a preformed milled coupler dispersion prior to coating the photographic element. They may also be incorporated in the milling step during preparation of the milled coupler dispersion along with a suitable dispersing surfactant, which preferably is an anionic surfactant.

Rank Xerox (UK) Business Services
(3.10/3.6/3.3.1)

FIG. 1


COUPLER + PERMANENT SOLVENT + AUXILLIARY SOLVENT
GELATIN + SURFACTANT + WATER
HEAT Δ
HEAT Δ
COUPLER SOLUTION
SURFACTANT SOLUTION
COARSE PREMIX
MECHANICAL MILLING
CHILL SET, NOODLED, WASHED
EVAPORATION OF AUXILLIARY SOLVENT
DIRECT DISPERSION
COLOR PAPERS
WASHED DISPERSIONS
FILMS
EVAPORATED DISPERSIONS
FILMS

This invention relates to color photographic elements and to a method of preparing the same. More particularly, it relates to photographic elements containing certain yellow coupler dispersions and silver halide having an unexpected increase in photographic activity of the yellow dispersion and also an unexpected increase of the stability of the developed yellow dye to light fade.

Ballasted photographic dye forming couplers are usually incorporated in photographic systems as a colloidal emulsion, usually called a dispersion in the photographic art. The various methods of preparation of photographic coupler dispersions of prior art are illustrated in Figure 1. The coupler is added to a high boiling water immiscible solvent (called a permanent solvent) such as tricresyl phosphate, dibutyl phthalate, etc. Some times a low boiling water miscible solvent (called an auxiliary solvent) such as ethylacetate, propanol, methyl-isobutyl ketone, etc. is also added to promote the solubility of less soluble couplers. The mixture is heated to form a true crystal free solution, called the "coupler solution" as indicated in Figure 1. A second solution of the stabilizing surfactant or surfactants is added to a mixture of gelatin and water and heated to produce a true solution called the "surfactant solution" as indicated in Figure 1. The surfactant used in the "surfactant solution" is usually an anionic surfactant. The "surfactant solution" and the "coupler solution" are then mixed together with mild stirring to form what is known as a "premix". The premix consists of a crude emulsion of the oil phase (i.e., the "coupler solution") in the aqueous phase (i.e., the "surfactant solution"). The crude "dispersion" is composed of droplets of very large particles, of the order of 5-15 μm in diameter and is as such not usable for high quality photographic products. It is necessary to further reduce the particle size by subsequent high shear milling procedures. The crude "premix" is then further milled in an appropriate high shear milling device. If the coupler solution is composed of only "permanent" solvent, then the dispersion is directly usable in photographic product and such dispersions are usually called "direct dispersions". The particle size of such dispersions are generally broadly distributed with an average diameter between 0.1 to 0.3 μm. As direct dispersions do not contain any auxiliary solvents, no water miscible solvent removal is necessary, resulting in a relatively less expensive dispersion preparation process. Such direct dispersions are then appropriate for price sensitive high volume products such as various types of color papers.

When dispersions are prepared with auxiliary solvents an additional step is necessary to remove the water miscible solvent such that it does not evaporate during the cooling operations to cause excessive evaporation load or create an environmentally hazardous situation. Those dispersions that are treated by some type of an evaporation procedure to remove the auxiliary solvent under a controlled condition are called "evaporated" dispersions. Alternatively, the crude premix can be chill set and noodled by extrusion through orifices and washed by cold water to remove the water soluble auxiliary solvent. Dispersions prepared by this process are usually called "washed" dispersions. Washed dispersions are in general more expensive than evaporated dispersions as they may involve up to 50 hours of tedious washing procedures. Both "washed" and evaporated dispersions lead to dispersion droplets that have broad size distribution with mean diameters ranging between 0.1 to 0.3 μm. "Washed" and "evaporated" dispersions are usually suitable for low volume film products.

U.S. Patent 3,860,425, issued June 14, 1975 to Ono et al teaches the use of a mixture of (1) a nonionic surface active agent containing polyoxypropylene units having a molecular weight greater than 500 and polyoxyethylene units, and at a molar ratio of said polyoxyethylene units to the polyoxypropylene units ranging from 0.1 to 0.6 and (2) an anionic surface active agent having an $-OSO_3M$ group or an $-SO_3M$ group, wherein M represents a monovalent cation, and a hydrophobic group in the preparation of a milled dispersion of oleophilic materials, for photographic use. Such dispersions have particle diameters between 0.67 to 0.19 μm. Between about 0.05 to about 0.10 gram of the anionic surfactant and between about 0.02 gram to about 0.10 gram of the nonionic surfactant per gram of the oleophilic dispersed phase of the coupler are used.

U.S. Patent 5,013,640, issued May 7, 1991 to Bagchi et al discloses the use of block oligomeric surfactants comprising hydrophobic polyoxyethylene block (A) and hydrophilic polyoxypropylene block (B) joined in the manner of A-B-A, B-A-B, A-B, $(A\text{-}B)_n{\cong}G{\cong}(B\text{-}A)_n$, a $(B\text{-}A){\cong}G{\cong}(A\text{-}B)_n$, where G is a connector organic moiety and n is between 1 and 3, as melt addenda to reduce viscosity of a microprecipitated dispersion melt in gelatin. The said microprecipitated dispersion being preprecipitated as a slurry in water before gelatin addition using preferably an anionic surfactant. The particle size of the microprecipitated dispersions have diameters between 0.01 to 0.05 μm.

In cost sensitive high volume products, such as Ektacolor® Paper or Eastman Color Print®, it is desirable to increase the dye yield of a coupler, as in such a case, it requires less coupler and/or silver, which translates to cost reduction. Further, cyan, magenta and yellow dyes that create photographic images, fade with time when exposed to various ambient lighting conditions such as sunlight, incandescent light or fluorescent light. Most damage is usually done by UV-radiation that may be present in any lighting source. It is therefore desirable to make photographic products, especially photographic paper that is used to display images of both personal and commercial scenes, as stable as possible to fade. There are various means of achieving improved dye stability. One way is to produce couplers that form dye with increased dye stability. Since products such as Ektacolor® Paper or Eastman Color Print® are high volume products that are highly price sensitive, it is not always commercially feasible to replace an existing coupler with settled down cost with a new coupler. Photographic papers contain a layer comprising a UV-absorbing compound dispersed in protective layers to absorb the damaging UV-radiation and prevent it from reaching the image dyes. Usually such UV-absorbing compounds have a slight yellow coloration, which when applied in large enough quantities cause the white areas of paper to appear yellow, which is highly undesirable. Therefore, there is a limit to the extent that such UV-absorptive materials can be applied in a photographic product such as paper. U.S. Patent 4,656,125 issued April 7, 1987, to Rinner et al discloses that dye stability can be achieved by the addition of stabilizer compounds to the coupler dispersions. A need to enhance the activity of photographic couplers and enhance the stability of image dyes from fade is desired.

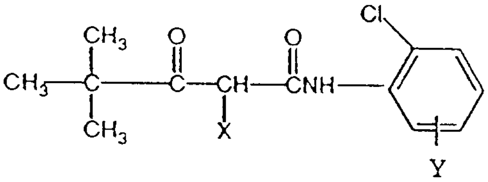
In photographic paper where the image resides on a reflective support light passes through the photographic layers twice for the visualization of the image. In transparency display products such as Duratrans® light passes through the image only once. Therefore, to produce enough visual density the couplers and the silver halide emulsions are coated at about 70% higher levels on a transparent support. In such case, where the component loading is very high, the bottom yellow layer develops up much more slowly compared to the top cyan and the magenta layers. This requires the use of a longer development time. Therefore, a more active bottom yellow layer in such products with faster development rates will provide a much improved product with shorter development time. Therefore, there is need for the invention of a more active yellow dispersion melt.

An object of this invention is to provide more active, (one yielding more dye-density per unit lay down) yellow couplers, dispersed by conventional milling procedures by the simple addition of polyoxyalkylene compounds to the dispersion melt just prior to coating of a photographic product.

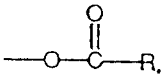
Another object of the invention is to provide more light-stable yellow dye-forming coupler dispersion melts for quality improvement of photographic products such as color papers and color display materials.

Another objective of this invention is to provide a multilayer photographic package, where the bottom slow-developing yellow layer is more active.

It has been discovered, quite unexpectedly, that when polymeric, polyoxyalkylene surface active compounds are added to conventional dispersions of pivalylacetanilide (PAA)-yellow couplers, such dispersions in a coated silver halide photographic element produce substantially higher dye yield compared to the conventional dispersion without any additive. Further, the yellow dye formed from such dispersions containing the addenda of this invention are substantially more light stable compared to dispersions that do not contain such addenda. The structure of PAA class yellow couplers to which this invention applies is as follows:

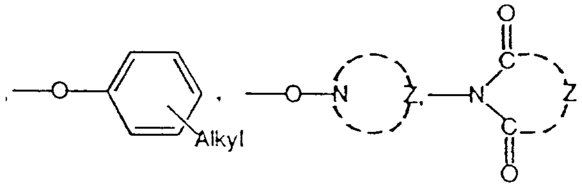


where X = -H, -Cl,



$$-O-\overset{\overset{O}{\|}}{C}-R.$$

-SAr(Ar = aryl group), $-SO_2R$ or $-OSO_2R$, where R is an alkyl group



(where Z is any organic moieties to complete the ring).
and Y is a ballasting group

Ballasting groups usually comprise one or more 5 to 25 carbon atom containing organic moiety whose function is to immobilize the coupler and the formed image dye during photographic development by imparting poor water diffusibility to the coupler compound. Kodachrome® type couplers, however, are unballasted and therefore are soluble in developer solutions. Such couplers are usually incorporated in the developer solutions. Fisher couplers usually contain a solubilizing $-SO_3^-$ group to impart base solubilizing characteristics to the coupler molecule. In polymeric couplers, the ballast is the polymer backbone which may also be gelatin. In some polymeric couplers the bonding to the ballasting polymeric backbone is achieved through the coupling off group rendering the formed dye more mobile and transferable by diffusion or by thermal evaporation after photographic development. A broad description of such coupler compounds can be found in "The Theory of the Photographic Process", 4th Edition, McMillan, New York, 1977 by T.H. James. Typical ballast group -Y- are extensively described in US 3,770,446 (1973), US 3,265,506 (1966) etc. and are hereby incorporated herein by reference. Broad groups of various ballast groups that can be used are disclosed in US patents 2,875,057; 2,407,210; 2,298,443; 3,048,194; 4,022,620; 4,443,536 and 3,447,928, which are also included herein by reference.

The invention is carried out by adding required amounts of the polymeric polyoxyalkylene surface active compound and preferably a surface active compound comprising at least a polyoxypropylene (POP) block and a polyethylene (POE) block to the dispersion melts, prepared by conventional milling procedure prior to coating the film product.

Drawings are included to illustrate the advantages of this invention. Briefly, the drawings are:

Fig. 1 is a diagrammatic flow chart illustrating prior art procedures for the preparation of conventional milled dispersions.

Fig. 2 is a graph of fresh sensitometric curves comparing several preparations in accordance with the invention to a control.

Fig. 3 is a graph of dye density vs. silver coverage comparing several preparations in accordance with the invention to a control.

Fig. 4 is a graph of fresh sensitometric curves comparing a preparation in accordance with the invention to a control.

The methods of preparation of conventional milled dispersions of photographic dye-forming couplers have been extensively described earlier. In the method and composition of this invention, the surfactant used to prepare the surfactant solution of Fig. 1 is any surfactant that will aid the formation of stable dispersions of particles.

Such surfactants for the preparation of the dispersion can be anionic and are in general defined as follows:

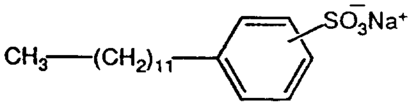
Class - A: Anionic Dispersion Surfactants:

The anionic dispersion surfactants of this invention comprise a 6 to 25 carbon atom hydrophobic moiety made up of either aliphatic, aromatic or of both types of hydrocarbons, or fluorocarbon groups terminated by single or multiple anionic charges arising from $-COO^-$, $-SO_3^-$ or $-OSO_3^-$ groups or a combination thereof.

Typical examples of such "Class-A Anionic Dispersion Surfactants" are as follow:

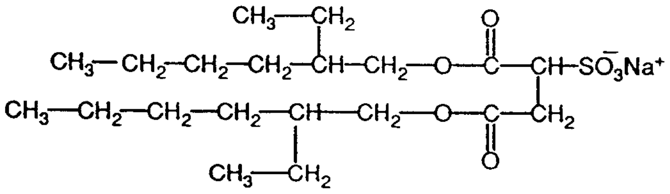
DS-A1 $CH_3-(CH_2)_{11}-\overline{S}O_4Na^+$ (Sodium Dodecyl Sulfate)

DS-A2



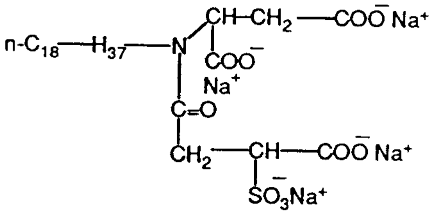
(Sodium Dodecyl Benzene Sulfonate)

DS-A3



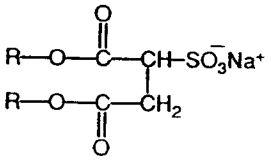
(Aerosol OT, Cyanamid)

DS-A4



(Aerosol 22, Cyanamid)

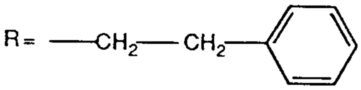
DS-A5



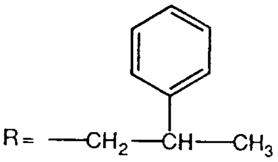
where R = $CH(CH_3)C_4H_9$

(Aerosol MA, Cyanamid)

DS-A6 —do—

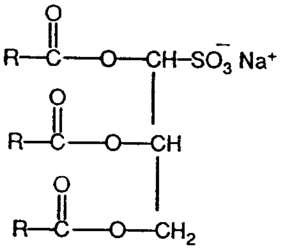


DS-A7 —do—



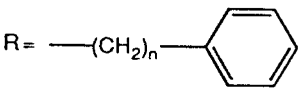
DS-A8 —do— R = $—CH_2—CH(CH_2CH_3)C_3H_7$

DS-A9



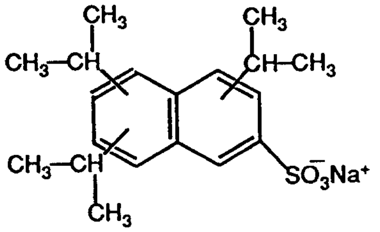
R = $—(CH_2)_nCH_3$ (n = 2, 3 & 5)

DS-A10 —do—



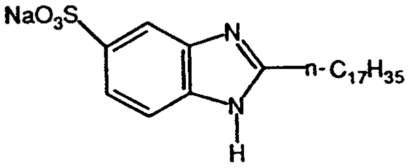
(n = 2 to 5)

DS-A11

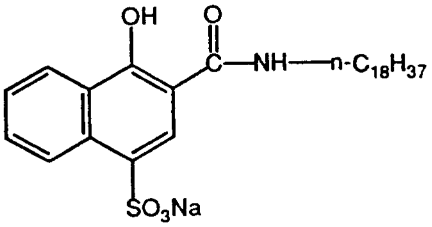


(Alkanol-XC, Du Pont)

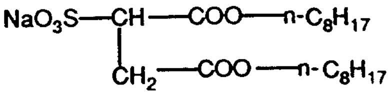
DS-A12



DS-A13



DS-A14



$$NaO_3S-\underset{\begin{array}{l}|\\ CH_2-COO-n\text{-}C_8H_{17}\end{array}}{CH}-COO-n\text{-}C_8H_{17}$$

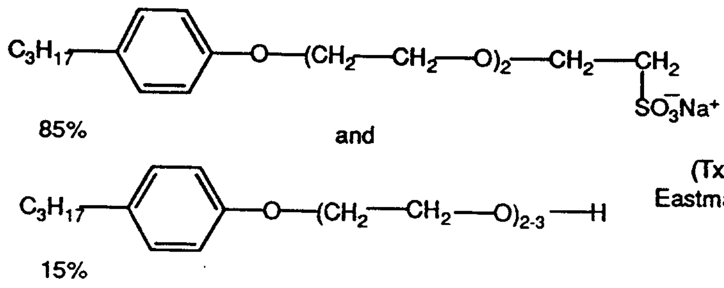
Such surfactants for the preparation of the dispersions can also be polyether surfactants definable as follows:

Class -B: Polyether Dispersion Surfactants:

The polyether dispersion surfactants of this invention comprise a 6 to 25 carbon atom hydrophobic moiety made up of either aliphatic, aromatic or of both types of hydrocarbon or fluorocarbon groups and at least 2 oxyethylene and/or glycidyl ether groups that may or may not be terminated with a single or multiple negative change arising from $-COO^-$, $-OSO_3^-$, or $-OSO_4^-$ groups or a combination thereof.

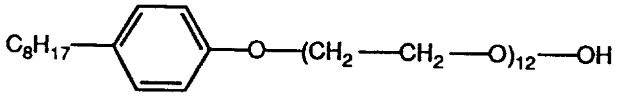
Typical examples of such "Class-B Polyether Dispersion Surfactants" are as follows:

DS-B1



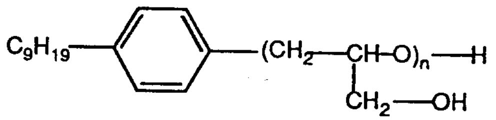
(Tx200E, Eastman Kodak Company)

DS-B2



(Triton X-102, Union Carbide)

DS-B3



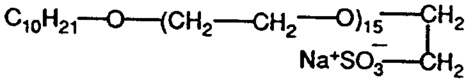
n = 5-12 (mixture)

(Olin 10G, Olin)

DS-B4 n-$C_{12}H_{25}-O-(CH_2-CH_2-O)_{12}-SO_3^-Na^+$ (Polystep B-23, Stepan)

DS-B5 n-$C_{12}H_{25}-O-(CH_2-CH_2-O)_{23}-OH$ (Trycol 5964, Henkel)

DS-B6



$C_{10}H_{21}-O-(CH_2-CH_2-O)_{15}-CH_2-CH_2-SO_3^-Na^+$

(Avanel S-150, PPG/Mazer)

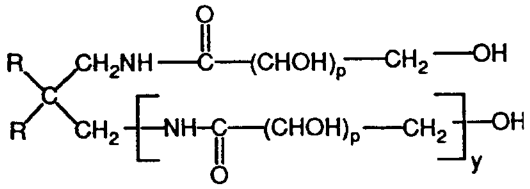
Such surfactants for the preparation of the dispersion can also be sugar surfactants defined as follows:

Class -C: Sugar Dispersion Surfactants:

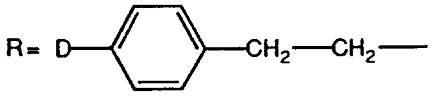
The sugar dispersion surfactants of this invention are characterized by having one to three hydrophobic tails, each tail containing from about 6 to 25 carbon atoms comprising either aliphatic, aromatic or a combination of both types of hydrocarbon or fluorocarbon groups and also having one or more attached hydrophilic mono- or oligosacharidic hydrophilic chains that may or may not be terminated by single or multiple anionic charges arising from $-COO^-$, $-OSO^-_3$ or $-SO^-_3$ groups or a combination thereof.

Typical examples of such "Class -C Sugar Dispersion Surfactants" are as follows:

DS-C1



where, R = H(CH), and z = 0 - 10

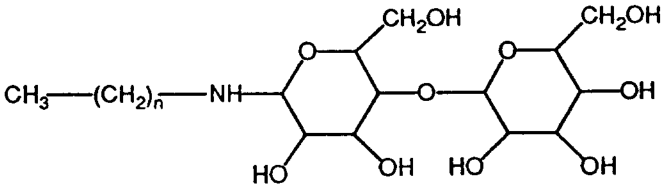


$p = 3$ to 10

$D = (CH_2)_z$

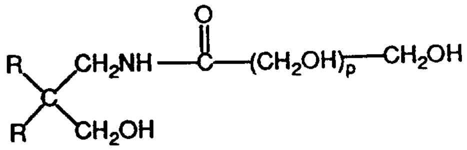
$y = 0$ or 1

DS-C2



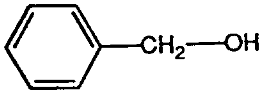
where, $n = 3$ to 15

DS-C3



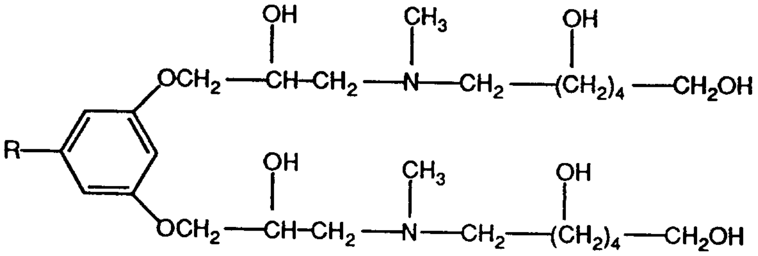
where, R = n-CH_3—$(CH_2)_x$— (where x = 3 to 10)

R =



p = 3 to 15

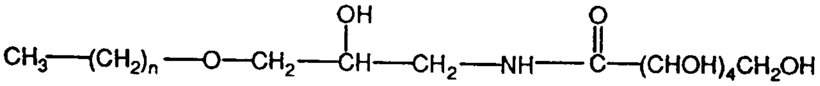
DS-C4



where, R = n—CH_3—$(CH_2)_x$—

(where, x = 1 to 5)

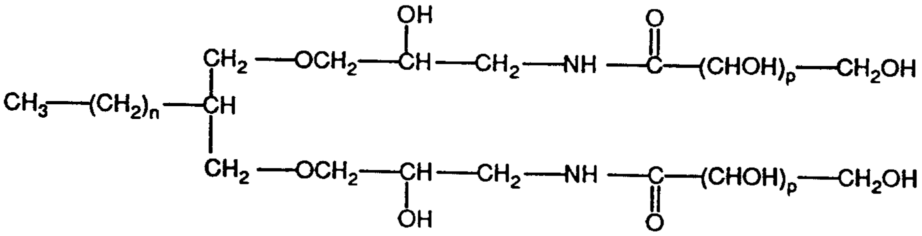
DS-C5



$$CH_3-(CH_2)_n-O-CH_2-\overset{OH}{CH}-CH_2-NH-\overset{O}{\overset{\|}{C}}-(CHOH)_4CH_2OH$$

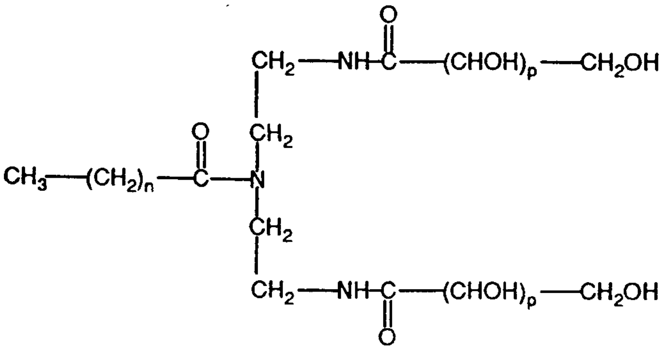
where, n = 3 to 15

DS-C6



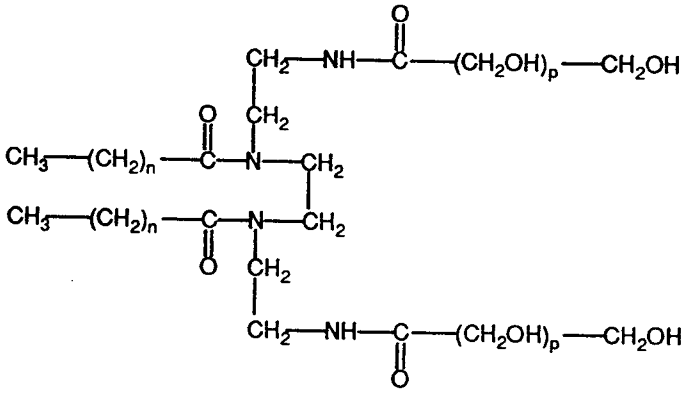
where, n = 2 to 12
p = 3 to 10

DS-C7



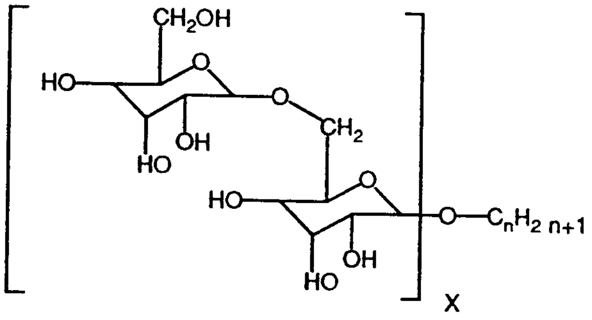
where, n = 6 to 18
p = 3 to 10

DS-C8



where, n = 2 to 18
p = 3 to 10

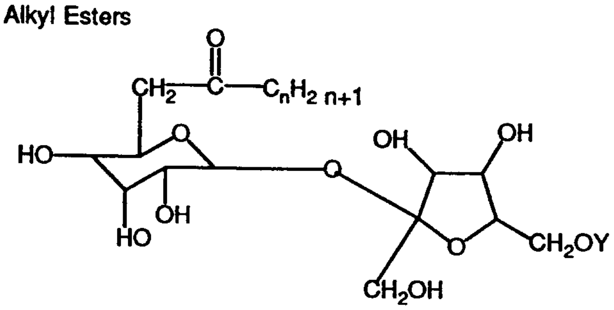
DS-C9 Alkyl Polyglycosides



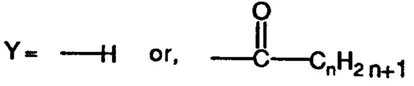
n is 8 to 14

APG 225	n is	8 and	10 and	x = 1.8
APG 300	n is	9 and	11 and	x = 1.4
APG 325	n is	9 and	11 and	x = 1.6
APG 600FP	n is	12 and	14 and	x = 1.4
APG 625	n is	12 and	14 and	x = 1.6

DS-C10 Sucrose Alkyl Esters

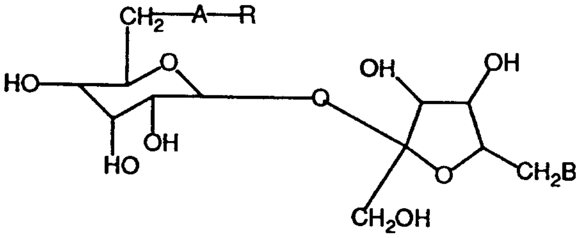


where n = 9 to 17



$Y = -H$ or, $-\overset{O}{\overset{\|}{C}}-C_nH_{2n+1}$

DS-C11 Sucrose Alkyl Amide and Ether



where R = $-C_{10}H_{21}$

to $-C_{18}H_{37}$

and $-A-$

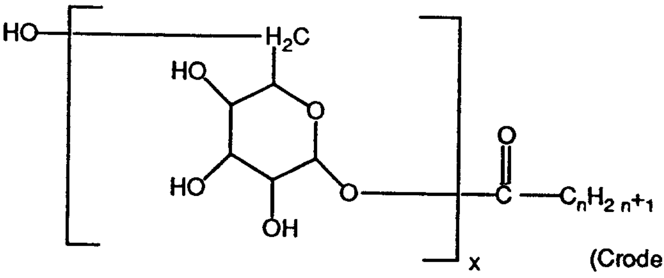
is $-O-\overset{O}{\overset{\|}{C}}-NH-$

or $-O-$

and B is $-OH$

or $-A-R$

DS-C12



(Crodesta, Croda, Inc.)

wherein

n = 5 to 20 and

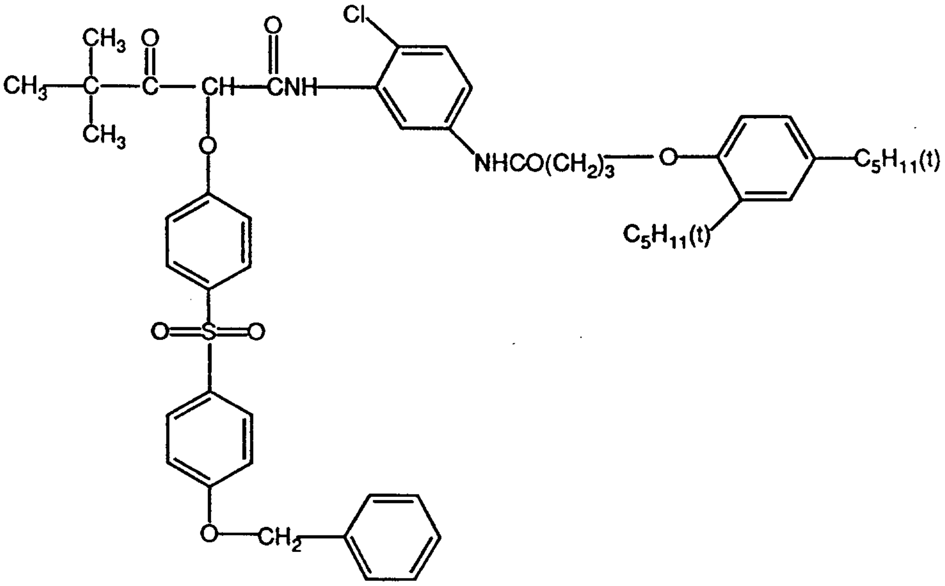
x = 1 to 4.

The dispersion surfactant or surfactants can be used by themselves or as any combination of mixtures of different classes or different individual surfactants at a level performing between about 0.03g to about 0.1g of total surfactant, as a single surfactant or in combination for the preparation of the dispersion per g of the coupler to be dispersed. The preferred surfactant is Alkanol-XC (DS-A11).

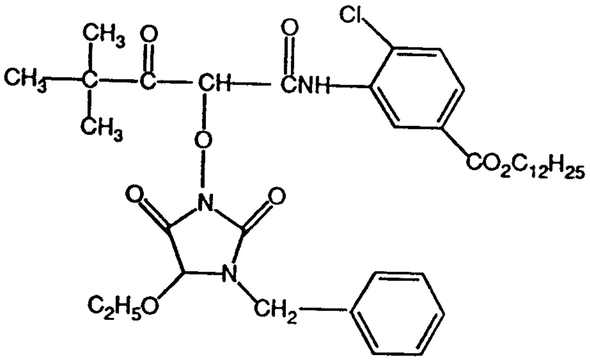
Other surfactants of class-A, B or C set forth in "McCutcheon's", Vol. 1, "Emulsifiers and Detergents", International Edition and North American Edition, McCutcheon's Division of the Manufacturing Confectioner Publishing Co., N.J. (1991), incorporated herein by reference, may be used.

The couplers of this invention are yellow-dye forming pivalylacetanilide (PAA) couplers of general structure as indicated earlier. Specific examples of such class of couplers are as follows:

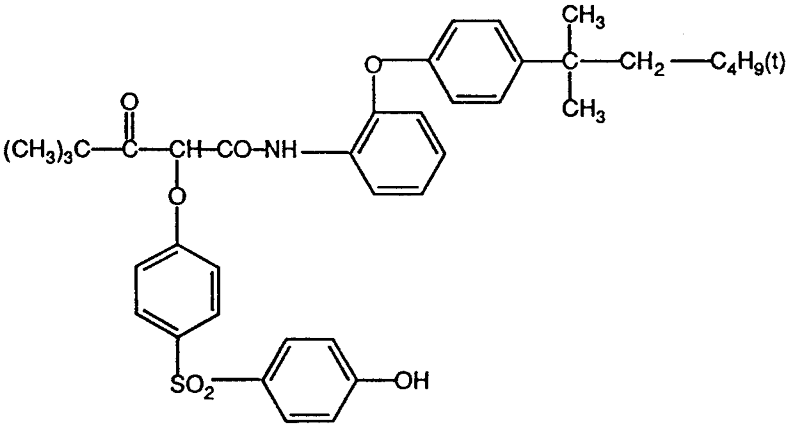
CY-1



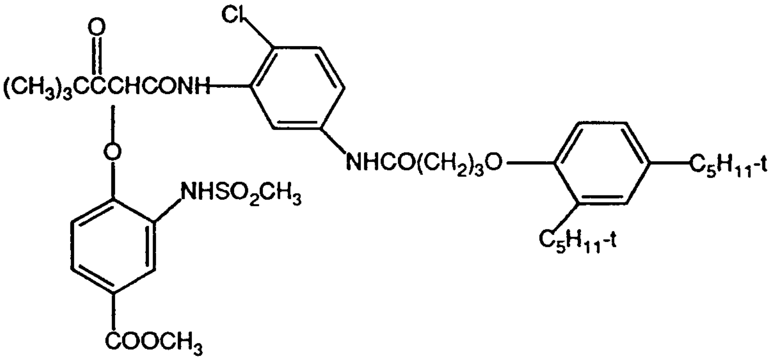
CY-2



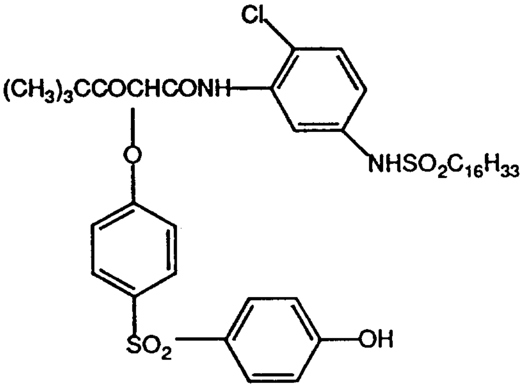
CY-3



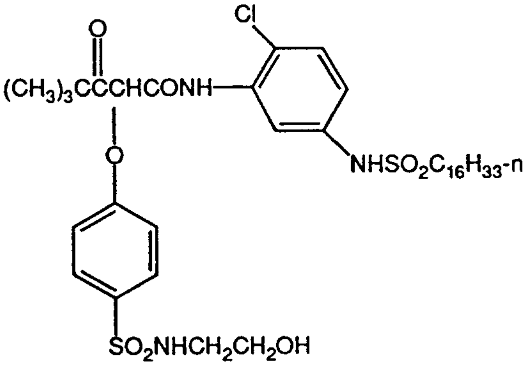
CY-4



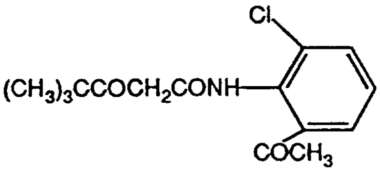
CY-5


Cl
(CH3)3CCOCHCONH
O
NHSO2C16H33
SO2
OH

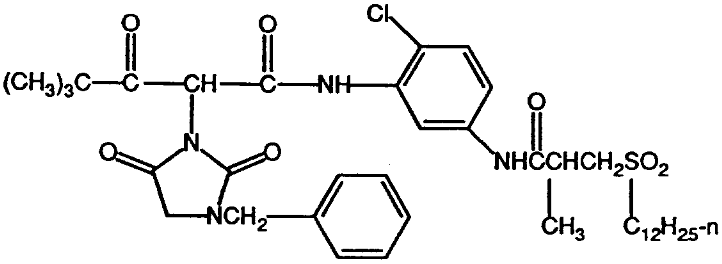
CY-6


O
Cl
(CH3)3CCCHCONH
O
NHSO2C16H33-n
SO2NHCH2CH2OH

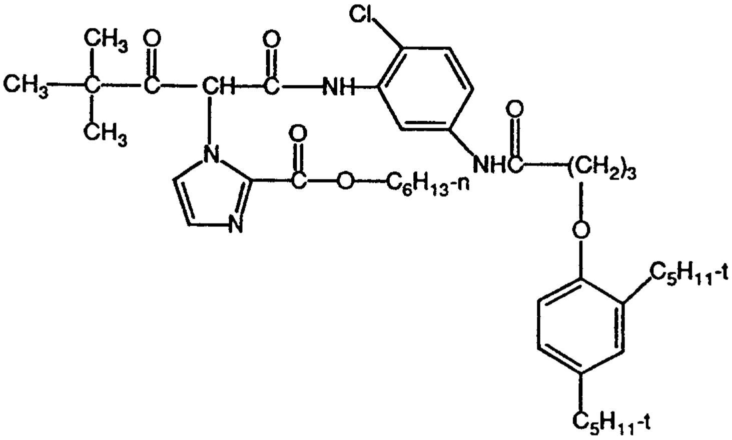
CY-7


Cl
(CH3)3CCOCH2CONH
COCH3

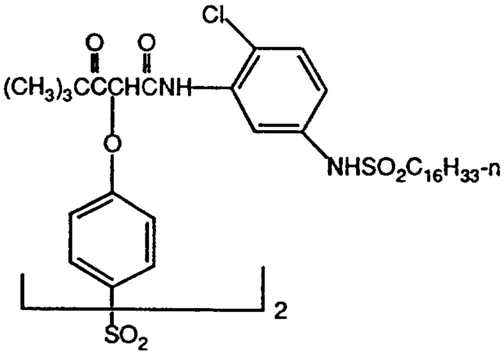
CY-8


Cl
O
O
(CH3)3C
C
CH
C
NH
N
O
O
NCH2
O
NHCCHCH2SO2
CH3
C12H25-n

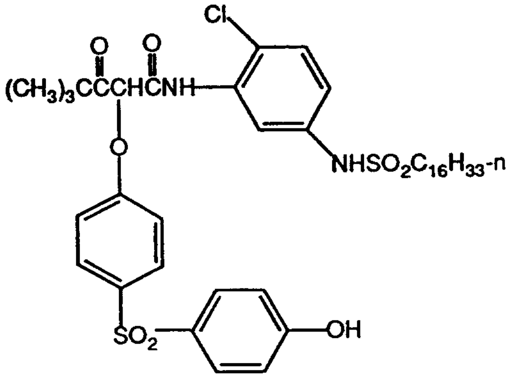
CY-9


Cl
CH3
O
O
CH3
C
C
CH
C
NH
CH3
N
O
C
O
C6H13-n
N
O
NHC
(CH2)3
O
C5H11-t
C5H11-t

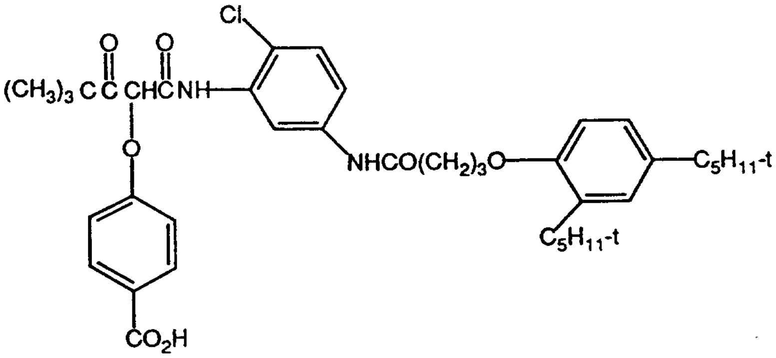
CY-10


Cl
O
O
(CH3)3CCCHCNH
O
NHSO2C16H33-n
2
SO2

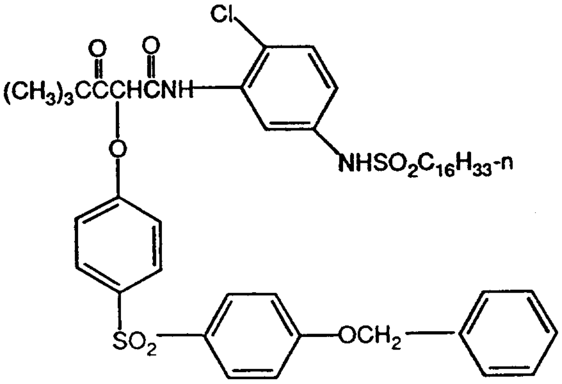
CY-11



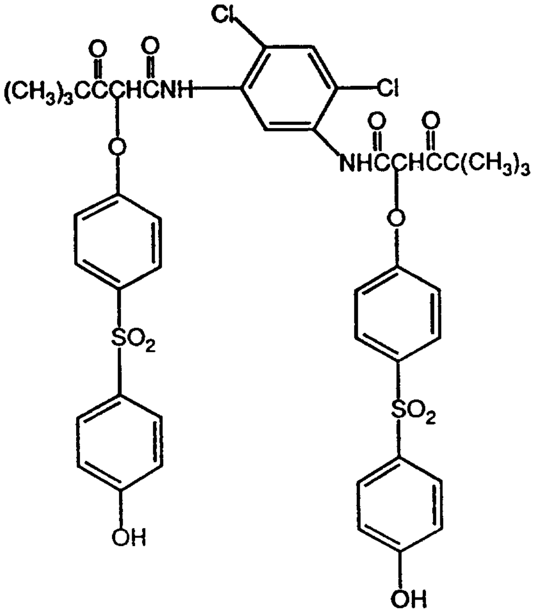
CY-12



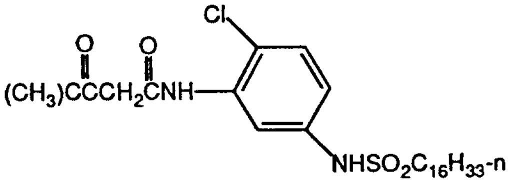
CY-13



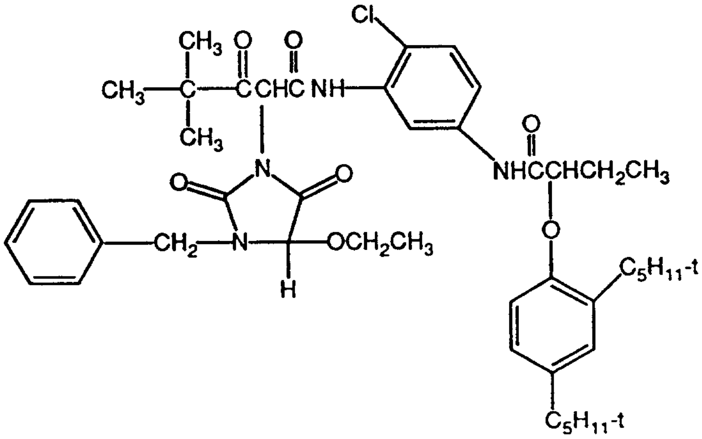
CY-14



CY-15



CY-16



Suitable surface active polyoxyalkylene polymers and preferably block polymeric compounds containing polyoxyethylene and polyoxypropylene blocks or block polymers with multiple polyoxyethylene-polyoxypropylene blocks connected together by an organic moiety that impart high activity and high dye-stability when added to a silver halide gelatino coating melt containing conventionally predispersed PAA couplers of this invention, are given to Table I.

Table I: Polymeric, Block Polymeric and Block Oligomeric Addenda of this Invention

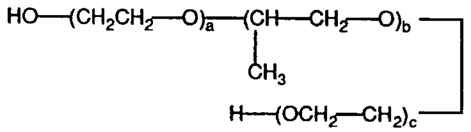
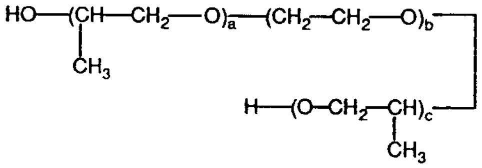
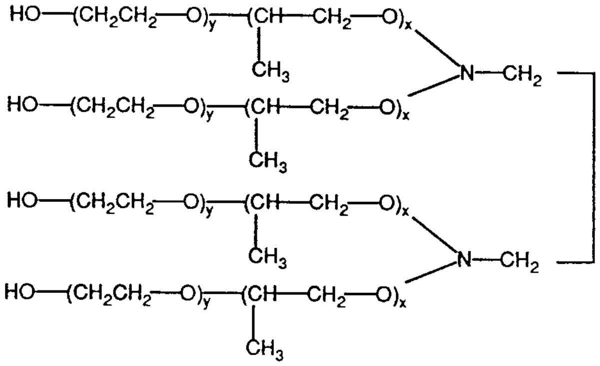
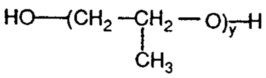
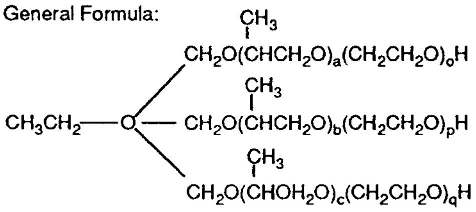
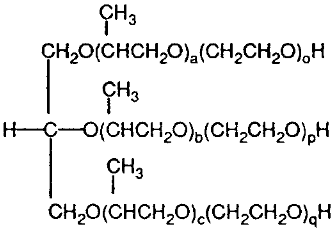
ID	Name (Manufacturer)	Structure	Molecular Weight Range
P-1	Pluronic™ Polyols (BASF)		1,100 to 14,000
P-2	Pluronic™-R Polyols (BASF)		1,900 to 9,000
P-3	Plurodot™ Polyols (BASF)	Liquid Polyethers Based on Alkoxylated Triols	3,200 to 7,500
P-4	Tetronic™ Polyols (BASF)		3,200 to 27,000
P-5	Pluracol E™	$HO-(CH_2-CH_2-O)_y-H$	200 to 45,000
P-6	Pluracol P™	 $HO-(CH_2-\underset{CH_3}{CH_2}-O)_y-H$	400 to 2,000

Table I: Continued

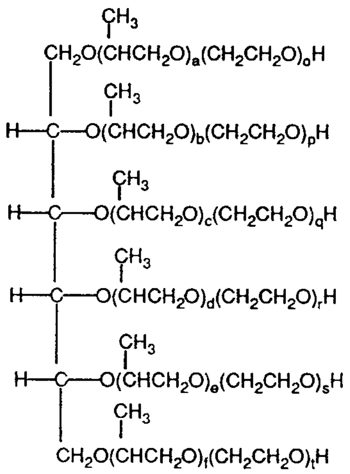
ID	Name (Manufacturer)	Structure	Molecular Weight Range
P-7	—	General Formula: 	

	Molecular Weight	
	Entire Cmpd	Polyoxypropylene Fragment
Compound (P-7a) (a+b+c): (o+p+q) = 1:0.43	4500	3400
Compound (P-7b) (a+b+c): (o+p+q) = 1:0.25	4000	3400
Compound (P-7c) (a+b+c): (o+p+q) = 1:0.10	4000	3700

ID	Name (Manufacturer)	Structure	Molecular Weight Range
P-8	—	General Formula:  In the general formula (B):	

	Molecular Weight	
	Entire Cmpd	Polyoxypropylene Fragment
Compound (P-8a) (a+b+c): (o+p+q) = 1:0.3	3000	2400
Compound (P-8b) (a+b+c): (o+p+q) = 1:0.2	1500	1300

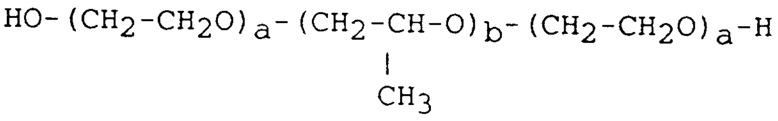
Table I: Continued

ID	Name (Manufacturer)	Structure	Molecular Weight Range
P-9	—	General Formula (C):  In the general formula:	

	Molecular Weight	
	Entire Cmpd	Polyoxypropylene Fragment
Compound (P-9a) (a+b+c+d+e+f): (o+p+q+r+s+t) = 1:0.5	3000	2200
Compound (P-9b) (a+b+c+d+e+f): (o+p+q+r+s+t) = 1:0.3	1000	300
Compound (P-9c) (a+b+c+d+e+f): (o+p+q+r+s+t) = 1:0.1	1000	900

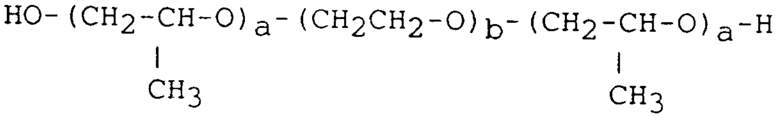
Other polyethylene/polypropylene block containing compounds disclosed in McCutcheon's, Vol 1, "Emulsifiers and Detergents" mention previously may be employed in this invention.

The block polymeric addenda of this invention is added to a coating melt to the extent of 0.1 to 0.6g per gram of the PAA coupler of this invention. The preferred amount is between 0.1 to 0.3g of the block polymeric compound per gram of the PAA coupler. The preferred block polymeric materials of this invention are (P-1) through (P-6). Particularly preferred are polyoxyalkylene polymers of the formula:



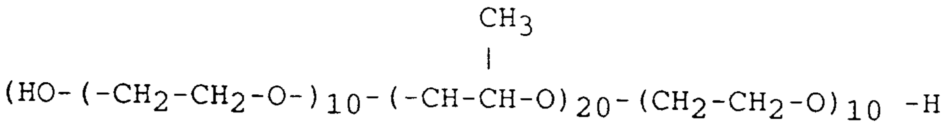
$$HO-(CH_2-CH_2O)_a-(CH_2-\underset{CH_3}{\underset{|}{CH}}-O)_b-(CH_2-CH_2O)_a-H$$

or



$$HO-(CH_2-\underset{CH_3}{\underset{|}{CH}}-O)_a-(CH_2CH_2-O)_b-(CH_2-\underset{CH_3}{\underset{|}{CH}}-O)_a-H$$

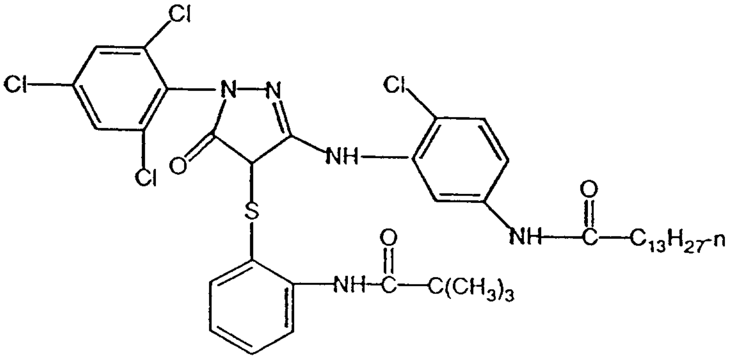
where a has a value of 5 to 500 and, b has a value of 5 to 500. Most preferred is Pluronic L44 which has the following structure. Pluronic L44



$$(HO\text{-}(\text{-}CH_2\text{-}CH_2\text{-}O\text{-})_{10}\text{-}(\text{-}CH\text{-}\overset{\overset{CH_3}{|}}{C}H\text{-}O)_{20}\text{-}(CH_2\text{-}CH_2\text{-}O)_{10}\ \text{-}H$$

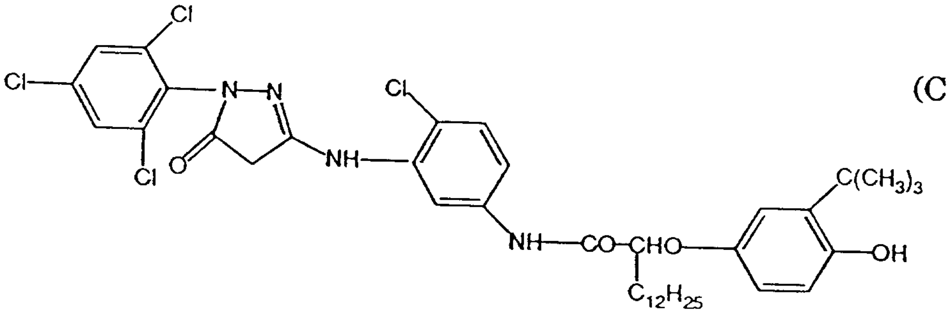
This invention is very specific to couplers of the PAA class. The addition of the surface active materials of this invention produce no activity advantage or dye stability advantage to other couplers. The noninventive coupler combinations with the surface active addenda of this invention exemplified hereinafter are as follows:

4-Thiopyrazolones (Magenta)



(C-1)

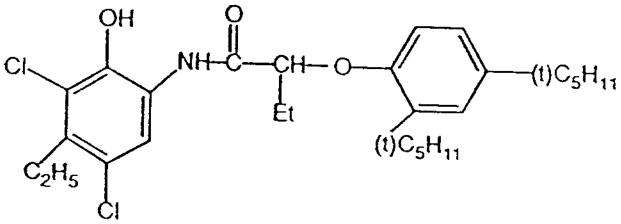
Pyrazolones (Magenta)

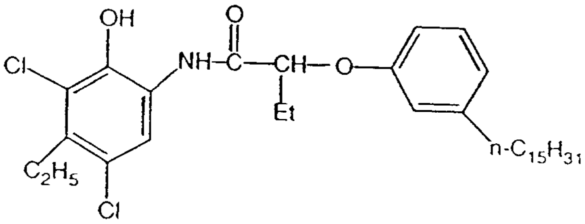


(C-2)

Phenolic (Cyan)

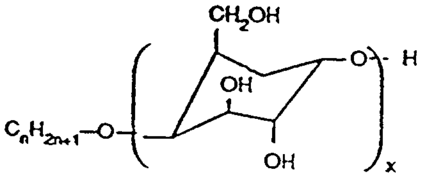
(C-3)





(C-4)

Not all nonionic surface active materials show this unique simultaneous effect of increased activity and added dye stability. The noninventive, nonionic surfactant used in this example is the alkyl polyglycoside (APG-225), which has the following structure.



(APG 225)

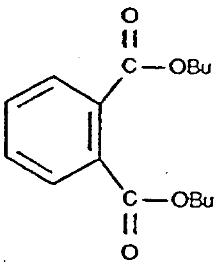
Examples

The following examples are intended to be illustrative and not exhaustive of the invention. Parts and percentages are by weight unless otherwise specified.

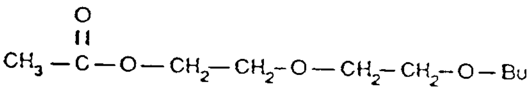
Coating laydowns are given in "mg/ft^2". Multiplication of these numbers by 10.7 will convert them to "mg/m^2".

Examples 1 - 7: Dispersions Utilized

Conventional dispersions of the compounds indicated in Table II were prepared according to the description given earlier by the direct method for the reduction to practice of this invention. The various solvents used in preparing these dispersions are as follows:

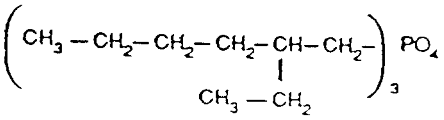


(S-1)



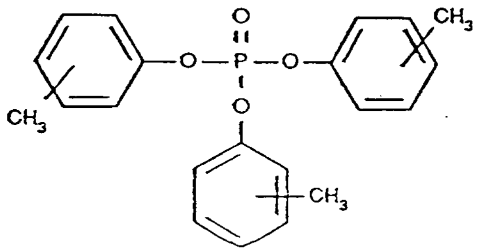
$CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_2-O-CH_2-CH_2-O-Bu$

(S-2)



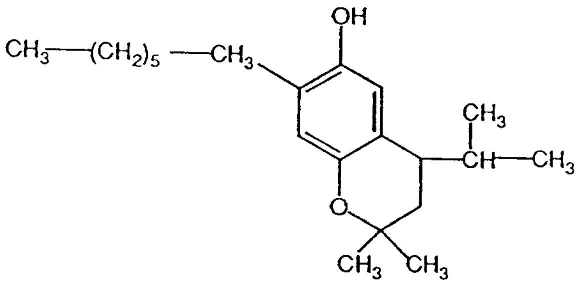
$\left(CH_3-CH_2-CH_2-CH_2-\underset{\underset{CH_3-CH_2}{|}}{CH}-CH_2-\right)_3 PO_4$

(S-3)

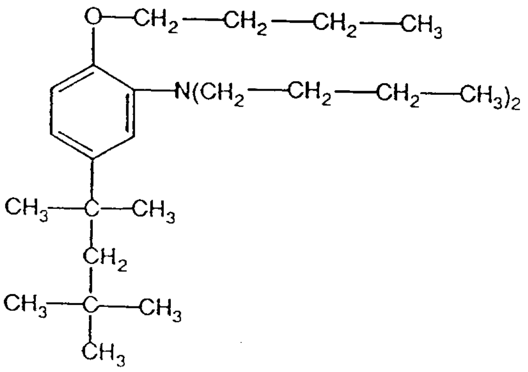


(S-4)

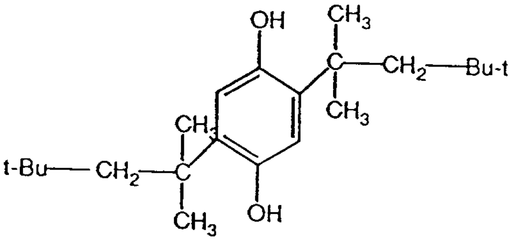
Dye stabilizers and associated scavengers used in preparation of these dispersions are as follows:



(ST-1)



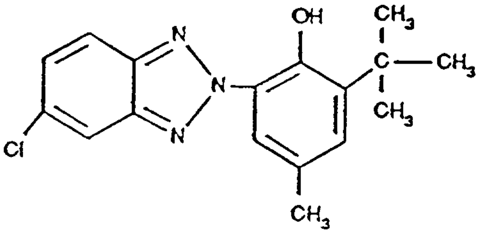
(ST2)



(ST-3)

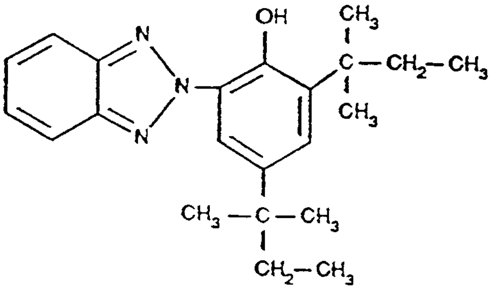
The UV-absorbing compounds used in the layers over the sensitized layers are as follows:

Tinuvin 326



(UV-1)

Tinuvin 328



(UV-2)

Table II. Compositions of Conventional Dispersions

Example #	Coupler # or UV-Compd. #	Coupler wt %	Coupler Solvent	Wt. % of Coupler Solvent	Surfactant Name	Wt. % of Surfactant	Stabilizer Compound	Wt. % of Stabilizer Compound	Gelatin Wt. %	Water Wt. %
1	(CY-1)	12.9	(S-1)	3.2	(DS-A11)	0.9	none	none	8.8	71.0
			(S-2)	3.2						
2	(CY-2)	9.0	(S-1)	3.0	(DS-A11)	0.9	none	none	9.0	78.1
3	(C-2)	8.7	(S-1)	8.7	(DS-A11)	1.0	(ST-1)	3.7	8.7	76.3
							(ST-3)	0.9		
4	(C-1)	6.7	(S-3)	4.9	(DS-A11)	0.9	(ST-2)	7.8	8.4	76.4
			(S-4)	2.2	(DS-A11)		(ST-3)	0.7		
5	(C-3)	9.5	(S-1)	5.2	(DS-A11)	0.7	(ST-3)	0.03	9.5	75.1
			(S-2)	0.8	(DS-A11)					
6	(C-4)	8.3	(S-1)	4.0	(DS-A11)	0.4	none	none	9.9	77.4
7	(UV-2)	11.8	none	none	(DS-A11)	0.5	none	none	7.8	77.4
	(UV-1)	2.1								

It is to be noted that the dispersion of Example 7 does not contain any coupler solvent. The compounds (UV-1) and (UV-2) at elevated temperatures form an utectic mixture that is liquid and than can be dispersed in aqueous gelatin solution like other conventional dispersions.

Examples 8-15: Photographic Coatings and Evaluation Using PAA-Coupler (CY-1)

The coating format for testing these PAA-yellow couplers, from the base up, is as follows:
Base: Titanium dioxide loaded polyethylene resin coated photographic paper stock.

Blue Sensitized Layer: Blue sensitized cubic silver chloride emulsion with up to about 1% surface iodide having an average cubic edge length of about 0.6 microns at 30 mg/ft^2. Yellow dye-forming coupler (CY-1) at 100 mg/ft^2 dispersion of Example 1, gelatin at 115 mg/ft^2, added surfactant (inventive and noninventive at 0, 0.2, and 0.6 g of coupler (CY-1).

UV-Absorbing Layer: UV-absorbing compounds (UV-2) and (UV-1) in dispersion of Example 7 at 80 mg/ft^2, gelatin at 121 mg/ft^2.

Overcoat: 125 mg/ft^2 of gelatin and gelatin hardener bis(vinylsulfonylmethyl)ether (BVSME) at the level of 2% based upon total gel in the packet.

In all layers the spreading agent Olin 10G (Dixie Corporation) was used at a level of 0.3% of the melt volume of each layer.

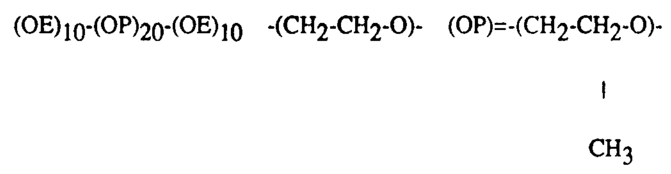
The coatings were exposed to white light through a gray wedge chart and then processed by the Kodak RA-4 process (Kodak is a trademark of the Eastman Kodak Co.). The resultant image was then read by a color densitometer and the results are summarized in Table III. It is observed in Table III, that in the inventive coatings where the material of this invention, L44, was spiked in at levels of 0.2 and 0.6g per gram of the coupler, large increases in Dmax and contrast (gradient) are shown, with other photographic parameters such as Dmin, and speed remaining the same. Such large boost in limiting reflection density levels indicate large increases in dye density yield. Extraction of the dye from the coatings and determination of their yield with a known extinction coefficient of the dye for the two invention Examples 9 and 10 are also shown in Table III in comparison with the control Example 8. It is seen that in Example 9 there is about a 46% and in Example 10 about 60% increased dye yield. The addition of L44 increased the dye yield for coupler (CY-1). APG 225 which is also a nonionic amphiphile did not show any increase in dye density (Table III). The actual sensitometric curves of the control Example 8 and the invention Examples 9 and 10 are also shown in Fig. 2, where it is seen that the spiking of L44 produces a very large boost in the Dmax of the coating of PAA coupler (CY-1). It is also seen that the boost in activity is nonlinear. That is, the major increase occurs up to a level of 0.2 g per g of coupler (CY-1) and beyond this amount the effect levels off. Fig. 3 shows plots of the dye density yield vs silver formed in the step wedge image as measured by x-ray fluorescence, after fixing out the Ag halide following the color development step. The invention examples show larger dye density for the same amount of silver developed in comparison to the control coatings.

Another advantage of this invention, is high dye stability of the formed dye image. This was demonstrated by exposing the images for 2 and 4 weeks to high intensity (50 K Lux) light balanced to the color temperature of sunshine under ambient humidity and temperature conditions. The density losses measured from a density of 1.7 are also listed in Table III. It is observed that in the inventive Examples 9 and 10 where L44 was present dye density losses were considerably smaller compared to the control Example 8 and the noninventive Example 11 which contained the noninventive material APG 224. It is observed that control Example 8 did not contain any L44.

Table III. Fresh Sensitometry and Dye Stability Results of Photographic Coatings with PPA Coupler (CY-1)

	Addenda		Blue Sensitometers						50 K Lux Sunshine Fade from Density 1.7				
									2 Week Fade		4 Week Fade		
Example #	Name	g per g of coupler	Dmax	Dmin	Average Gradient	Speed	Dmax from Control	Gradient from Control	D	Dye Stability Factor[2]	D	Dye Stability Factor[2]	Dye Yield Micro-Mole/ft^2
8	none control	0.0	2.447	0.052	2.560	182	0.000	0.000	-0.340	1.00X	-0.722	0.00X	57
9	Pluronic L44[1] inventive	0.2	2.963	0.063	2.963	180	0.516	0.043	-0.166	2.04X	-0.476	1.52X	83
10	Pluronic L44[1] inventive	0.6	3.024	0.061	3.024	180	0.577	0.464	-0.125	2.72x	-0.431	1.68x	91
11	APG non-inventive	0.2	2.460	0.059	2.460	182	0.013	-0.100	-0.323	1.052X	-0.695	1.04X	

[1] Pluronic L44



$(OE)_{10}\text{-}(OP)_{20}\text{-}(OE)_{10}$ $\text{-}(CH_2\text{-}CH_2\text{-}O)\text{-}$ $(OP)=\text{-}(CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH_2}}\text{-}O)\text{-}$

[2] Dye Stability Factor Ratio of fade from density of 1.7 of example to that of the control.

In a second coating set, similar spiking experiments were done with other polyalkylene compounds such as polyethylene oxide (MW 1500), and polyalkylene block oligomers such as Pluronic P-75 and Tetronic T-304. Table IV shows that these compounds in accordance with this invention with PAA coupler (CY-1) produced increase Dmax, contrast and stability to dye fade under exposure of 50 K Lux sunshine temperature balanced illumination. From the extent of the effects observed, it appears that the block polyalkylene polymers are preferred over the polyoxyethylene compound examined.

Table IV: Enhancement of Dmas, Gradient and Dye Stability of PAA Coupler (CY-1) by the Addition of Various Compounds of this Invention

		Addenda		Increase Over Control in Blue Gradient	Increase Over	50 K Lux Sunshine Fade from Density 1.7		
		g per g of	Control in Blue Dmax		2 Week Fade		4 Week Fade	
Example #	Name	Coupler	Dmin	Gradient	D	Dye Stability Factor	D	Dye Stability Factor
12	none (control)	0.0	0.000	0.000	-0.474	1.00X	-0.937	1.00X
13	Pluronic[1] P-75 inventive	0.2	0.163	0.176	-0.298	1.63X	-0.671	1.62X
14	Tetronic[2] T-304	0.2	0.244	0.238	-0.271	1.75X	-0.602	1.38X
15	Polyethylene Oxide MW 1500 inventive	0.2	0.074	0.113	-0.369	1.28X	-0.796	1.17X

Examples 16 - 17: Photographic Coatings and Evaluation Using PAA-Coupler (CY-2)

The coating format for testing yellow coupler (CY-2), from the base up, is as follows:

Base: Resin coated paper stock as described in Examples 8 - 15.

Blue Sensitized Layer: Blue sensitized cubic silver chloride emulsion with up to about 1% surface bromide having an average cube edge length of about 0.6 micron at 24 mg/ft^2, yellow dye forming coupler (CY-2) at 50 mg/ft^2 (dispersion of Example 2), gelatin at 115 mg/ft^2, added surfactant L-44 0 and 0.2g per g f coupler (CY-2).

UV-Absorbing Layer: UV-absorbing compounds (UV-2) and (UV-1) in dispersion of Example 7 at 80 mg/ft^2, gelatin at 121 mg/ft^2.

Overcoat: 125 mg/ft^2 of gelatin and gelatin hardener bis(vinylsulfonylmethyl)ether (BVSME) at the level of 2% based upon total gel in the packet.

In all layers the spreading agent Olin 10G was used at a level of 0.3% of the melt volume of each layer.

The coatings were exposed and processed in the same manner as indicated earlier. Results are tabulated in Table V. It clearly shows that coupler (CY-2) shows enhancement of Dmax, gradient and dye stability with the addition of the combination agent of this invention, L44, in the layer where the coupler resides. The fresh sensitometry of the coatings of Examples 16 and 17 are shown in Fig. 4.

Table V: Fresh Sensitometry and Dye Stability of Photographic Coating with PAA Coupler (CY-2)

	Addenda		Blue Sensitometers						50 K Lux Sunshine Fade from Density 1.0			
									2 Week Fade		4 Week Fade	
Example #	Name	g per g of coupler	Dmax	Dmin	Average Gradient	Speed	Dmax from Control	Gradient from Control	D	Dye Stability Factor	D	Dye Stability Factor
16	none control	0.0	1.244	0.078	1.110	139	0.000	0.00	-0.412	1.00X	-0.706	1.00X
17	Pluronic L44 inventive	0.2	1.700	0.079	1.852	139	0.742	0.041	-0.230	1.79X	-0.540	1.31X

Example 18: Photographic Coating and Evaluation Using Thiopyrazolone Magenta Coupler (C-1) (Comparative)

The coating format for testing magenta coupler (C-1), from base up, is as follows:

Base: Resin coated paper stock as described in Examples 8 - 15.

Green Sensitized Layer: Green sensitized cubic silver chloride emulsion with up to about 1% surface bromide having an average cubic edge length of about 0.3 micron at 17 mg/ft^2, magenta dye-forming coupler (C-1) at 32 mg/ft^2, with associated image stabilizers as indicated in the dispersion of Example 4, gelatin at 115 mg/ft^2, added surfactant Pluronic L44 at 0, 20 and 60 mg/ft^2.

Overcoat: 125 mg/ft^2 of gelatin and gelatin and hardener BVSME at levels of 2% based upon total gel in the packet.

In all layers the spreading agent Olin 10G was used at a level of 0.3% of the melt volume of each layer.

The coatings were exposed and processed in the same manner as indicated earlier. Sensitometric data, both fresh and after exposure to prolonged high intensity illumination, did not show any activity or dye stability advantages.

Example 19: Photographic Coatings and Evaluation Using Pyrazolone Magenta Coupler (C-2) (Comparative)

The coating format for testing magenta coupler (C-2), from base up, is as follows:

Base: Resin coated paper stock as described in Examples 8 - 15.

Green Sensitized Layer: Green sensitized cubic silver chloride emulsion with up to 1% surface bromide having an average cubic edge length of about 0.3 micron at 26.5 mg/ft^2, magenta dye-forming coupler (C-2) at 41.5 mg/ft^2, with associated image stabilizers as indicated in dispersion of Example 3, gelatin at 115 mg/ft^2, added surfactant Pluronic L44 at 0, 20 and 60 mg/ft^2.

UV-Absorbing Layer: UV-absorbing compounds (UV-2) and (UV-1) in dispersion of Example 7 at 80 mg/ft^2, gelatin at 121 mg/ft^2.

Overcoat: 125 mg/ft^2 of gelatin and hardener BVSME at levels of 2% based upon total gel in the packet.

In all layers the spreading agent Olin 10G was used at a level of 0.3% of the melt volume of each layer.

The coatings were exposed and processed in the same manner as indicated earlier. Sensitometric data, both fresh and after exposure to prolonged high intensity illumination, did not show any activity or dye stability advantages.

Example 20: Photographic Coatings and Evaluation Using Phenolic Cyan Coupler (C-3) (Comparative)

The coating format for testing cyan coupler (C-3), from base up, is as follows:

Base: Resin coated paper stock as described in Examples 8 - 15.

Red Sensitized Layer: Red sensitized cubic silver chloride emulsion with up to 1% surface bromide having an average cubic edge length of about 0.38 micron at 16.7 mg/ft^2. Cyan dye-forming coupler (C-3) at 39.3 mg/ft^2 as indicated in dispersion of Example 5. Gelatin at 115 mg/ft^2, added surfactant Pluronic L44 at 0, 20, and 60 mg/ft^2.

UV-Absorbing Layer: UV-absorbing compounds (UV-2) and (UV-1) in dispersion of Example 7 at 40 mg/ft^2, gelatin at 61 mg/ft^2.

Overcoat: 126 mg/ft^2 of gelatin and hardener BVSME at levels of 2% based upon total gel in the packet.

In all layers the spreading agent Olin 10G was used at a level of 0.3% of the melt volume of each layer.

The coatings were exposed and processed in the same manner as indicated earlier. Sensitometric data, both fresh and after exposure to prolonged high intensity illumination did not show any activity or dye stability advantages.

Example 21: Photographic Coatings and Evaluation Using Phenolic Cyan Coupler (C-4) (Comparative)

The coating format for testing cyan coupler (C-4), from base up, is as follows:

Base: Resin coated paper stock as described in Examples 8 - 15.

Red Sensitive Layer: Red sensitive cubic chloride emulsion with up to 10% surface bromide having average cubic edge length of about 0.38 micron at 20 mg/ft^2, cyan dye-forming coupler (C-4) at 40 mg/ft^2 as indicated in dispersion of Example 6, gelatin at 100 mg/ft^2, addenda Pluronic L44 at 0, 20 and 60 mg/ft^2.

UV-Absorbing Layer: UV-absorbing compounds (UV-2) and (UV-1) in dispersion of Example 7 at 40 mg/ft^2, gelatin at 61 mg/ft^2.

Overcoat: 126 mg/ft^2 of gelatin and hardener BVSME at levels of 2% based upon total gel in the packet.

In all layers the spreading Olin 10G was used at a level of 0.3% of the melt volume of each layer.

The coatings were exposed and processed in the same manner as indicated earlier. Sensitometric data, both fresh and after exposure to prolonged high intensity illumination, did not show any activity or dye stability advantages.

A typical full multilayer photographic element in accordance with this invention has the following configuration:

(Numbers indicate coverage in mg per square ft.)

(Numbers within " " indicate same in mg per square meter)

LAYER 7

Overcoat:

125.0 Gelatin; "1336"
2.0 (ST-3) (Conventional Scavenger Dispersed in Solvent); "21"

LAYER-6

UV Protection Layer:

61.0 Gelatin; "653"
34.3 Tinuvin 328 (Co-dispersed) Ultraviolet light absorber; "364"
5.7 Tinuvin 326 (Co-dispersed) Ultraviolet light absorber; "60"
4.0 (ST-3) (Co-dispersed in Solvent); "43"

LAYER-5

Red Layer:

115.0 Gelatin; "1230"
39.3 (C-3) (Cyan Cplr. Co-dispersed in Solv.); "420"
0.5 (ST-3) (Scavenger Co-dispersed in Solvent); "5"
16.7 AgCl (In Red Sensitized AgCl Emulsion); "179"

LAYER-4

UV Protection Layer:

61.0 Gelatin; "653"
34.3 Tinuvin 328 (Co-dispersed); "364"
5.7 Tinuvin 326 (Co-dispersed); "60"
4.0 (ST-3) (Co-dispersed in Solvent); "43"

LAYER-3

Green Layer:

115.0 Gelatin; "1230"
41.5 (C-2) (Magenta Coupler Co-dispersed in Solvent); "444"
18.2 (ST-1) (Stabilizer Co-dispersed in Solvent); "195"
3.4 (ST-3) (Scavenger Co-dispersed in Solvent); "37"
24.5 AgCl (In Green Sensitized AgCl Emulsion); "262"

LAYER-2

Inter Layer:

70.0 Gelatin; "749"
9.0 (ST-3) (Scavenger Dispersed in Solvent); "96"

LAYER-1

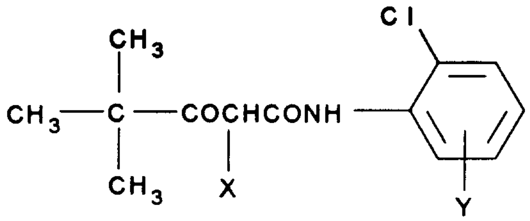
Blue Layer:

140.0 Gelatin; "1498"
100.0 (CY-1) (Yellow Coupler Dispersed in Solv.); "1070"
30.0 AgCl (In Blue Sensitized AgCl Emulsion); "321"
20.0 Pluronic L-44; "214"
Resin Coat: Titanox Dispersed in Polyethylene
Support: Paper
Resin Coat: Polyethylene

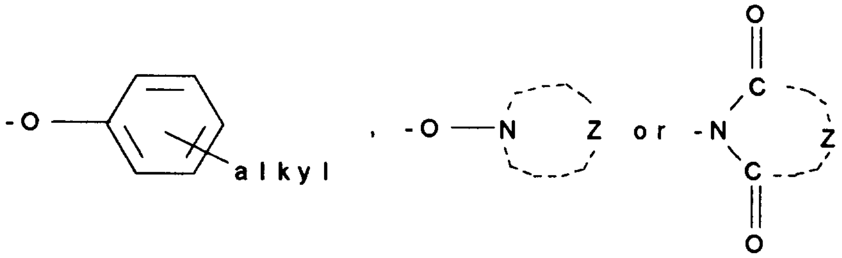
The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

Claims

1. A color photographic recording element comprising at least one blue-sensitive photographic silver halide emulsion layer comprising at least one yellow image-dye forming coupler dispersion characterized in that the yellow coupler has the formula:



where
X is -H, -Cl, -OCO-R, -SAr, -SO_2R or -OSO_2R,
R is an alkyl,



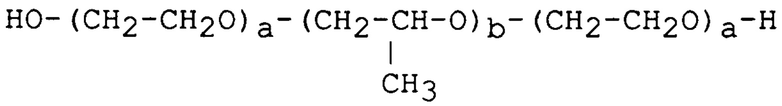
Ar is aryl, and
Z is any organic moieties to complete the ring,
Y is a ballasting group, and
the emulsion layer further comprises from about 0.1 to about 0.6 gram of a polyoxyalkylene polymer, per gram of the yellow coupler.

2. The color photographic recording element of Claim 1 wherein the polyoxyalkylene polymer is present in the amount of from about 0.1 to about 0.3 gram per gram of yellow coupler.

3. The color photographic recording element of Claim 1 wherein the yellow image-dye forming coupler dispersion contains a coupler solvent.

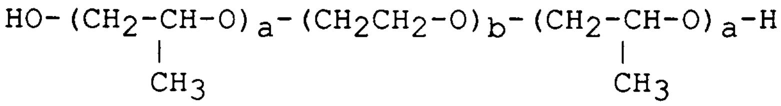
4. The color photographic recording element of Claim 1 or Claim 2 wherein the polyoxyalkylene polymer is a polyoxyethylene-polyoxypropylene block polymer.

5. The color photographic recording element of Claim 1 wherein the polyoxyalkylene polymer is



$$HO-(CH_2-CH_2O)_a-(CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}H-O)_b-(CH_2-CH_2O)_a-H$$

or



$$HO-(CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}H-O)_a-(CH_2CH_2-O)_b-(CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}H-O)_a-H$$

where a has a value of 5 to 500 and, b has a value of 5 to 500.

6. A method of preparing a blue sensitive layer in a silver halide photographic light sensitive element which comprises forming a dispersion of a yellow image dye-forming coupler in a hydrophilic colloid, mixing the dispersion with a silver halide emulsion and applying the resulting composition to form a layer characterized in that the yellow coupler is as defined in claim 1 and the method further comprises the step of adding a polyoxyalkylene polymer in the amount of from about 0.1 to about 0.6 gram per gram of yellow coupler in the dispersion.

7. The method of Claim 6 wherein the polyoxyalkylene polymer is added in the form of from about 0.1 to about 0.3 gram per gram of yellow coupler.

8. The method of Claim 6 or Claim 7 wherein the polyoxyalkylene polymer is a polyoxyethylene-polyoxypropylene block polymer.

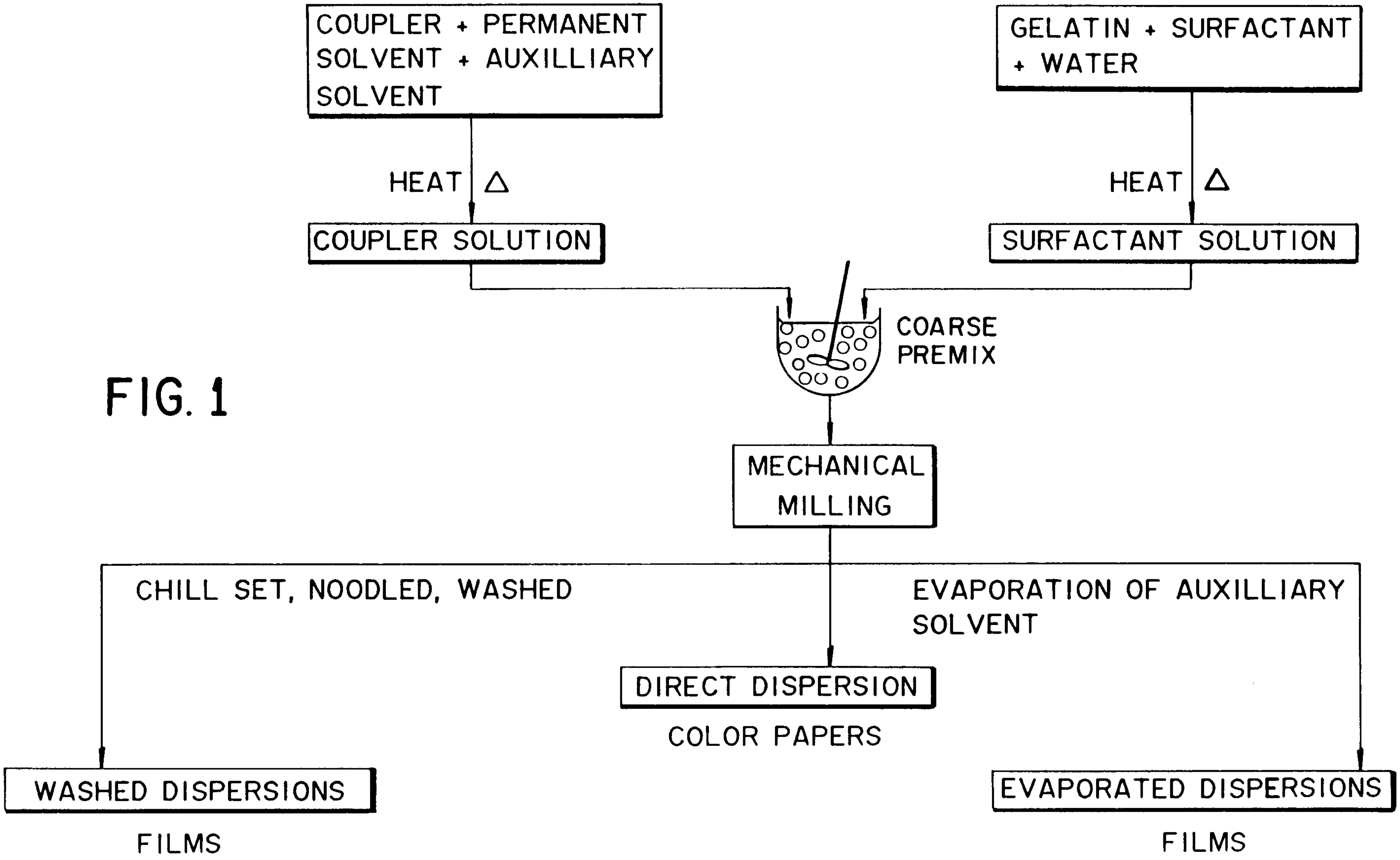

COUPLER + PERMANENT SOLVENT + AUXILLIARY SOLVENT
GELATIN + SURFACTANT + WATER
HEAT Δ
HEAT Δ
COUPLER SOLUTION
SURFACTANT SOLUTION
COARSE PREMIX
MECHANICAL MILLING
CHILL SET, NOODLED, WASHED
EVAPORATION OF AUXILLIARY SOLVENT
DIRECT DISPERSION
COLOR PAPERS
WASHED DISPERSIONS
FILMS
EVAPORATED DISPERSIONS
FILMS

FIG. 1

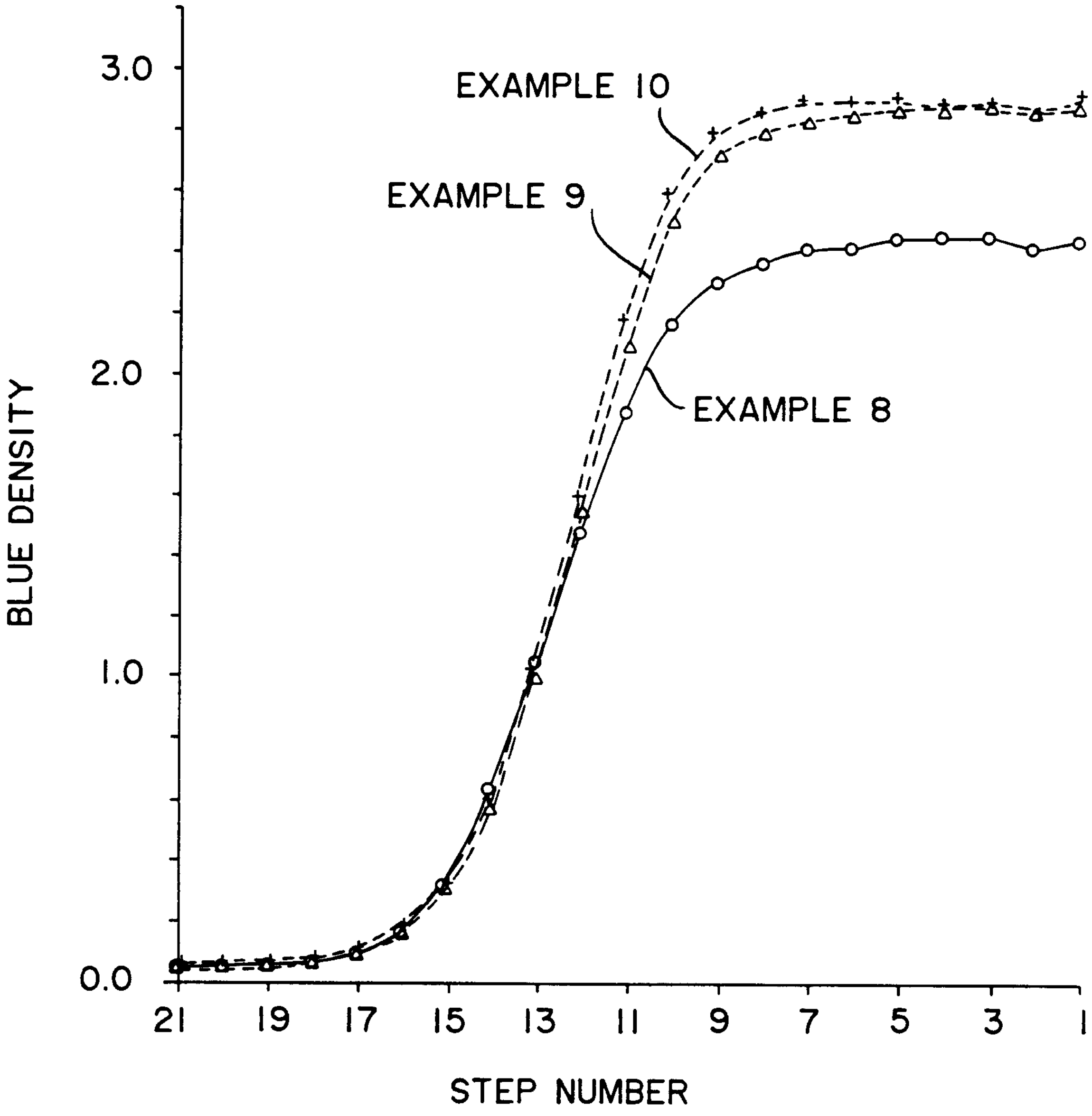

EXAMPLE 10
EXAMPLE 9
EXAMPLE 8
BLUE DENSITY
3.0
2.0
1.0
0.0
21
19
17
15
13
11
9
7
5
3
1
STEP NUMBER

FIG. 2

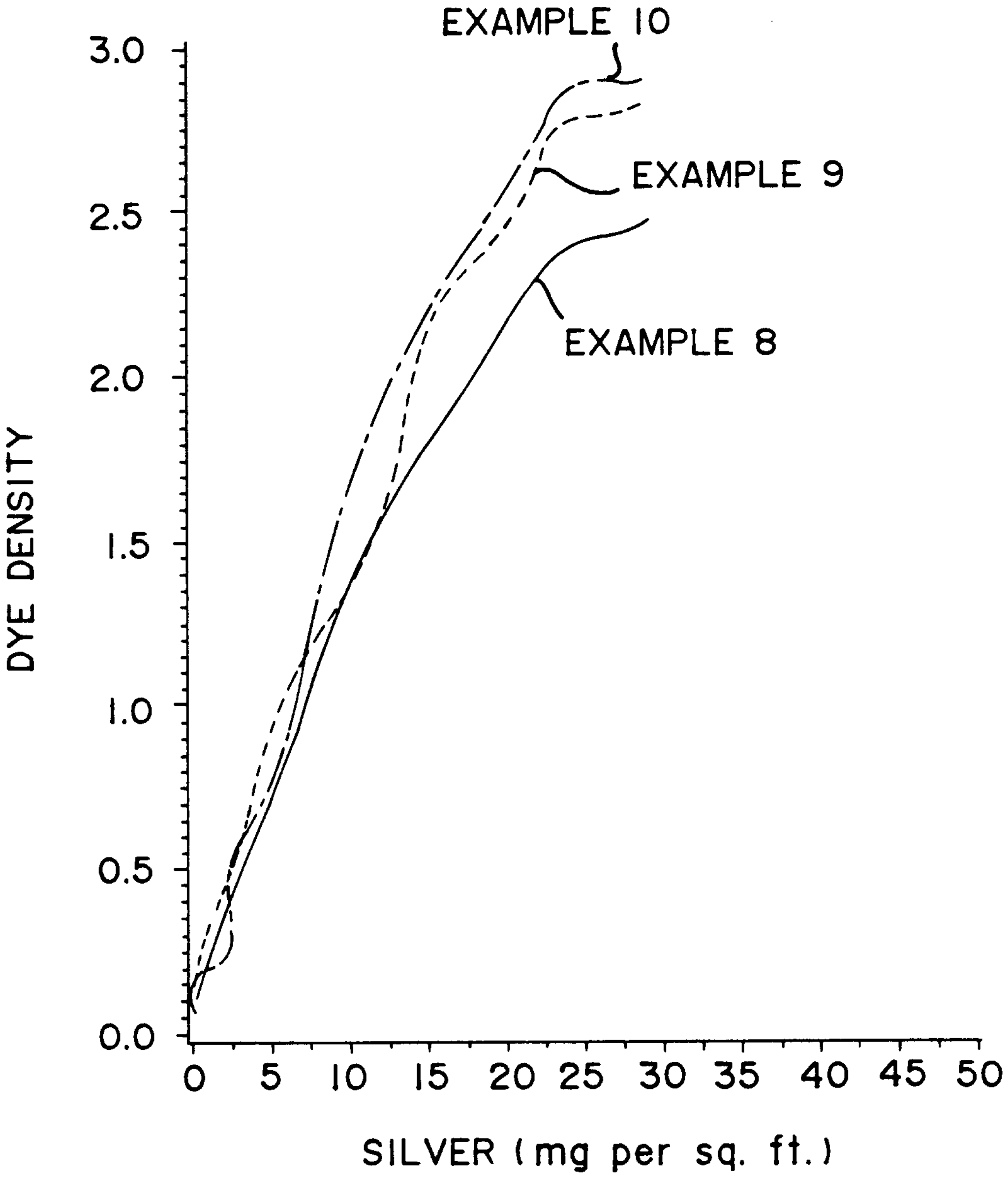

EXAMPLE 10
EXAMPLE 9
EXAMPLE 8
3.0
2.5
2.0
1.5
1.0
0.5
0.0
DYE DENSITY
0
5
10
15
20
25
30
35
40
45
50
SILVER (mg per sq. ft.)

FIG. 3

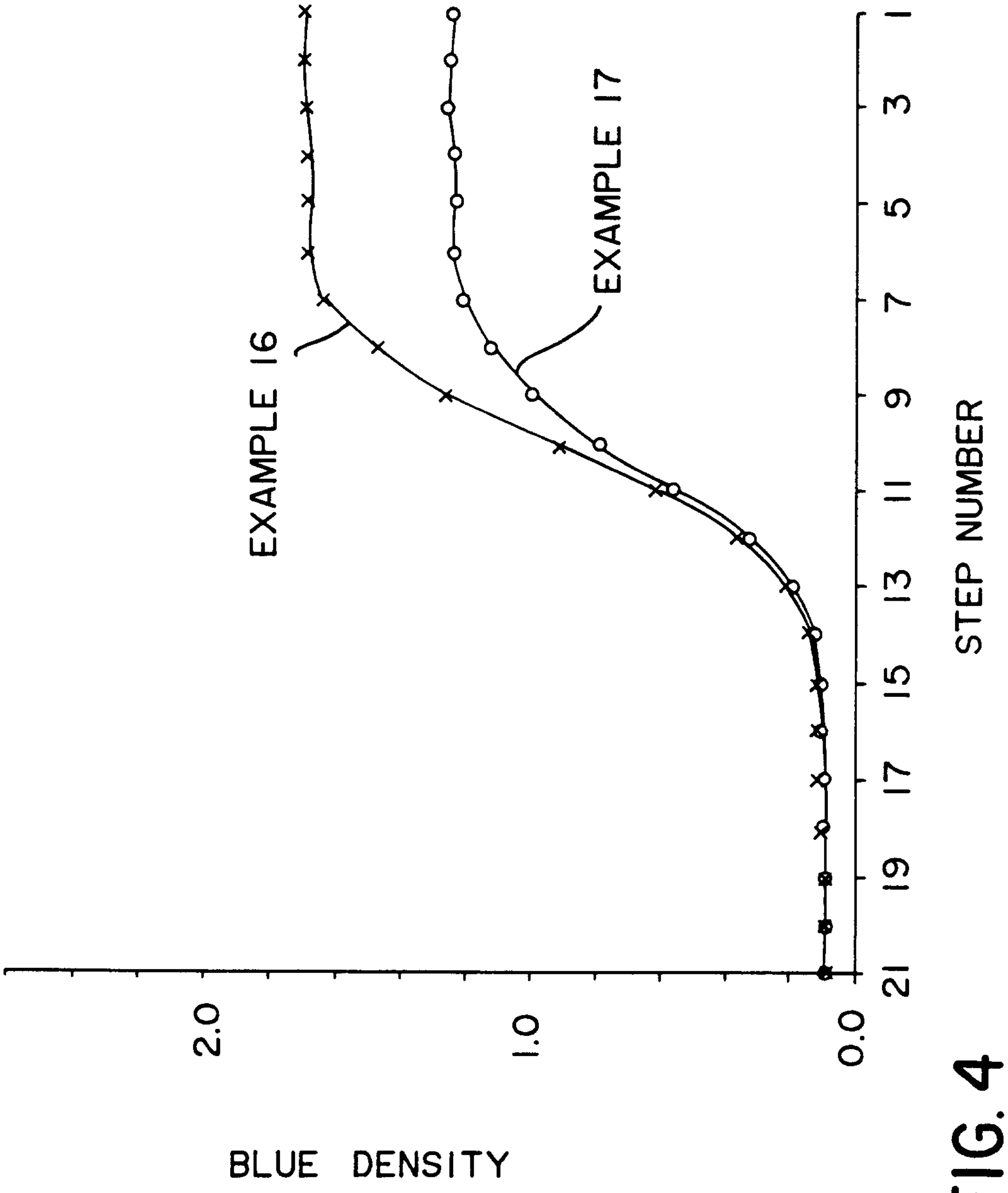

BLUE DENSITY
2.0
1.0
0.0
STEP NUMBER
21
19
17
15
13
11
9
7
5
3
1
EXAMPLE 16
EXAMPLE 17

FIG. 4

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 20 0701

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,X	WO-A-9 016 011 (EASTMAN KODAK COMPANY) * page 9, line 1 - line 20 * * page 16; table B * * page 38; example 8; table I * * page 32, line 17 - page 33, line 18 * ---	1-8	G03C7/388
D,Y	FR-A-2 150 505 (FUJI PHOTO FILM) * page 4, line 1 - line 16 * * page 7, line 16 - page 18, line 4; claims 1-4 * ---	1-8	
Y	EP-A-0 379 893 (AGFA-GEVAERT) * page 12, line 41 - page 16, line 30 * * page 18, line 51 - page 20; claims; table 4 * -----	1-8	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10 JUNE 1993	PHILOSOPH L.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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....
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