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⑤④ **Photographic coupler dispersions.**

⑤⑦ The dark stability of a photographic dye image formed by reaction between a coupler, dispersed in admixture with an involatile solvent, and oxidized p-phenylenediamine colour developing agent is impaired by the presence of a compound comprising a phenolic (or naphtholic moiety in which the acidity of the phenolic hydroxyl group is enhanced by at least one electron-withdrawing substituent in ortho and/or para positions relative to that group. Such a compound may be the coupler itself of the involatile solvent used for its incorporation. This loss in stability can be reduced by introducing into the dispersion a lipophilic anionic surfactant which comprises a sulphate or sulphonate group as the sole hydrophilic group and either a single aliphatic hydrocarbon group having at least 15 carbon atoms or two or more aliphatic hydrocarbon groups which together contain at least 17 carbon atoms. A conventional, i.e. less lipophilic, anionic surfactant may also be used in preparing the coupler dispersion.

EP 0 182 658 A2

PHOTOGRAPHIC COUPLER DISPERSIONS

This invention relates to dispersions of couplers useful in the manufacture of sensitive silver halide colour photographic materials.

It is well known to incorporate dye-forming couplers into photographic silver halide emulsion layers, or adjacent hydrophilic colloid layers, so that an imagewise distribution of oxidized colour developing agent obtained by developing silver halide in the emulsion layer reacts with the coupler to form a dye image. In a colour photographic material having red-, green- and blue-sensitive emulsion layers for providing, respectively, cyan, magenta and yellow dye images, it is necessary, in order to prevent contamination of each dye image with one or both of the other dyes, to ensure that the cyan, magenta and yellow couplers cannot diffuse from their positions in or near their respective emulsion layers. A common method of preventing coupler diffusion, and that with which the present invention is concerned, comprises providing the coupler with a water-insoluble 'ballast' group and, before mixing it with the relevant coating composition, dispersing it as a uniform mixture with a water-insoluble high-boiling organic solvent, termed a coupler solvent or an 'oil-former', in an aqueous gelatin solution. A surface-active agent is used to facilitate the dispersion process and to help stabilise the dispersion obtained.

A great variety of surface active agents have been made available and many types have been suggested for use in photographic materials. However, relatively hydrophobic surface active agents have been suggested for this purpose much less frequently than surfactants of other classes. Instances concerning the preparation of dispersions of water-insoluble addenda, such as colour couplers are to be found in

U.S. patents 3,676,141 and 3,912,517. Both of these patents propose use of an anionic surfactant containing a sulphonate or sulphate group and a hydrophobic radical of 8 to 30 carbon atoms with a
5 non-ionic surface active compound for aiding dispersion by a conventional high-speed mixing process.

Many photographic coupler dispersions contain compounds with phenolic or naphtholic groups of which the acidity is enhanced by the presence of
10 electron-withdrawing substituents in the ortho and/or para positions relative to the hydroxyl group. Well-known compounds of this kind are certain phenolic and naphtholic cyan dye-forming couplers, but couplers for producing dyes of other colours are known which
15 contain such acidic groups. It has been found that the dark stability of dyes formed by colour development of photographic materials containing dispersions of phenolic or naphtholic compounds with enhanced acidity is not as good as is desirable. The
20 present invention is based upon the discovery that the adverse effect on dye stability of the phenolic or naphtholic compound can be mitigated to a useful extent by the use of certain lipophilic anionic surfactants in preparing the relevant dispersions.
25 Additional anionic surfactants of more conventional type may be used to aid the dispersion process but non-ionic surfactants have been found to reduce the beneficial effect of the lipophilic surfactant and so are excluded.

30 According to the present invention there is provided a method of making a photographic coupler dispersion by dispersing a mixture containing the coupler and an oil-former in an aqueous hydrophilic colloid solution in the presence of an anionic
35 surfactant, the coupler and/or the oil-former comprising a phenolic or naphtholic moiety of which

the acidity is enhanced by the presence of at least one electron-withdrawing group at a position ortho or para to the phenolic hydroxyl group, wherein there is added at any stage a anionic surfactant which

5 comprises a sulphate or sulphonate group as the sole hydrophilic group and either a single aliphatic hydrocarbon group having at least 15 carbon atoms or two or more aliphatic hydrocarbon groups which together contain at least 17 carbon atoms, but wherein

10 no non-ionic surfactant is used.

The anionic surfactant defined above is referred to below simply as the lipophilic anionic surfactant.

The present invention concerns coupler

15 dispersions which contain in the oily, dispersed, phase, at least one compound comprising a phenolic or naphtholic moiety, each such compound having at least one electron-withdrawing substituent in a position ortho or para to the phenolic hydroxyl group which

20 enhances the acidity of that group. As is well known, many substituents have an electron-withdrawing effect and the following are listed as examples:

	cyano,	$-\text{COOR}^1$
	nitro,	$-\text{CONR}^1\text{R}^2$
25	halogen	$-\text{SO}_2\text{NR}^1\text{R}^2$
	(especially F, Cl or Br)	$-\text{SO}_2\text{R}$
	$-\text{CCl}_3$ or $-\text{C}_n\text{F}_{2n+1}$	$-\text{SO}_3\text{M}$
	$-\text{COR}$	$-\text{OSO}_3\text{M}$
	$-\text{OCOR}$	$-\text{N}=\text{N}-\text{R}^3$

30 wherein R is an alkyl or aryl group, each of R^1 and R^2 is hydrogen or an alkyl or aryl group, R^3 is an aryl or heterocyclic group and M is a cation, any group R, R^1 , R^2 and R^3 possibly being itself

35 substituted with such substituents as alkyl, alkoxy, aryl, aryloxy, halogen, nitro, and carboxylic acid, ester and amide groups. A suitable substituent for

the phenolic or naphtholic moiety has a Hammett p-Substituent Constant greater than zero: See, for instance, the article by Exner in the book 'Advances in Linear Free Energy Relationships', edited by
5 Chapman and Shorter, Plenum Press (London) 1972.

The compound comprising the acidic phenolic, or naphtholic, moiety may be the coupler itself, in which case it may be a suitably substituted member of one of the various classes of cyan dye-forming
10 coupler. Such couplers are described in, for example:

UK Patent	562,205	825,311
	586,211	843,497
	627,814	1,077,873
	649,660	1,165,563
15	737,104	1,377,233
	797,141	1,541,075

Alternatively the compound comprising the acidic phenolic or naphtholic moiety may be a coupler giving, on colour development, a magenta or yellow
20 dye, coupling taking place preferentially at a pyrazolone or active methylene coupling position rather than at a position para to the hydroxyl group of the phenolic or naphtholic moiety. Couplers of this kind are described in, for instance:

25 U.K. Patent Specification 1,474,128.

Another alternative is for the compound comprising the acidic phenolic or naphtholic moiety to be a coupler solvent, in which case the coupler itself need not contain such a moiety. Coupler solvents
30 having acidic phenolic or naphtholic moieties are described in, for instance:

US Patent 4,207,393
and 4,228,235.

Any of the usual coupler solvents may be
35 employed as the oil-former in a dispersion of the

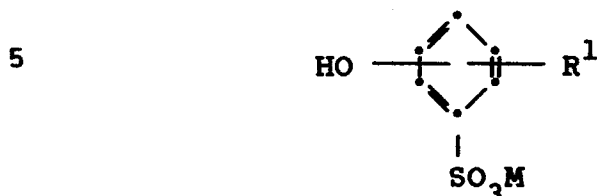
invention. Suitable solvents are inert high-boiling liquids or low-melting solids, well-known examples being dibutyl phthalate and tricresyl phosphate.

Numerous other coupler solvents are described in UK
5 Patent Specification 541,589.

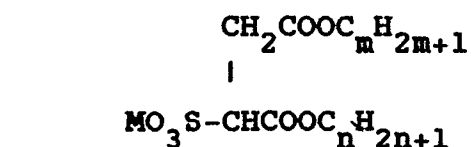
A coupler dispersion of the invention contains an anionic surfactant which comprises, as the sole hydrophilic group, a group of formula $-\text{SO}_3\text{M}$ or $-\text{OSO}_3\text{M}$ (where M is any convenient cation) and either
10 a single aliphatic hydrocarbon group having at least 15 carbon atoms or two or more aliphatic hydrocarbon groups which together contain at least 17 carbon atoms. The aliphatic hydrocarbon group or groups may contain unsaturation and the surfactant molecule may
15 contain such non-hydrophilic features as ether, amide or sulphonamide linkages and ester groups. Classes of surfactant having at least some members in accordance with these requirements include:

- i) alkane sulphonates,
- 20 ii) alcohol sulphates,
- iii) ether alcohol sulphates,
- iv) sulphated polyol esters,
- v) sulphated alkanolamides,
- vi) sulphated amides,
- 25 vii) sulphated esters,
- viii) sulphonated esters,
- ix) alkylarylsulphonates,
- x) olefin sulphonates,
- xi) sulphopolycarboxylic esters
- 30 xii) sulphonalkylesters of fatty acids,
- xiii) sulphoalkylamides of fatty acids.
- ix) petroleum sulphonates as described in our copending application based on British Application 8428678.

Preferred surfactants from these classes are alkane sulphonates (class i) of formula: R^1SO_3M and alkylphenol sulphonates (class ix) of formula:



wherein R^1 is a straight chain alkyl or alkenyl group of at least 15 carbon atoms, and M is a cation, and dialkylsulphosuccinates (class xi) of formula:



wherein $m+n$ is at least 17, m and n being the same or different, M in the above formulae is a hydrogen ion, an alkali metal ion or any other suitable cation.

Instead of using a single compound for any constituent of a dispersion of the invention, a mixture of two or more compounds may be used. Thus two or more couplers, coupler solvents or lipophilic surfactants may be employed, it being necessary for only one of these compounds to comprise an acidic phenolic or naphtholic moiety.

The dispersing agent used in a method of the invention may also include a second, and less lipophilic, anionic surfactant. This may be from the classes (i) to (xiii) listed above, the reduced lipophilic character being achieved through the presence of fewer carbon atoms in the aliphatic hydrocarbon group or groups present or through the presence of more than one hydrophilic group, any additional group being, for instance an hydroxyl, or a carboxylic acid or salt, group. Thus a second anionic surfactant may contain a single group $-SO_3M$ or $-OSO_3M$ and either a single aliphatic hydrocarbon

group having fewer than 15 carbon atoms or two or more aliphatic hydrocarbon groups which together contain fewer than 17 carbon atoms. Alternatively, a second anionic surfactant may be of some other class such as
5 a sulphated monoglyceride, a sulphated fat or oil having a free carboxyl group, an α -sulphocarboxylic acid, an alkyl glyceryl ether sulphonate or an N-acylated-amino acid.

The coupler-coupler solvent solution or
10 mixture is dispersed, with the aid of a surfactant or surfactant mixture, in an aqueous hydrophilic colloid solution. The colloid is preferably gelatin or a simple derivative such as phthalated gelatin.

The dispersion step in a method of the
15 invention may be effected conventionally using any high-speed mixing device. A water-miscible or volatile water-immiscible 'auxiliary solvent' may be present, being removed by washing with water from the set dispersion or when volatile, by evaporation under
20 reduced pressure. Auxiliary solvents and their use are described in, for example, U.S. Patent 2,801,171.

In carrying out a method of the invention, the compound comprising a phenolic or naphtholic moiety of enhanced acidity, or mixture of such
25 compounds, preferably constitutes at least 5% by weight of the oil phase (i.e. the coupler, water-immiscible solvent and lipophilic anionic surfactant) and the lipophilic anionic surfactant preferably constitutes at least 1% by weight of the
30 oil phase. Relatively to the weight of coupler, the weight of lipophilic surfactant is usually present at a concentration of from 1 to 100% by weight, the preferred range being 3 to 20%.

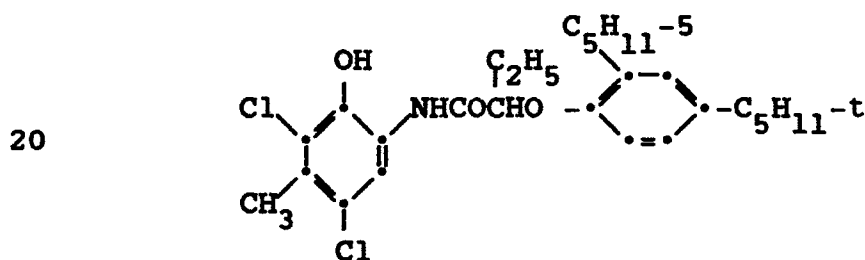
A coupler dispersion made by a method of the
35 invention is employed conventionally in the

manufacture of incorporated-coupler silver halidecolour photographic materials, both negative and positive. Numerous references to patent specifications and other publications relating to silver halide photographic materials, including colour materials and their processing, are given in Research Disclosure December 1978, Item 17643 (see especially sections VII, XI, XIV and XIX). Thus the dispersion is mixed with the appropriate coating composition, usually a gelatino-silver halide photographic emulsion, prior to coating.

The invention is illustrated by the following Examples.

Example 1

Dispersions of coupler I having the structure:



were prepared by dissolving the coupler, 0.60g, in di-n-butyl phthalate, 0.60g, and mechanically dispersing the resulting oily solution in 9.4ml of 6.6% w/v gelatin solution to which had been added surfactant as in Table 1. The result was an oil-in-water dispersion having an average droplet diameter of less than 1µm.

Photographic coatings were prepared by combining together, under safelight conditions, 1.5g of coupler dispersion, 1.5g of 12.1/2% w/v aqueous gelatin solution, 0.20ml of photographic paper type silver chlorobromide emulsion (approximately 1.0M in silver halide) and 5.5ml water. 5% w/v chromic

sulphate solution, 0.30ml, was added immediately prior to coating on photographic film base at a wet thickness of approximately 0.1mm.

Portions of dried coating were exposed to room light for 5s and then developed for 210 s in a p-phenylenediamine developer (KODAK 'Ektaprint 2', trade mark) at 31°C, bleach-fixed for 120s in a bleach-fix solution (KODAK 'Ektaprint'), washed for 30 minutes in running water, and dried.

The resulting cyan density of each sample was measured with a transmission densitometer through a red filter. The samples were then incubated in an oven at 60°C and 70% relative humidity and the dye density measured from time to time. The initial optical density (D_i) and the percentage density loss at the various times are recorded in Table 1.

TABLE 1

20	Surfactant added (sodium salt)	D_i	% density loss at stated time in days			
			7	14	28	42
Control:						
tri-isopropylnaphthalene sulphonate						
25	0.03g	1.56	5.8	12	26	37
	0.06g	1.85	6.3	12	26	39
	0.12g	1.92	7.3	15	30	43
Invention						
bis (tridecyl) sulphosuccinate						
30	0.04g	1.37	1.5	5.1	11	18
	0.08g	1.57	0.6	4.0	10	18
	pentadecylphenolsulphonate					
	0.06g	1.26	2.4	5.5	12	20
	0.12g	1.70	1.2	4.1	11	19

It will be seen that the image dyes from dispersions made according to the invention faded at less than half the rate of the dyes from the prior art dispersions (sodium tri-isopropylnaphthalene sulphonate peptised) in this accelerated dark keeping test.

Example 2

This example illustrates the use of a combination of hydrophilic and hydrophobic surfactants according to the invention.

A coupler dispersion was prepared by dissolving coupler I, 5.0g, in di-n-butyl phthalate, 2.8g together with 2 - (2 - butoxyethoxy) ethyl acetate, 0.4g, and mechanically dispersing the resulting oily solution in 11.5% w/v gelatin solution, 42g, containing sodium tri-isopropylnaphthalene sulphonate, 0.18g. Portions of 10g were withdrawn, and 10% w/v solutions of sodium bis (tridecyl) sulphasuccinate in 1:2 methanol:water were added as in Table 2 and mechanically dispersed into the dispersion.

Photographic coatings were prepared by combining together, under safelight conditions, 1.0g of coupler dispersion, 1.5g of 12.1/2% w/v aqueous gelatin solution, 0.20ml of photographic paper type silver chlorobromide emulsion (approximately 1.0M in silver halide), and 6.0ml water. 5% w/v chromic sulphate solution, 0.30ml, was added immediately prior to coating on photographic film base at a wet thickness of approximately 0.1mm.

Portions of dried coating were exposed, processed and tested as in Example 1: the results are given in Table 2. A low humidity accelerated keeping test was also carried out by placing processed strips in an oven at 77°C with no added humidity, and measuring the dye density at intervals as before. These results are given in Table 3.

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TABLE 2

60°C 70% R.H. results

5	10% sodium bis(tridecyl) sulphosuccinate solution added	D_i	% density loss at stated time		
			7	14	28 days
	None	1.71	8.2	19	36
	0.1ml	1.80	6.1	12	26
	0.2	1.52	4.6	10	23
	0.4	1.08	1.9	6.5	18
	0.8	1.95	*3.5	0	9.7

10 *increase

TABLE 3

77°C low humidity results

15	10% sodium bis (tridecyl) sulphosuccinate solution added	D_i	% density loss at stated time		
			3	7	16 days
	None	1.78	13	30	55
	0.1ml	1.79	9.5	23	49
	0.2	1.48	10	22	47
	0.4	1.82	6.6	17	43
	0.8	1.91	4.7	14	39

20 Example 3

This example illustrates another combination of hydrophilic and hydrophobic surfactants according to the invention.

25 Coupler dispersions were prepared by dissolving together 1.0g of coupler I, 0.6g of tricresyl phosphate, and 0.10g of sodium bis (tridecyl) sulphosuccinate, and mechanically dispersing the resulting oily solution into 5.0g of a
30 12.1/2% w/v aqueous gelatin solution mixed with 3.0ml water and 10% w/v aqueous sodium dioctyl sulphosuccinate (a non-lipophilic anionic surfactant) as stated in Table 4. The dispersion prepared for Example 2 was used for the control.

35 Coatings were prepared as in Example 2, except that 0.9ml of dispersion and 6.1ml of water were added. Testing was as in Example 2, and results are given in Tables 4 and 5.

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TABLE 4

60°C 70% R.H. results

5	10% sodium dioctylsulpho- succinate soln. added	D_i	% density loss at stated time	
			6	14
			days	
	(control)			
	None (as Example 2)	2.62	5.0	13
	0.60 ml	1.49	2.0	5.4
	0.75 ml	2.17	1.4	4.6
	1.0 ml	2.63	2.17	1.9

10

TABLE 5

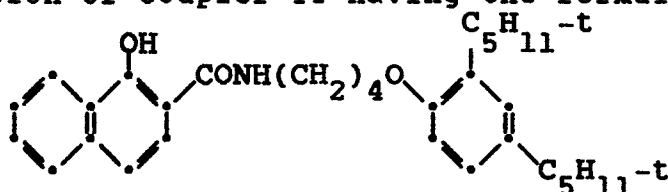
77°C low humidity results

15	10% sodium dioctylsulpho- succinate soln. added	D_i	% density loss at stated time	
			3	6
			days	
	(control)			
	None (as Example 2)	2.55	5.9	15
	0.60 ml	1.50	2.0	6.0
	0.75 ml	2.18	2.7	7.8
	1.0 ml	2.61	1.17	4.6

20

Example 4

A dispersion of coupler II having the formula



25

was prepared by dissolving 3.5g of coupler into a
 mixture of 2.0g of di-n-butyl phthalate and 8.0g of
 2-(2-butoxyethoxy) ethyl acetate, and mechanically
 dispersing the resulting oily solution into 40g of
 9.0% w/v gelatin solution to which had been added 0.5g
 of sodium tri-isopropyl naphthalene sulphonate. The
 dispersion was then cooled, and when set was cut into
 small cubes of approximately 0.5 cm edge. The chopped
 dispersion was washed for 5 hours in chilled (5°C)

35

demineralised water which was maintained at approximately pH5.5 by addition of a small quantity of propionic acid. The washed dispersion was melted at 40°C and to a 5.0g portion was added 0.2g of a 70% w/w solution of sodium bis (tridecyl) sulphosuccinate ('Aerosol TR 70' - trade mark - supplied by Cyanamid of Great Britian Limited). This solution was mechanically dispersed into the dispersion sample.

Coatings were prepared as in Example 2, except that 1.3g of dispersion and 4.9 ml of water were used for each coating. Testing was carried out as in Example 2 and the results are shown in Table 6.

TABLE 6

Condition A: 60°C, 70% R.H.
Condition B: 77°C, low humidity

	Fading Condition	70% sodium bis(tridecyl) sulphosuccinate added	D _i	% density loss after (days)	
				7	14
	A	-	1.90	1.6	4.2
	A	0.1g	2.10	0	1.9
	B	-	1.88	2.1	6.4
	B	0.1g	2.15	0.5	2.3

Example 5

This is a comparative example in which no acidic phenol or naphthol was present.

Dispersions of coupler were prepared by dissolving coupler, 1.5g, in di-n-butyl phthalate, 0.9g, and ethyl acetate, 0.9g, and mechanically dispersing the resultant solution in 15g of 9.2% w/w gelatin to which had been added 10% sodium tri-isopropyl naphthalene sulphonate, 0.6 ml.

1.0g portions of dispersion were taken and 0.3 ml of water or of a solution of hydrophobic surfactant added (see Table 7) and the mixture held for 20 minutes at 40°C.

Photographic coatings were prepared by

combining together, under safelight conditions, the treated portion of coupler dispersion, 1.5g of 12 1/2 w/v aqueous gelatin solution, 0.25 ml of photographic paper type silver chlorobromide emulsion (approximately 1.0M in silver halide) and 5.7 ml water.

5% w/v chromic sulphate solution, 0.30 ml, was added immediately prior to coating on photographic film base at a wet thickness of approximately 0.1 mm.

Portions of dried coating were exposed to room light for 5s and then developed for 210s at 31°C. bleach-fixed for 60s, washed for 10 minutes in running water, and dried. The processing solutions used were as for Example 1.

The resulting dye density of each sample was measured with a transmission densitometer through an appropriate filter: green for a magenta image, blue for a yellow image. The samples were then incubated in the dark in an oven at 60°C and 70% relative humidity for four weeks and the dye densities again measured. The percentage fades which had occurred are listed in Table 7. It will be seen that the presence of the surfactants did not improve the dark stability.

TABLE 7

Coupler	Addition	Image Hue	Original Density	% Fade (4 Weeks)
III	Water	Yellow	1.11	0.0
	A		1.14	1.8
IV	Water	Magenta	1.63	0.6
	A		1.65	1.2
V	Water	Magenta	1.80	2.8
	A		2.06	9.7

Notes : Addition 0.3 ml of water or

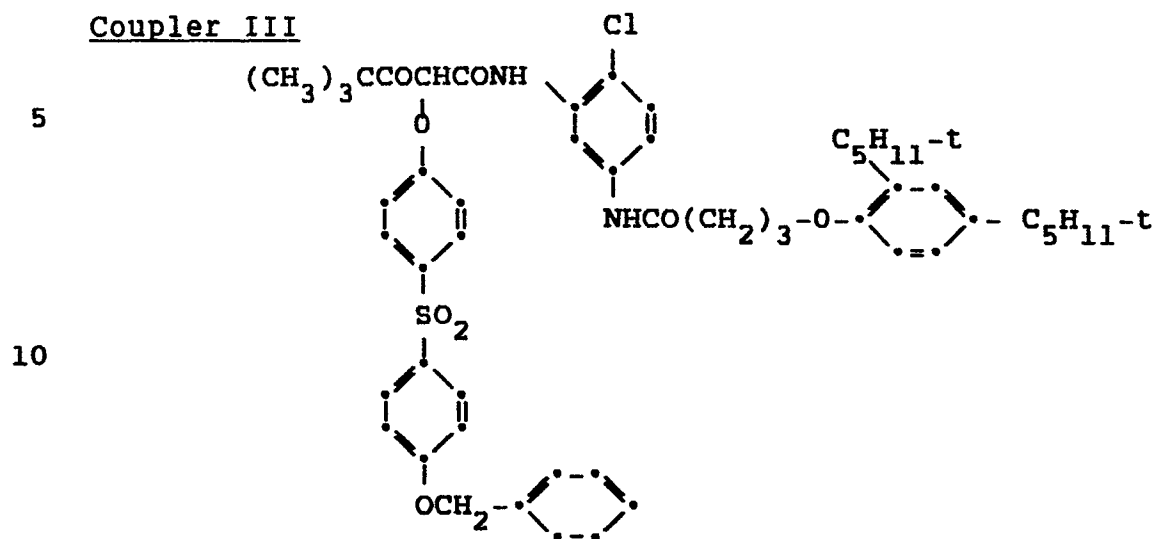
A : 7% Aerosol TR70

(Sodium bis-tridecyl sulphsuccinate)

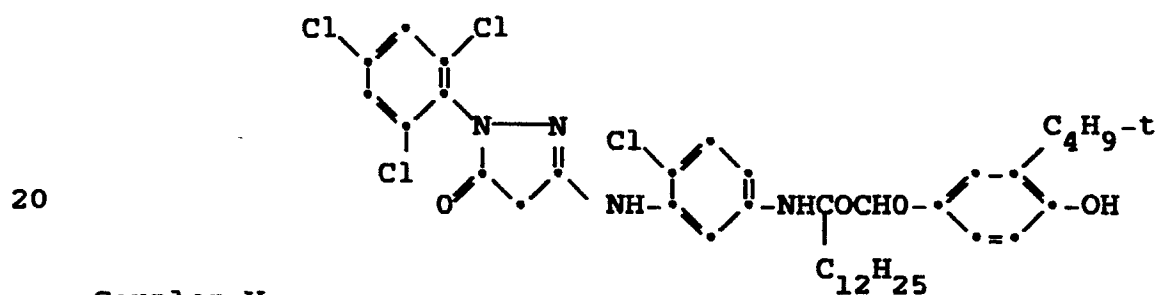
(Aerosol TR70 is a trade mark for a surfactant manufactured by the American Cyanamid Company)

Couplers III to V had the structures:

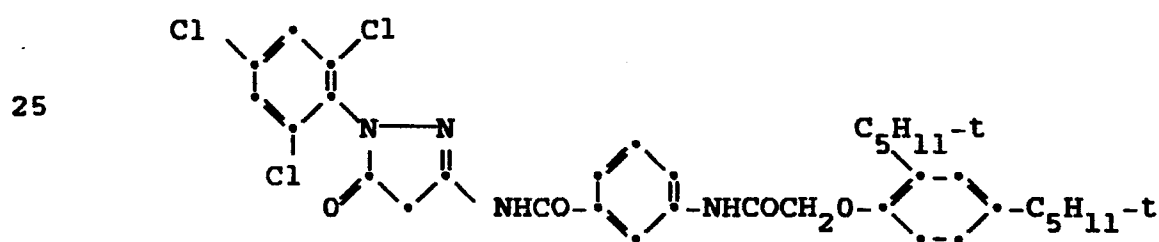
Coupler III



Coupler IV



Coupler V



Example 6

30 This Example illustrates the use of the surfactants of the invention when coupler IV was dispersed in the presence of an acidic phenol coupler solvent.

35 Coupler IV, 1.0g; n-dodecyl-p-hydroxybenzoate, 0.33g; n-octyl-p-hydroxybenzoate, 0.33g; and .

N,N-diethyl lauramide, 0.33g, were melted together to form an oily solution. This solution was mechanically dispersed into 7.6g of 10.5% w/w gelatin solution, to which had been added 0.8g of 10% w/w sodium dioctyl sulphosuccinate aqueous solution and other surfactants as stated in Table 9.

Photographic coatings were prepared by combining together under safelight conditions, 0.8g of coupler dispersion, 0.25g of silver chlorobromide photographic paper emulsion (approximately 1.0M in silver halide), 1.0g of 12% w/w gelatin aqueous solution, and 6.6 ml of water. 5% w/v chromic sulphate solution, 0.30 ml, was added immediately prior to coating on photographic film base at a wet thickness of approximately 0.10 mm.

Portions of dried coating were exposed, processed and tested as in Example 5: results are given in Table 8. It will be seen that the presence of the surfactant of the Invention improved the dark stability of the dye in the presence of the acidic phenols.

TABLE 8

25	Coating Surfactant Added	Original Density	% Fade in 12 weeks
	----	1.24	6.5
	A, 0.10g	1.29	3.1
	A, 0.20g	1.26	2.4
	A, 0.30g	1.72	-1.2 (density increase)

Note: surfactant A, 70% sodium bis-tridecyl sulphosuccinate

Example 7

The coupler used in this Example had an acidic phenol leaving group. The results show how the dark stability of the image dye was most diminished in areas of low image density, where most acidic phenol remained. The stabilising effect of the surfactants of the Invention is illustrated: the effects varied with the humidity at which the accelerated dark fading was carried out.

10 A coupler dispersion and coatings were prepared as in Example 5, except that coupler VI was used. The coatings were exposed to a photographic step wedge and processed as in Example 5. The image densities of the various steps of the image were
15 measured (blue filter). The strips were incubated either for 60 days at 60°C, 70% RH or for 28 days at 77°C, low RH. Results are given in Table 10: coating A had 0.3 ml water added, B had 0.3 ml 7% Aerosol TR70, as in Example 5.

20 Coupler VI

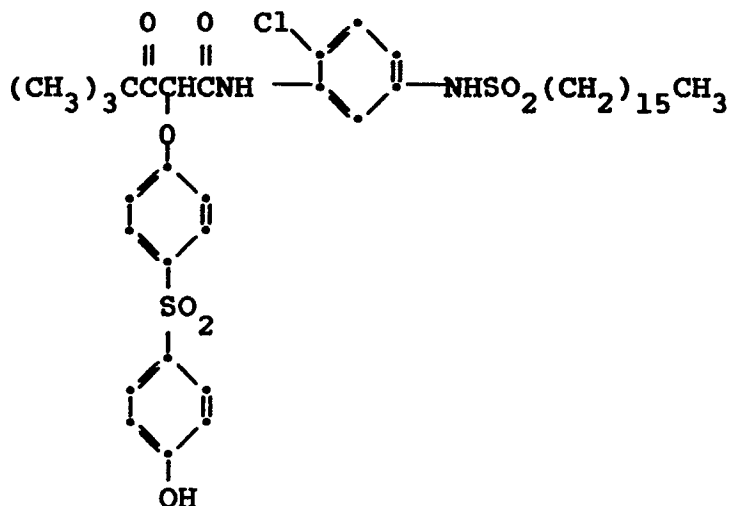


TABLE 9

Coating	60 Days 60°C 70% RH		28 Days 77°C. low RH	
	Initial Density	Step % Fade	Initial Density	Step % Fade
5 A	0.35	26	0.39	38
	0.67	33	0.71	37
	0.97	28	1.02	34
	1.37	20	1.42	23
	1.76	11	1.82	12
	1.90	7	1.98	3
10 B	0.47	13	0.46	11
	0.78	15	0.76	9
	1.10	18	1.08	8
	1.52	18	1.49	6
	1.90	17	1.87	4
	2.02	14	1.95	2

Example 8

Coatings were prepared and tested as in Example 5, using the acidic phenol cyan coupler VII. The surfactant additions were different: these and the results are given in Table 10.

TABLE 10

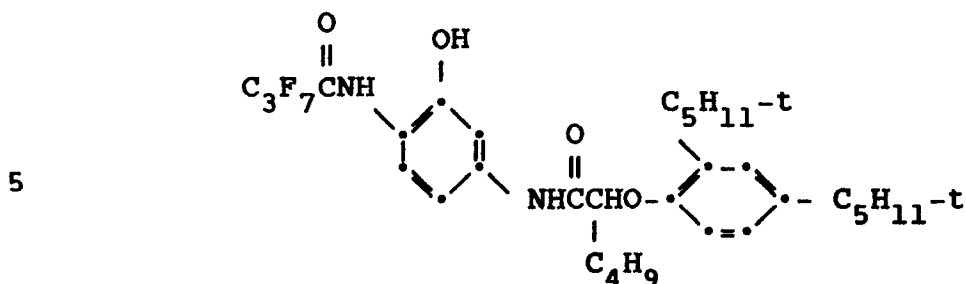
Surfactant Addition	Original (red) Density	% Fade (4 wks)
0.3ml water	1.64	4.3
0.1ml A	1.24	1.6
0.2ml A	1.01	3.0
0.1ml C	1.09	0.9
0.1ml D	1.69	0.6

Note:

surfactant solutions:

A, 7% sodium bis-tridecyl sulphosuccinate
 C, 10%, Hostapur SAS 60 (Trade Mark) (This is a mixture of C₁₃ - C₁₈ sodium alkyl sulphonates)

D, 10% sodium pentadecyl phenol sulphonate.

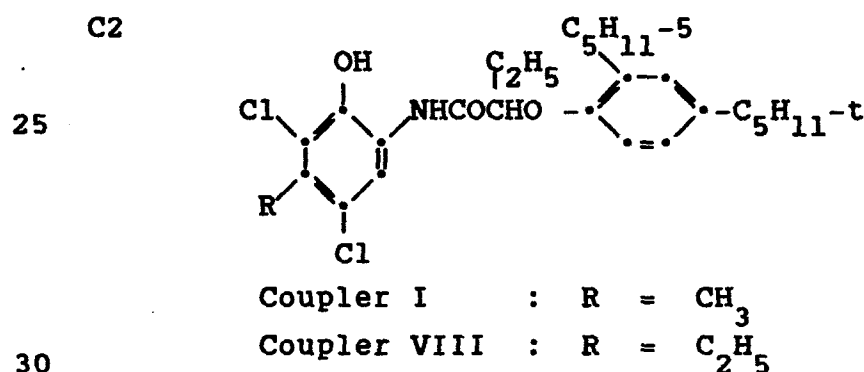
Coupler VIIExample 9

10 Multilayer coatings were made on a paper support according to the following summary. The numbers in parenthesis are coverages expressed as mg/m². In the case of the silver halide in the emulsion layers, the coverages relate to the silver present.

- 15 Layer 6 - Gelatin (1076)
- Layer 5 - Gelatin (1679), red-sensitive silver chlorobromide emulsion (281), cyan coupler (1076) and hydrophobic surfactant (301) (see Table 11).
- 20 Layer 4 - Gelatin (1313), UV-absorber (861), dioctylhydroquinone (58)
- Layer 3 - Gelatin (1851), green-sensitive silver chlorobromide emulsion (418), magenta coupler IV (522)
- 25 Layer 2 - Gelatin (753), dioctylhydroquinone (54)
- Layer 1 - Gelatin (1690), blue-sensitive silver chlorobromide emulsion (403), yellow coupler III (990), gelatin hardener.
- 30 Support - Electron - bombarded polyethylene coated paper.

The couplers were incorporated in the layers as dispersions, being mixed with di-n-butyl phthalate (one half the coupler weight in the case of the cyan and magenta couplers and one quarter the coupler weight in the case of the yellow coupler) and dispersed in aqueous gelatin solutions with the aid of sodium tri-isopropyl naphthalene sulphonate. The UV absorber in layer 4 comprised a mixture of 84.1% (by weight) of 2-(2-hydroxy-3,5-di-tert-pentyl-phenyl) benzotriazole, 15% 2-(2-hydroxy-3-tert-butyl-5-methylphenyl) benzotriazole and 0.9% dioctylhydroquinone dispersed in 2-(2-butoxyethoxy) ethyl acetate. The gelatin hardener in layer 1 was bis(vinylsulphonylmethyl) ether and was added in an amount equal to 1.75% of the total weight of the gelatin in the multilayer coating.

Four different multilayer coatings were made using two different couplers, each coated with or without the lipophilic anionic surfactant sodium bis (tridecyl) sulphosuccinate. The couplers were numbers I and VIII defined by the formula:



Samples of the four coatings were exposed, processed as described in Example 1 and then used for determining the stability of the cyan dye image under incubation test conditions. In all the tests the loss

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in red-light reflection density of an image having an initial value of 1.7 was measured as a function of the incubation time. Two different test conditions were used, 77°C and 15% relative humidity for the two week tests and 60°C and 70% relative humidity for 16 week tests.

The results obtained are given in Table 11.

Table 11

10	Coupler	Lipophilic surfactant (mg/m ²)	% density loss after (weeks incubation)					
			4	6	8	12	16	2
15	I	0	17	32	35	48	55	28
	I	301	10	19	24	36	45	25
	VIII	0	3	4	4	8	9	4
	VIII	301	0	2	1	5	4	2

These show that the lipophilic surfactant reduced the density loss of both cyan image dyes for both incubation test conditions. The stability of the image dyes to light exposure was unimpaired by the presence of the lipophilic surfactant.

CLAIMS

1. A method of making a photographic coupler dispersion by dispersing a mixture containing the coupler and an oil-former in an aqueous hydrophilic colloid solution in the presence of an anionic surfactant, the coupler and/or the oil-former comprising a phenolic or naphtholic moiety of which the acidity is enhanced by the presence of at least one electron-withdrawing group at a position ortho or para to the phenolic hydroxyl group, wherein there is added at any stage a anionic surfactant which comprises a sulphate or sulphonate group as the sole hydrophilic group and either a single aliphatic hydrocarbon group having at least 15 carbon atoms or two or more aliphatic hydrocarbon groups which together contain at least 17 carbon atoms (hereafter called the lipophilic anionic surfactant), but wherein no non-ionic surfactant is used.
2. A method according to claim 1 wherein the lipophilic anionic surfactant is an alkylphenol sulphonate or a dialkylsulphosuccinate.
3. A method according to either of the preceding claims wherein the anionic surfactant present during the dispersion step comprises a surfactant less lipophilic than the specified lipophilic anionic surfactant.
4. A method according to any of the preceding claims wherein the lipophilic anionic surfactant is added before the dispersion step.
5. A method according to any of the preceding claims wherein the coupler is a phenolic or naphtholic cyan dye-forming coupler.
6. A method according to any of the preceding claims wherein the coupler solvent comprises a phenolic or naphtholic moiety of enhanced acidity.

7. A method according to any of the preceding claims wherein the compound comprising a phenolic or naphtholic moiety of enhanced acidity, or mixture of such compounds, constitutes at least 5% by weight of the dispersed substances.
8. A method according to any of the preceding claims wherein the total lipophilic surfactant constitutes at least 1% by weight of the dispersed substances.
9. A dye-forming coupler dispersion made by a method according to any of the preceding claims.
10. A sensitive photographic material comprising a support bearing a photographic hydrophilic colloid-silver halide emulsion layer and, dispersed in that layer or in a hydrophilic colloid layer adjacent thereto a dye-forming coupler dispersion according to claim 9.
11. A sensitive photographic material which comprises a support bearing a photographic hydrophilic colloid - a silver halide emulsion layer and, dispersed in that layer or in a hydrophilic colloid layer adjacent thereto, a water-insoluble dye-forming coupler, a water-immiscible solvent therefor, and a dispersing agent for the coupler-coupler solvent mixture, the coupler and/or the solvent comprising a phenolic or naphtholic moiety of which the acidity is increased by an electron-withdrawing group at the o or p-position relative to the phenolic hydroxyl group and the dispersing agent containing a lipophilic anionic surfactant which comprises a sulphate or sulphonate group as the sole hydrophilic group and either a single aliphatic hydrocarbon group having at least 15 carbon atoms or two or more aliphatic hydrocarbon groups which together contain at least 17 carbon atoms but no non-ionic surfactant.

12. A material according to claim 11 wherein the surfactant is an alkanesulphonate, an alkylphenyl sulphonate or a dialkyl sulphosuccinate.

13. A material according to claim 11 or 12

5 wherein the dispersing agent also comprises an anionic surfactant which contains an aliphatic hydrocarbon group having fewer than 15 carbon atoms or two or more aliphatic hydrocarbon groups which together contain fewer than 17 carbon atoms.

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