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PRODUCTION OF COLORED COLLOID LAYERS

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This invention relates to the production of coloured colloid layers and particularly to the production of such layers as elements in light-sensitive photographic materials.

Photographic materials frequently include, in addition to a support layer and one or more light-sensitive layers, a coloured colloid layer which serves to prevent halation, i. e. a so-called anti-halation layer. Where the support is transparent this is usually coated on the side of the support remote from the emulsion layer, but if the element is intended to be exposed through the support the anti-halation layer may be applied to the outer surface of the light-sensitive layer. Where the support is not transparent the anti-halation layer is usually coated between the light-sensitive layer and the support.

Further, many photographic materials, especially those used for colour photography, include coloured colloid layers between emulsion layers, such layers serving as light filters.

It is of particular importance, especially where such coloured colloid layers are coated adjacent to light-sensitive layers, that the colouring material employed should not diffuse from the coloured colloid layer into any adjacent layer of the photographic material.

The present invention provides a method of producing coloured colloid layers which may serve as anti-halation or filter layers and which are strongly resistant to such diffusion, and in addition provides a method whereby an originally colourless colloid layer of the photographic material may be converted, when required, to a coloured colloid layer without, at the same time, colouring other layers of the material.

According to the present invention a method of forming a coloured colloid layer comprises forming a layer of a water-permeable colloid containing a surface-active compound and thereafter applying to such layer an aqueous solution of a dyestuff which has an opposite electrostatic charge to that carried by the said surface-active agent.

More specifically, according to this invention, (*a*) a water-permeable colloid layer containing an anion-active agent is treated with an aqueous solution of a basic dyestuff; or (*b*) a water-permeable colloid layer containing a kation-

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active agent is treated with an aqueous solution of an acid dyestuff.

It is found that, under the conditions specified, the dyestuff is firmly held in the layer and is not removed by prolonged washing in water. Where the water-permeable colloid layer containing the surface-active agent forms a layer in a photographic element which contains other water-permeable colloid layers not containing such surface-active agent, such other layers, though they may temporarily absorb some dyestuff, may be washed free of such dyestuff by washing in water.

Examples of anion-active agents which may be employed according to this invention are:

(*a*) Soluble salts of long-chain alkyl carboxylic acids, e. g. soluble salts of fatty acids containing eight or more carbon atoms, as, for example, oleic, ricinoleic, linoleic, stearic and palmitic acids. These, however, are generally less preferable than

(*b*) Soluble salts of long-chain alkyl sulphonic acids,

(*c*) Soluble salts of sulphated higher fatty alcohols, e. g. soluble salts of fatty alcohol sulphates of which the alkyl group contains at least eight carbon atoms, as, for example, the soluble salts of lauryl hydrogen sulphate and oleyl hydrogen sulphate,

(*d*) Soluble salts of sulphated secondary alcohols containing at least eight carbon atoms in the chain,

(*e*) Soluble salts of alkylated aromatic sulphonic acids, e. g. soluble salts of alkyl benzene sulphonic acids, of alkyl naphthalene sulphonic acids and of alkylated hydroxy diphenyl sulphonic acids,

(*f*) Soluble salts of long-chain alkyl esters of succinic acid.

The soluble salts may be formed from alkali metals, e. g. sodium and potassium, from ammonium or from amines, e. g. triethanolamine and cyclohexylamine.

The compounds may contain amino residues in the anion, as for example in the sodium salt of oleoyl, amino ethane sulphonic acid which contains a carbonamide group (—NH.CO—).

Very many anion-active agents are commercially marketed as detergents and these commercial products may conveniently be employed in

the process of this invention. Thus, suitable commercial products are those sold under the trade names:

Trade Name	Believed to be—
Aerosol OT	the sodium salt of a sulphated dicarboxylic ester.
Agral N	the sodium salt of an alkyl naphthalene sulphonic acid.
Aresklene 375	the sodium salt of an alkyloxy-diphenyl disulphonic acid.
Dispersol L	the sodium salt of dinaphthyl-methane disulphonic acid.
Gardinol	a sodium alkyl sulphate.
Igepon T	the sodium salt of oleoyl-methyl-amino-ethane sulphonic acid.
Lissapol A	sodium hexadecyl sulphate.
Lissapol C	Do.
Lissatan A	a derivative of sodium hexadecyl sulphate.
Lohrinol	a sulphonated fatty acid.
Nekal A	the sodium salt of an alkyl naphthalene sulphonic acid.
Nekal BX	Do.
Perminal W	Do.
Santomerse D	the sodium salt of an alkyl benzene sulphonic acid.
Sulphonated Lorol TA	triethanolamine dodecyl sulphate.
Sulphonated Lorol NH	ammonium dodecyl sulphate.
Sulphonated Lorol CY	cyclohexylamine dodecyl sulphate.
Sulphonated Ocenol	a sulphonated fatty alcohol.
Teepol X	a sodium alkyl sulphate.
Tergitol 4	a sodium secondary alkyl sulphate.
Tergitol 7	Do.

Kation-active agents which may be employed are, for example, alkyl-, aryl- and aralkyl-substituted ammonium compounds and quaternary salts of heterocyclic nitrogen compounds. Specific examples are dodecyl pyridinium sulphate, cetyl pyridinium bromide and the materials sold under the trade names Lissolamine A (believed to be cetyl trimethyl ammonium bromide), Sapamine MS (believed to be a diethyl aminoethyl long-chain alkyl amide ester), Fixanol C (believed to be cetyl pyridinium bromide) and octadecylamine.

The water-permeable colloid layer which is to be coloured may be composed of gelatin, casein, agar-agar or other natural material, or may be a synthetic polymeric material such as a polyvinyl acetate having a low degree of esterification or a partially hydrolysed methyl methacrylate resin, or may be a water-permeable cellulose ether or cellulose ester, e. g. cellulose acetate, having a low degree of esterification.

Large numbers of acid dyes and basic dyes are well known and described in Rowe's colour index, and it is unnecessary to list them. The following are, however, examples of the type of dyestuff which may be employed:

Surface-Active Agent	Dye	Colour
Anion-active—	Basic dyes:	
Teepol X, Agral N	Auramine O (C. I. No. 655)	Yellow.
	Rhodamine B (C. I. No. 749)	Magenta.
	Rosaniline hydrochloride (C. I. No. 677)	Red.
	Chrysaniline (C. I. No. 793)	Yellow-brown.
Cation-active—	Acid dye:	
Fixanol C, Lissolamine A.	Tartrazine (C. I. No. 640)	Yellow.
	Eosine (C. I. No. 768)	Magenta.

The proportion of surface-active agent added to the colloid layer may vary over a wide range according to the results desired, but generally speaking will not exceed 50% of the total weight of the colloid layer and will usually be much less, e. g. 5 or 10%.

Similarly the strength of the dye solution applied to the layer may vary widely, but generally solutions of ½ to 2% strength are suitable.

The following examples illustrate the invention:

EXAMPLE 1

An 8% solution of gelatin in water was prepared, and to portions of it was added a range of quantities of Teepol X. The resulting solutions were coated on photographic film base and dried. The sample coatings thus prepared were then bathed in a ½% solution of Auramine O (colour index No. 655) for periods of one to eight minutes, and then washed for one hour in running water and dried. The density of the dye-layers was then determined and the following results were obtained:

Table 1

Concentration of Teepol X in ccs. per 100 cc. 8% gelatin solution	Time (in minutes) of bathing in ½% Auramine O Solution			
	1	2	4	8
None				0.09
2%	0.96	1.03	1.07	1.07
4%	0.80	0.85	0.89	0.94
8%	0.91	0.95	1.03	1.24

EXAMPLE 2

The procedure of Example 1 was followed, using Lissolamine A as the surface-active agent and Tartrazine as acid dye. The following density figures were obtained:

Table 2

Concentration of Lissolamine A in gms. per 100 cc. of 8% gelatin	Time (in minutes) of bathing in ½% Tartrazine Solution			
	1	2	4	8
None				0.07
1%	0.97	1.00	1.00	1.07
2%	1.71	1.77	1.78	1.78
4%	1.75	1.97	2.05	2.10
8%	2.01	2.17	2.16	2.25

EXAMPLE 3

The procedure of Example 1 was followed, using octadecylamine hydrochloride as the surface-active agent and Tartrazine as the dye. The following density figures were obtained:

Table 3

Concentration of Octadecylamine hydrochloride in gms. per 100 cc. of 8% gelatin solution	Time (in minutes) of bathing in ½% Tartrazine Solution			
	1	2	4	8
None				0.07
½%	0.81	0.82	0.88	0.89
1%	1.32	1.41	1.45	1.50

EMAMPLE 4

The procedure of Example 1 was followed using Dispersol L as the surface-active agent and

Auramine as the dye. The following densities were obtained:

Table 4

Concentration of Dispersol L in ccs. per 100 cc. of 8% gelatin solution	Time (in minutes) of bathing in ½% Auramine O Solution			
	1	2	4	8
None				0.09
1%	1.4	1.5	1.5	1.6
2%	2.2	2.4	2.4	2.3

EXAMPLE 5

The procedure of Example 1 was followed using sodium dodecyl sulphate as the surface-active agent and Auramine O as the dye. The following densities were obtained:

Table 5

Concentration of Sodium dodecyl sulphate in gms. per 100 cc. of 8% gelatin solution	Time (in minutes) of bathing in ½% Auramine O Solution			
	1	2	4	8
None				0.09
½%	1.1	1.3	1.4	1.4
1%	2.1	2.4	2.3	2.4
2%	2.8	2.7	2.9	2.9

It will be observed from the density figures given in the foregoing examples that, whilst after an hour's washing a strong density of dyestuff is held in the layers containing the surface-active agents, virtually none of the dye remains in a similar layer not containing the surface-active agent.

The density figures in the foregoing examples were determined in a standard type densitometer, the specimens being viewed through a filter transmitting only between 3800 Å. and 5000 Å.

The surface-active agents are themselves usually colourless and the invention therefore affords a method of producing a photographic material in which one or more layers containing surface-active agents are present and are initially colourless but can be coloured at any desired stage in the processing of the material.

What we claim is:

1. A method of forming a photographic element comprising a film support and a water-permeable coloured colloid layer which comprises (1) coating a film support with a layer of a water-permeable colloid containing an uncoloured salt selected from the group consisting of (*a*) anion-active alkali metal, ammonium and amine salts of long chain sulphonic and sulphuric acids which contain an alkyl radical of at least 8 carbon atoms in the anion, and (*b*) cation-active alkyl substituted ammonium salts and quaternary salts of heterocyclic nitrogen compounds each of which contains a long chain alkyl radical of at least 8 carbon atoms in the cation, and thereafter (2) applying to such layer an aqueous solution of a dye, a basic dye being selected when the uncoloured salt is anion-active and an acid dye being selected when the uncoloured salt is cation-active, thereby forming in said colloid layer a relatively stable, water insoluble dye complex between said dye and said salt.

2. A method of forming a photographic element comprising a film support, a water-permeable coloured colloid layer and a light-sensitive colloid-silver halide layer which comprises (1) coating a film support with a layer of a water-permeable colloid containing an uncoloured salt selected from the group consisting of (*a*) anion-active alkali metal, ammonium and amine salts of long chain sulphonic and sulphuric acids which contain an alkyl radical of at least 8 carbon atoms in the anion, and (*b*) cation-active alkyl substituted ammonium salts and quaternary salts of the heterocyclic nitrogen compounds each of which contains a long chain alkyl radical of at least 8 carbon atoms in the cation, and thereafter (2) applying to such layer an aqueous solution of a dye, a basic dye being selected when the uncoloured salt is anion-active and an acid dye being selected when the uncoloured salt is cation-active, thereby forming in said colloid layer a relatively stable, water-insoluble dye complex between said dye and said salt, and applying a light-sensitive colloid silver halide layer thereto.

3. A method of forming a photographic element comprising a film support and a water-permeable coloured colloid layer which comprises coating a film support with a layer of a water-permeable colloid containing an uncoloured anion-active alkali metal salt of an aliphatic sulphonic acid containing an alkyl radical of at least 8 carbon atoms in the anion, and thereafter applying to such layer an aqueous solution of a basic dye, thereby forming in said colloid layer a relatively stable, water-insoluble dye complex between said dye and said salt.

4. A method of forming a photographic element comprising a film support and a water-permeable coloured colloid layer which comprises coating a film support with a layer of a water-permeable colloid containing an uncoloured anion-active alkali metal salt of an alkyl sulphate containing an alkyl radical of at least 8 carbon atoms in the anion, and thereafter applying to such layer an aqueous solution of a basic dye, thereby forming in said colloid layer a relatively stable, water-insoluble dye complex between said dye and said salt.

5. A method of forming a photographic element comprising a film support and a water-permeable coloured colloid layer which comprises coating a film support with a layer of a water-permeable colloid containing an uncoloured cation-active alkyl-substituted ammonium salt containing an alkyl radical of at least 8 carbon atoms in the cation, and thereafter applying to such layer an aqueous solution of an acid dye, thereby forming in said colloid layer a relatively stable, water-insoluble dye complex between said dye and said salt.

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