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(54) Viscosity reduction in a photographic melt

(57) An aqueous photographic coating composition comprises an aqueous solution comprising gelatin and an anionically charged, hydrophobic group-containing compound that is (a) soluble in water or a mixture of water and a water-miscible organic solvent, and (b) which confers an undesirably high viscosity to aqueous gelatin solutions, wherein the composition further comprises a cyclodextrin in an amount sufficient to reduce the viscosity of the solution.

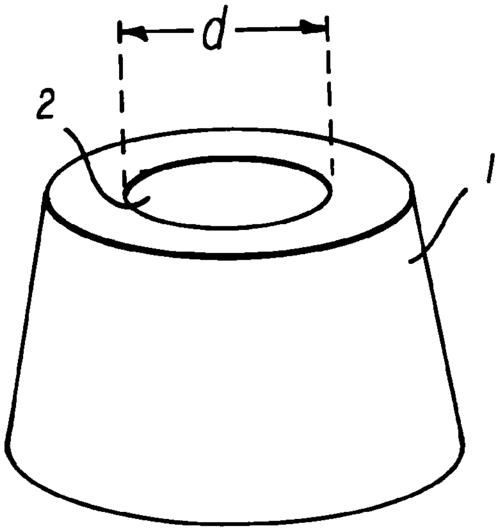

FIG. 1

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Description

Field of the Invention

This invention relates to a method for the preparation of a photographic element, and in particular to a method of controlling the viscosity of a photographic melt.

Background of the Invention

Photographic elements typically comprise a support having thereon at least one light-sensitive layer. Color photographic elements typically comprise at least one layer sensitive to blue light, at least one layer sensitive to green light and at least one layer sensitive to red light. Generally, a color photographic element also contains various other layers, such as subbing layers, interlayers, antihalation layers and the like. Each layer of a photographic element is applied, generally simultaneously with other layers, to an appropriate support in a coating process.

In conventional photographic coatings, photographic coating compositions comprising emulsions, dispersions, and/or other photographic addenda for each layer are coated from aqueous solutions which contain a hydrophilic colloid, such as gelatin. Usually, coating takes place at temperatures between about 35° to about 50°C. Generally, the photographic emulsions and dispersions are prepared, chill-set and stored until needed for coating. At that time they are then heated to about 35° to about 50°C to melt the chill-set emulsion or dispersion to provide the fluid coating compositions which are frequently called "melts", "coating melts" or "photographic melts".

Generally, in the photographic art there are two primary methods of coating photographic materials. One is the bead coating process. U.S. Patent 2,761,417 - Russell et al, U.S. Patent 2,681,294 - Beguin, and U.S. Patent 4,525,392 - Ishizaki, illustrate simultaneously applying multiple layers of photographic materials by the bead coating process, and apparatus for practicing that process.

The second primary method is the curtain coating process. U.S. Patent 3,632,374 - Greiller, and U.S. Patent 4,569,863 - Koepke et al, illustrate apparatus and process for curtain coating.

It is well known that adjustment and control of viscosities of melts of individual layers can improve layer thickness uniformity of finished coated products. It is also known that layer viscosities outside optimum ranges may cause undesired variations in layer thickness during flow on the slides of the coating hopper or on a non-horizontal web path after coating.

Certain photographic addenda, such as masking couplers, oxidized developer scavengers, filter dyes, optical brighteners, ultraviolet radiation absorbers, dye transfer dyes, etc., when admixed in a melt containing a hydrophilic colloid, produce excessively high viscosity, which can result in non-uniform coatings. Such photographic addenda are in general molecules with large hydrophobic groups and are usually solubilized with one or more fully ionized anionic groups, such as $-SO_3^-$ (i.e., sulfonate) groups, $-SO_4^=$ (i.e.,sulfate) groups or COO^- (i.e., carboxy) groups. Such materials are usually fully water soluble, or are soluble to the extent of about 5-20% by weight, in water containing 5 to 20% by weight of a water miscible auxiliary solvent such as methanol, ethanol, propanol, isopropanol, acetone, methyl ethyl ketone, ethyl acetate, or the like. Such materials behave also in a similar manner in the presence of a hydrophilic colloid.

It is known from U.S. Patent No. 3,409,435, that certain amphiphilic addenda, such as polyalkylene oxide block oligomers or polymers, when added to melts containing the mentioned viscosity-increasing photographic addenda, produce moderation of melt viscosity. The amphiphilic addenda disclosed in the '435 patent are block oligomeric compounds comprising hydrophobic polyoxypropylene blocks (A) and hydrophilic polyoxyethylene blocks (B) joined in the manner of A-B-A, B-A-B, A-B, $(A\text{-}B)_n\text{-}G\text{-}(B\text{-}A)$, or $(B\text{-}A)_n\text{-}G\text{-}(A\text{-}B)$, where G is a connective organic moiety and n is between 1 and 3.

Other examples of such amphiphilic addenda are disclosed in Ono et al. U.S. Patent No. 3,860,425 and in Visconte et al. US Patent 5,300,418.

However, such prior art materials that contain a large number of polyalkylene oxide groups produce adverse photographic (sensitometric) effects in some photographic products. Sugar surfactants discussed by Visconte et al. U.S. Patent No. 5,300,418 do not have the adverse photographic effects, but because they, and other amphiphiles, are surface active, they are unable to reduce the viscosity without reducing the surface tension of the melt.

One of the ways of reducing high viscosities of melts is by dilution with water. However, such a procedure leads to increased water load in the drier, which is undesirable under high speed coating conditions, used for high volume film and paper products. Therefore, dilution is not always a desirable approach.

Problem to be Solved by the Invention

Therefore, there is a need for photographic melts (of the aforesaid photographic addenda) which have sufficiently low viscosity, and adequate concentration of the hydrophilic colloid, such that no excessive drier wet load is encountered during manufacturing of photographic paper and film products, and such that no, or substantially no, adverse effect is produced on the desired sensitometric behavior of the photographic element. Furthermore, it is desirable to be able to reduce viscosity without reducing surface tension as the relative values of surface tension (including dynamic surface tension under flow conditions) of individual layers in multilayer packs coated simultaneously (as taught in the above mentioned patents) are important in order to avoid undesired non-uniformities in thicknesses of layers during the coating process caused by surface tension driven flow.

Summary of the Invention

An object of this invention is to reduce the high viscosity of photographic gelatin-containing melts, which contain an anionically charged, hydrophobic group-containing photographic addenda that are water soluble, or rendered water soluble by assistance of a water-miscible organic auxiliary solvent.

One aspect of this invention comprises an aqueous photographic coating composition comprising an aqueous solution comprising gelatin and an anionically charged, hydrophobic group-containing compound that is (a) soluble in water or a mixture of water and a water-miscible organic solvent, and (b) which confers an undesirably high viscosity to aqueous gelatin solutions, wherein the composition further comprises a cyclodextrin in an amount sufficient to reduce the viscosity of the solution.

Another aspect of this invention comprises a photographic element comprising a support having thereon a layer comprising:

(i) gelatin,
(ii) an anionically charged, hydrophobic-group containing compound that is (a) soluble in water or a mixture of water and a water- miscible organic solvent, and (b) which confers an undesirably high viscosity to aqueous gelatin solutions, and
(iii) a cyclodextrin.

Another aspect of this invention is a method of reducing the viscosity of an aqueous gelatin solution containing an anionically charged, hydrophobic group-containing compound that is (a) soluble in water or a mixture of water and a water-miscible organic solvent, and (b) which confers an undesirably high viscosity to aqueous gelatin solutions, which method comprises adding to said solution a cyclodextrin in an amount sufficient to reduce the viscosity of the solution.

A further aspect of this invention is a method of reducing the viscosity of an aqueous gelatin solution containing an anionically charged, hydrophobic group-containing compound that is (a) soluble in water or a mixture of water and a water-miscible organic solvent, and (b) which confers an undesirably high viscosity to aqueous gelatin solutions, which method comprises adding to said solution a cyclodextrin in an amount sufficient to reduce the viscosity of the solution without reducing in the surface tension of the composition.

Advantageous Effect to the Invention

This invention enables one to adjust the viscosity of a photographic coating composition without using undesirably large amounts of water to dilute the composition or adding a nonionic surfactant, including sugar based surfactants, as taught by the prior art, which may reduce the surface tension of the composition and/or cause undesired sensitometric changes in the resulting photographic element.

Brief Description of the Drawing

Fig. 1 illustrates the physical configuration of a cyclodextrin molecule.

Fig. 2 is a graph showing the surface tension of an aqueous solution of the anionically charged, hydrophobic group-containing compound, SC-1, obtained as described in the examples provided below.

Fig. 3 is a graph showing shows the effect of adding α-cyclodextrin to an aqueous solution of SC-1, obtained as described in the examples provided below.

Detailed Description of Invention

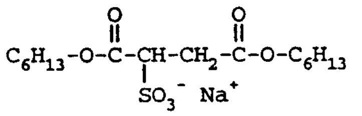
The invention is generally accomplished by providing a melt for coating of a layer of a photographic element and which contains a hydrophilic colloid and an anionically charged, hydrophobic group-containing compound that is (a) soluble in water or a mixture of water and a water-miscible organic solvent, and (b) which confers an undesirably high viscosity to aqueous gelatin solutions, and adding to the solution an amount of a cyclodextrin effective to reduce the viscosity of the solution.

Illustrative hydrophilic colloids include water-soluble polymers, gelatin, gelatin derivatives, cellulose esters, casein, agar, sodium alginate, starch, polyvinyl alcohol, polyacrylic acid copolymers and maleic anhydride copolymers and mixtures thereof. The cellulose esters include hydroxyl propyl cellulose, carboxymethyl cellulose and hydroxyethyl cellulose.

The latex polymers include vinyl chloride copolymers, vinylidene chloride copolymers, acrylic ester copolymers, vinyl acetate copolymers and butadiene copolymers. Among them, gelatin is most preferred.

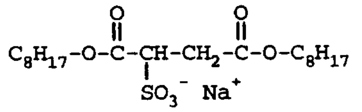
The amount of hydrophilic colloid in the solution is preferably about 2 to about 20 wt.%, based on the weight of the solution.

Illustrative anionically charged, anhydrophobic group-containing addenda include sodium dodecyl sulfate, sodium octyl sulfate, sodium decyl sulfate, sodium tetradecyl sulfate, sodium or potassium salt of octadecyl hydroquinone sulfate, or a compound of the formula:



$$C_6H_{13}-O-\overset{\overset{O}{\|}}{C}-\underset{\underset{SO_3^-\ Na^+}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-O-C_6H_{13}$$

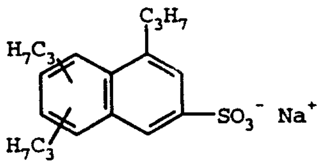
Aerosol MA



$$C_8H_{17}-O-\overset{\overset{O}{\|}}{C}-\underset{\underset{SO_3^-\ Na^+}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-O-C_8H_{17}$$

Aerosol OT

or

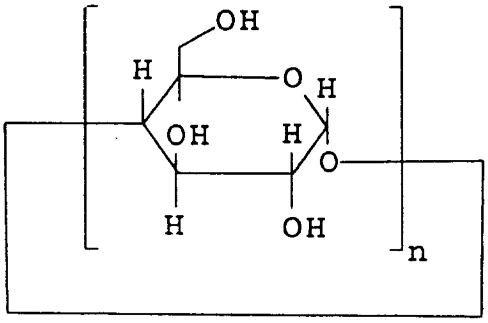


Alkanol XC.

The anionically charged hydrophobic group-containing compound is preferably present in the solution in an amount of from about 0.1 to about 10 wt.%, based on the weight of the solution.

In accordance with this invention the viscosity of the aqueous hydrophilic colloid solution is decreased by addition of a cyclodextrin.

Cyclodextrins are torus shaped cyclic oligosaccharides formed by the linking of 6, 7 or 8 glucopyranose units by a, (1-4) linkages (called α-, β- and γ-cyclodextrin respectively). Cyclodextrins have the following structural formula:



wherein n is as defined below.

The torroidal shape of a cyclodextrin is illustrated in Fig. 1. In Fig 1, a cyclodextrin molecule is shown as torus, 1, having a cavity 2, which has a diameter d. The cyclodextrins are defined as:

α-cyclodextrin: wherein n=6, d=4.5Å

β-cyclodextrin: wherein n=7, d=7.0Å

γ-cyclodextrin: wherein n=8, d=8.5Å

Cyclodextrins can be thought of as "molecular buckets" as they are toroidal-shaped, rigid structures with a well-defined cavity as illustrated in Fig. 1. Due to the hydrophobic nature of the cavity, cyclodextrins are known to form various inclusion complexes in aqueous solutions and solid state with apolar (hydrophobic) molecules which fit into cyclodextrin's cavity without teh formation of a covalent bond. Further, polar compounds and certain inorganic ions have also been found to bind with cyclodextrin. (Takisawa, N.; Shirahama, K.; Tanaka, I. *Colloid and Polymer Science* 271(1993)499-503; Bender, K. L.; Komiyama, M. in *Cyclodextrin Chemistry*, Springer-Verlag, Berlin.; Saenger, W., *Angew Chem. Int. Ed. Engl.* 19 (1980) 344. Kaifer, A. E. in A*dvances in Supramolecular Chemistry*, volume 2, pages 1-24, 1992, JAI Press Inc.; Satake, I; Ikenoue, T; Takeshita, *T. Bull. Chem Soc. Jpn.* 58 (1985) 2746; Schlenk, H; Sand, *D. J. Am. Chem Soc.* 83 (1961) 2312). While not wishing to be bound by any theory, it is believed that the cyclodextrins bind the anionically charged, hydrophobic group-containing addenda within the cavity of the cyclodextrin toroidal structure. Since cyclodextrins are not surface active, they thus reduce the viscosity of the gelatin melt without reducing the surface tension thereof.

The cyclodextrin is added in an amount effective to reduce the viscosity of the melt. The cyclodextrin is added to the melt preferably in an amount sufficient to provide a mole ratio of cyclodextrin to anionically charged, hydrophobic group-containing addenda of 1 to about 6, more preferably 1 to about 4 and most preferably about 3 to about 4.

The cyclodextrin is generally added after the photographic emulsion or dispersion has been heated to form a coating melt. As mentioned above, the viscosity of one layer of a multiple layer coating depends of the viscosities of the adjacent layers.

The photographic composition or melt of the invention can be used in any of the ways and in any of the combinations known in the art. Typically, the invention materials are coated as a layer on a support to form part of a photographic element. The photographic elements can be single color elements or multicolor elements. Multicolor elements contain image dye-forming units sensitive to each of the three primary regions of the spectrum. Each unit can comprise a single emulsion layer or multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element, including the layers of the image-forming units, can be arranged in various orders as known in the art. In an alternative format, the emulsions sensitive to each of the three primary regions of the spectrum can be disposed as a single segmented layer.

A typical multicolor photographic element comprises a support bearing a cyan dye image-forming unit comprised of at least one red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming coupler, a magenta dye image-forming unit comprising at least one green-sensitive silver halide emulsion layer having associated therewith at least one magenta dye-forming coupler, and a yellow dye image-forming unit comprising at least one blue-sensitive silver halide emulsion layer having associated therewith at least one yellow dye-forming coupler. The element can contain additional layers, such as filter layers, interlayers, overcoat layers, subbing layers, and the like.

If desired, the photographic element can be used in conjunction with an applied magnetic layer as described in Research Disclosure, November 1992, Item 34390 published by Kenneth Mason Publications, Ltd., Dudley Annex, 12a North Street, Emsworth; Hampshire P010 7DQ, ENGLAND.

In the following discussion of suitable materials for use in the photographic elements of this invention, reference will be made to Research Disclosure, December 1989, Item 308119, available as described above, which will be identified hereafter by the term "Research Disclosure." The Sections hereafter referred to are Sections of the Research Disclosure.

The silver halide emulsions employed in the elements of this invention can be either negative-working or positive-working. Suitable emulsions and their preparation as well as methods of chemical and spectral sensitization are described in Sections I through IV. Color materials and development modifiers are described in Sections V and XXI. Vehicles are described in Section IX, and various additives such as brighteners, antifoggants, stabilisers, light absorbing and scattering materials, hardeners, coating aids, plasticizers, lubricants and matting agents are described , for example, in Sections V, VI, VIII, X, XI, XII, and XVI. Manufacturing methods are described in Sections XIV and XV, other layers and supports in Sections XIII and XVII, processing methods and agents in Sections XIX and XX, and exposure alternatives in Section XVIII.

Coupling-off groups are well known in the art. Such groups can determine the chemical equivalency of a coupler, i.e., whether it is a 2-equivalent or a 4-equivalent coupler, or modify the reactivity of the coupler. Such groups can advantageously affect the layer in which the coupler is coated, or other layers in the photographic recording material, by performing, after release from the coupler, functions such as dye formation, dye hue adjustment, development acceleration or inhibition, bleach acceleration or inhibition, electron transfer facilitation, color correction and the like.

The presence of hydrogen at the coupling site provides a 4-equivalent coupler, and the presence of another coupling-off group usually provides a 2-equivalent coupler. Representative classes of such coupling-off groups include, for example, chloro, alkoxy, aryloxy, hetero-oxy, sulfonyloxy, acyloxy, acyl, heterocyclyl, sulfonamido, mercaptotetrazole, benzothiazole, mercaptopropionic acid, phosphonyloxy, arylthio, and arylazo. These coupling-off groups are described in the art, for example, in U.S. Pat. Nos. 2,455,169, 3,227,551, 3,432,521, 3,476,563, 3,617,291, 3,880,661, 4,052,212 and 4,134,766; and in U.K. Patents and published application Nos. 1,466,728, 1,531,927, 1,533,039, 2,006,755A and 2,017,704A.

Image dye-forming couplers may be included in the element such as couplers that form cyan dyes upon reaction with oxidized color developing agents which are described in such representative patents and publications as: U.S. Pat. Nos. 2,772,162, 2,895,826, 3,002,836, 3,034,892, 2,474,293, 2,423,730, 2,367,531, 3,041,236, 4,883,746 and "Farbkuppler-eine LiteratureUbersicht," published in Agfa Mitteilungen, Band III, pp. 156-175 (1961). Preferably such couplers are phenols and naphthols that form cyan dyes on reaction with oxidized color developing agent.

Couplers that form magenta dyes upon reaction with oxidized color developing agent are described in such representative patents and publications as: U.S. Pat. Nos. 2,600,788, 2,369,489, 2,343,703, 2,311,082, 3,152,896, 3,519,429, 3,062,653, 2,908,573 and "Farbkuppler-eine LiteratureUbersicht," published in Agfa Mitteilungen, Band III, pp. 126-156 (1961). Preferably such couplers are pyrazolones, pyrazolotriazoles, or pyrazolobenzimidazoles that form magenta dyes upon reaction with oxidized color developing agents.

Couplers that form yellow dyes upon reaction with oxidized and color developing agent are described in such representative patents and publications as: U.S. Pat. Nos. 2,875,057, 2,407,210, 3,265,506, 2,298,443, 3,048,194, 3,447,928 and "Farbkuppler-eine LiteratureUbersicht," published in Agfa Mitteilungen, Band III, pp. 112-126 (1961). Such couplers are typically open chain ketomethylene compounds.

It may be useful to use a combination of couplers any of which may contain known ballasts or coupling-off groups such as those described in U.S. Patent 4,301,235; U.S. Patent 4,853,319 and U.S. Patent 4,351,897. The coupler may also be used in association with "wrong" colored couplers (e.g. to adjust levels of interlayer correction) and, in color negative applications, with masking couplers such as those described in EP 213.490; Japanese Published Application 58-172,647; U.S. Patent 2,983,608; German Application DE 2,706,117C; U.K. Patent 1,530,272; Japanese Application A-113935; U.S. Patents 4,070,191 and 4,273,861; and German Application DE 2,643,965. The masking couplers may be shifted or blocked.

The photographic element may also contain materials that accelerate or otherwise modify the processing steps e.g. of bleaching or fixing to improve the quality of the image. Bleach accelerator releasing couplers such as those described in EP 193,389; EP 301,477; U.S. 4,163,669; U.S. 4,865,956; and U.S. 4,923,784, may be useful. Also contemplated is use of the compositions in association with nucleating agents, development accelerators or their precursors (UK Patent 2,097,140; U.K. Patent 2,131,188); electron transfer agents (U.S. 4,859,578; U.S. 4,912,025); antifogging and anti color-mixing agents such as derivatives of hydroquinones; aminophenols, amines, gallic acid; catechol; ascorbic acid; hydrazides; sulfonamidophenols; and non color-forming couplers.

For example, in a color negative element, the materials of the invention may replace or supplement the materials of an element comprising a support bearing the following layers from top to bottom:

(1) one or more overcoat layers containing ultraviolet absorber(s);
(2) a two-coat yellow pack with a fast yellow layer containing "Coupler 1": Benzoic acid, 4-chloro-3-((2-(4-ethoxy-2,5-dioxo-3-(phenylmethyl)-1- imidazolidinyl)-3-(4-methoxyphenyl)-1,3-dioxopropyl)amino)-, dodecyl ester and a slow yellow layer containing the same compound together with "Coupler 2": Propanoic acid, 2-[[5-[[4-[2-[[[2,4-bis(1,1-dimethylpropyl)phenoxy]acetyl]amino]-5-[(2,2,3,3,4,4,4-heptafluoro-1-oxobutyl)amino]-4-hydroxyphenoxy]-2,3-dihydroxy-6-[(propylamino)carbonyl]phenyl]thio]-1,3,4-thiadiazol-2-yl]thio]-, methyl ester and "Coupler 3": 1-((dodecyloxy)carbonyl) ethyl(3-chloro-4-((3-(2-chloro-4-((1-tridecanoylethoxy) carbonyl)anilino)-3-oxo-2-((4)(5)(6)-(phenoxycarbonyl)-1H-benzotriazol-1-yl)propanoyl)amino))benzoate;
(3) an interlayer containing fine metallic silver;
(4) a triple-coat magenta pack with a fast magenta layer containing "Coupler 4": Benzamide, 3-((2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-N-(4,5-dihydro-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl)-,"Coupler 5": Benzamide, 3-((2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-N-(4',5'-dihydro-5'-oxo-1'-(2,4,6-trichlorophenyl) (1,4'-bi-1H-pyrazol)-3'-yl)-,"Coupler 6": Carbamic acid, (6-(((3-(dodecyloxy)propyl) amino)carbonyl)-5-hydroxy-1-naphthalenyl)-, 2-methylpropyl ester , "Coupler 7": Acetic acid, ((2-((3-(((3-(dodecyloxy)propyl)amino) carbonyl)-4-hydroxy-8-(((2-methylpropoxy)carbonyl) amino)-1-naphthalenyl)oxy)ethyl)thio)-, and "Coupler 8" Benzamide, 3-((2-(2,4-bis(1,1-dimethylpropyl) phenoxy)-1-oxobutyl)amino)-N-(4,5-dihydro-4-((4-methoxyphenyl) azo)-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl)-; a mid-magenta layer and a slow magenta layer each containing "Coupler 9": a ternary copolymer containing by weight in the ratio 1:1:2 2-Propenoic acid butyl ester, styrene, and N-[1-(2,4,6-trichlorophenyl)-4,5-dihydro-5-oxo-1H-pyrazol-3-yl]-2-methyl-2-propenamide; and "Coupler 10": Tetradecanamide, N-(4-chloro-3-((4-((4-((2,2-dimethyl-1-oxopropyl) amino)phenyl)azo)-4,5-dihydro-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl)amino)phenyl)-, in addition to Couplers 3 and 8;
(5) an interlayer;
(6) a triple-coat cyan pack with a fast cyan layer containing Couplers 6 and 7; a mid-cyan containing Coupler 6 and "Coupler 11": 2,7-Naphthalenedisulfonic acid, 5-(acetylamino)-3-((4-(2-((3-(((3-(2,4-bis(1,1-dimethylpropyl)phenoxy) propyl)amino)carbonyl)-4-hydroxy-1-naphthalenyl) oxy)ethoxy)phenyl)azo)-4-hydroxy-, disodium salt; and a slow cyan layer containing Couplers 2 and 6;
(7) an undercoat layer containing Coupler 8; and
(8) an antihalation layer.

In a color paper format, the photographic elemtns may comprise a support bearing the following layers from top to bottom:

(1) one or more overcoats;
(2) a cyan layer containing "Coupler 1": Butanamide, 2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-N-(3,5-dichloro-2-hydroxy-4-methylphenyl)-, "Coupler 2": Acetamide, 2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-N-(3,5-dichloro-2-hydroxy-4-, and UV Stabilizers: Phenol, 2-(5-chloro-2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylethyl)-;Phenol, 2-(2H-benzotriazol-2-yl)-4-(1,1-dimethylethyl)-;Phenol, 2-(2H-benzotriazol-2-yl)-4-(1,1-dimethylethyl)-6-(1-methylpropyl)-; and Phenol, 2-(2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylpropyl)- and a poly(t-butylacrylamide) dye stabilizer;
(3) an interlayer;
(4) a magenta layer containing "Coupler 3": Octanamide, 2-[2,4-bis(1,1-dimethylpropyl)phenoxy]-N-[2-(7-chloro-6-methyl-1H-pyrazolo[1,5-b][1,2,4]triazol-2-yl)propyl]- together with 1,1'-Spirobi(1H-indene), 2,2',3,3'-tetrahydro-3,3,3',3'-tetramethyl-5,5',6,6'-tetrapropoxy-;
(5) an interlayer; and
(6) a yellow layer containing "Coupler 4": 1-Imidazolidineacetamide, N-(5-((2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-2-chlorophenyl)-.alpha.-(2,2-dimethyl-1-oxopropyl)-4-ethoxy-2,5-dioxo-3-(phenylmethyl)-.

In a reversal format, the photographic element may comprise a support bearing the following layers from top to bottom:

(1) one or more overcoat layers;
(2) a nonsensitized silver halide containing layer;
(3) a triple-coat yellow layer pack with a fast yellow layer containing "Coupler 1": Benzoic acid, 4-(1-(((2-chloro-5-((dodecylsulfonyl)amino)phenyl) amino)carbonyl)-3,3-dimethyl-2-oxobutoxy)-, 1-methylethyl ester; a mid yellow layer containing Coupler 1 and "Coupler 2": Benzoic acid, 4-chloro-3-[[2-[4-ethoxy-2,5-dioxo-3-(phenylmethyl)-1-imidazolidinyl]-4,4-dimethyl-1,3-dioxopentyl]amino]-, dodecylester; and a slow yellow layer also containing Coupler 2;
(4) an interlayer;
(5) a layer of fine-grained silver;
(6) an interlayer;
(7) a triple-coated magenta pack with a fast magenta layer containing "Coupler 3": 2-Propenoic acid, butyl ester, polymer with N-[1-(2,5-dichlorophenyl)-4,5-dihydro-5-oxo-1H-pyrazol-3-yl]-2-methyl-2-propenamide; "Coupler 4": Benzamide, 3-((2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-N-(4,5-dihydro-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl)-; and "Coupler 5": Benzamide, 3-(((2,4-bis(1,1-dimethylpropyl)phenoxy)acetyl)amino)-N-(4,5- dihydro-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl)-; and containing the stabilizer 1,1'-Spirobi(1H-indene), 2,2',3,3'-tetrahydro-3,3,3',3'-tetramethyl-5,5',6,6'-tetrapropoxy-; and in the slow magenta layer Couplers 4 and 5 with the same stabilizer;
(8) one or more interlayers possibly including fine-grained nonsensitized silver halide;
(9) a triple-coated cyan pack with a fast cyan layer containing "Coupler 6": Tetradecanamide, 2-(2-cyanophenoxy)-N-(4-((2,2,3,3,4,4,4-heptafluoro-1-oxobutyl)amino)-3-hydroxyphenyl)-; a mid cyan containing"Coupler 7": Butanamide, N-(4-((2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-2-hydroxyphenyl)-2,2,3,3,4,4,4-heptafluoro- and "Coupler 8": Hexanamide, 2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-N-(4-((2,2,3,3,4,4,4-heptafluoro-1-oxobutyl)amino)-3-hydroxyphenyl)-;
(10) one or more interlayers possibly including fine-grained nonsensitized silver halide; and
(11) an antihalation layer.

The invention materials may also be used in combination with filter dye layers comprising colloidal silver sol or yellow, cyan, and/or magenta filter dyes, either as oil-in-water dispersions, latex dispersions or as solid particle dispersions. Additionally, they may be used with "smearing" couplers (e.g. as described in U.S. 4,366,237; EP 96,570; U.S. 4,420,556; and U.S. 4,543,323.) Also, the compositions may be blocked or coated in protected form as described, for example, in Japanese Application 61/258,249 or U.S. 5,019,492.

The photographic element may also contain image-modifying compounds such as "Developer Inhibitor-Releasing" compounds (DIR's). DIR's useful in conjunction with the compositions of the invention are known in the art and examples are described in U.S. Patent Nos. 3,137,578; 3,148,022; 3,148,062; 3,227,554; 3,384,657; 3,379,529; 3,615,506; 3,617,291; 3,620,746; 3,701,783; 3,733,201; 4,049,455; 4,095,984; 4,126,459; 4,149,886; 4,150,228; 4,211,562; 4,248,962; 4,259,437; 4,362,878; 4,409,323; 4,477,563; 4,782,012; 4,962,018; 4,500,634; 4,579,816; 4,607,004; 4,618,571; 4,678,739; 4,746,600; 4,746,601; 4,791,049; 4,857,447; 4,865,959; 4,880,342; 4,886,736; 4,937,179; 4,946,767; 4,948,716; 4,952,485; 4,956,269; 4,959,299; 4,966,835; 4,985,336 as well as in patent publications GB 1,560,240; GB 2,007,662; GB 2,032,914; GB 2,099,167; DE 2,842,063, DE 2,937,127; DE 3,636,824; DE 3,644,416 as well as the following European Patent Publications: 272,573; 335,319; 336,411; 346, 899; 362, 870; 365,252; 365,346; 373,382; 376,212; 377,463; 378,236; 384,670; 396,486; 401,612; 401,613. Such compounds are also disclosed in

"Developer-Inhibitor-Releasing (DIR) Couplers for Color Photography," C.R. Barr, J.R. Thirtle and P.W. Vittum in Photographic Science and Engineering, Vol. 13, p. 174 (1969).

It is also contemplated that the concepts of the present invention may be employed to obtain reflection color prints as described in Research Disclosure, November 1979, Item 18716, available from Kenneth Mason Publications, Ltd, Dudley Annex, 12a North Street, Emsworth, Hampshire P0101 7DQ, England. Materials of the invention may be coated on pH adjusted support as described in U.S. 4,917,994; with epoxy solvents (EP 0 164 961); with nickel complex stabilizers (U.S. 4,346,165; U.S. 4,540,653 and U.S. 4,906,559 for example); with ballasted chelating agents such as those in U.S. 4,994,359 to reduce sensitivity to polyvalent cations such as calcium; and with stain reducing compounds such as described in U.S. 5,068,171. Other compounds useful in combination with the invention are disclosed in Japanese Published Applications described in Derwent Abstracts having accession numbers as follows: 90-072,629, 90-072,630; 90-072,631; 90-072,632; 90-072,633; 90-072,634; 90-077,822; 90-078,229; 90-078,230; 90-079,336; 90-079,337; 90-079,338; 90-079,690; 90-079,691; 90-080,487; 90-080,488; 90-080,489; 90-080,490; 90-080,491; 90-080,492; 90-080,494; 90-085,928; 90-086,669; 90-086,670; 90-087,360; 90-087,361; 90-087,362; 90-087,363; 90-087,364; 90-088,097; 90-093,662; 90-093,663; 90-093,664; 90-093,665; 90-093,666; 90-093,668; 90-094,055; 90-094,056; 90-103,409; 83-62,586; 83-09,959.

Especially useful in the photographic elements of this invention are tabular grain silver halide emulsions. Specifically contemplated tabular grain emulsions are those in which greater than 50 percent of the total projected area of the emulsion grains are accounted for by tabular grains having a thickness of less than 0.3 micron (0.5 micron for blue sensitive emulsion) and an average tabularity (T) of greater than 25 (preferably greater than 100), where the term "tabularity" is employed in its art recognized usage as $T = ECD/t^2$ where ECD is the average equivalent circular diameter of the tabular grains in microns and t is the average thickness in microns of the tabular grains.

The average useful ECD of photographic emulsions can range up to about 10 microns, although in practice emulsion ECD's seldom exceed about 4 microns. Since both photographic speed and granularity increase with increasing ECD's, it is generally preferred to employ the smallest tabular grain ECD's compatible with achieving aim speed requirements.

Emulsion tabularity increases markedly with reductions in tabular grain thickness. It is generally preferred that aim tabular grain projected areas be satisfied by thin ($t < 0.2$ micron) tabular grains. To achieve the lowest levels of granularity it is preferred that aim tabular grain projected areas be satisfied with ultrathin ($t < 0.06$ micron) tabular grains. Tabular grain thicknesses typically range down to about 0.02 micron. However, still lower tabular grain thicknesses are contemplated. For example, Daubendiek et al U.S. Patent 4,672,027 reports a 3 mole percent iodide tabular grain silver bromoiodide emulsion having a grain thickness of 0.017 micron.

As noted above tabular grains of less than the specified thickness account for at least 50 percent of the total grain projected area of the emulsion. To maximize the advantages of high tabularity it is generally preferred that tabular grains satisfying the stated thickness criterion account for the highest conveniently attainable percentage of the total grain projected area of the emulsion. For example, in preferred emulsions, tabular grains satisfying the stated thickness criteria above account for at least 70 percent of the total grain projected area. In the highest performance tabular grain emulsions, tabular grains satisfying the thickness criteria above account for at least 90 percent of total grain projected area.

Suitable tabular grain emulsions can be selected from among a variety of conventional teachings, such as those of the following:

Research Disclosure, Item 22534, January 1983, published by Kenneth Mason Publications, Ltd., Emsworth, Hampshire P010 7DD, England; U.S. Patent Nos. 4,439,520; 4,414,310; 4,433,048; 4,643,966; 4,647,528; 4,665,012; 4,672,027; 4,678,745; 4,693,964; 4,713,320; 4,722,886; 4,755,456; 4,775,617; 4,797,354; 4,801,522; 4,806,461; 4,835,095; 4,853,322; 4,914,014; 4,962,015; 4,985,350; 5,061,069 and 5,061,616. In addition, use of [100] silver chloride emulsions as described in EP 534,395 are specifically contemplated.

The emulsions can be surface-sensitive emulsions, i.e., emulsions that form latent images primarily on the surfaces of the silver halide grains, or the emulsions can form internal latent images predominantly in the interior of the silver halide grains. The emulsions can be negative-working emulsions, such as surface-sensitive emulsions or unfogged internal latent image-forming emulsions, or direct-positive emulsions of the unfogged, internal latent image-forming type, which are positive-working when development is conducted with uniform light exposure or in the presence of a nucleating agent.

Photographic elements can be exposed to actinic radiation, typically in the visible region of the spectrum, to form a latent image and can then be processed to form a visible dye image. Processing to form a visible dye image includes the step of contacting the element with a color developing agent to reduce developable silver halide and oxidize the color developing agent. Oxidized color developing agent in turn reacts with the coupler to yield a dye.

With negative-working silver halide, the processing step described above provides a negative image. The described elements can be processed in the known C-41 color process as described in The British Journal of Photography Annual of 1988, pages 191-198. Where applicable, the element may be processed in accordance with color print processes such a the RA-4 process of Eastman Kodak Company as described in the British Journal of Photography Annual of 1988, Pp 198-199. To provide a positive (or reversal) image, the color development step can be preceded by development with a non-chromogenic developing agent to develop exposed silver halide, but not form dye, and followed by uniformly fogging the element to render unexposed silver halide developable. Alternatively, a direct positive emulsion can be employed to obtain a positive image.

Preferred color developing agents are p-phenylenediamines such as:

4-amino-N,N-diethylaniline hydrochloride,
4-amino-3-methyl-N,N-diethylaniline hydrochloride,
4-amino-3-methyl-N-ethyl-N-(β-(methanesulfonamido) ethyl)aniline sesquisulfate hydrate,
4-amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)aniline sulfate,
4-amino-3-β-(methanesulfonamido)ethyl-N,N-diethylaniline hydrochloride and
4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine di-p-toluene sulfonic acid.

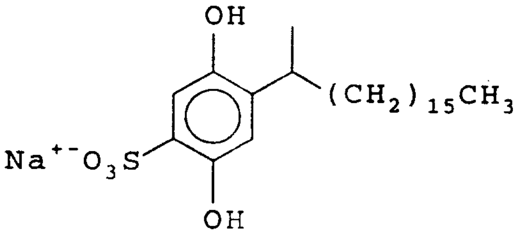
Development is usually followed by the conventional steps of bleaching, fixing, or bleach-fixing, to remove silver or silver halide, washing, and drying.

It is understood thoroughout this specification and claims that any reference to a substituent by the identification of a group containing a substitutable hydrogen (e.g. alkyl, amine, aryl, alkoxy, heterocyclic, etc.), unless otherwise specifically stated, shall encompass not only the substituent's unsubstituted form, but also its form substituted with any photographically useful substituents. Usually the substituent will have less than 30 carbon atoms and typically less than 20 carbon atoms.

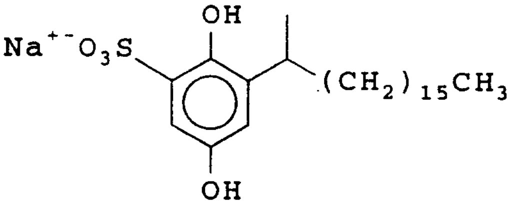
The following Example illustrates the reduction of viscosities of a coating melts by the addition of cyclodextrins.

Examples 1-6

Solutions of gelatin, water and an isomeric mixture of a sulfonated oxidized developer scavenger (SC-1) having the structural formulas (a) and (b), given below, were prepared in the proportions given in Table 1.



(a)



(b)

Table I

Summary of Effect of α-cyclodextrin on viscosity of gelatin melt containing SC-1					
Example	Gelatin (wt %)	SC-1 (wt %)	Viscosity reducing agent (α-CD, wt %)	Mole ratio α-CD/SC-1	Viscosity at 40°C (cP)
1, no SC-1 (control)	10.1	0	0	-	23.1
2, (control)	10.1	0.21	0	∞	44.5
3, invention	10.1	0.21	0.42	1.05	44.5
4, invention	10.1	0.21	0.85	1.93	41.7
5, invention	10.1	0.21	1.28	2.91	31.3
6, invention	10.1	0.21	1.68	3.82	25.6

Example 1 is a melt that has no SC-1, and shows the aqueous gelatin solution containing 10.1 wt.% gelatin has a viscosity of 23.1 cP RBT (Rolling Ball Time). Incorporation of SC-1 (0.21 wt %, based on the weight of the solution) in the melt raises the viscosity to 44.5 cP. However, it is seen that the addition of the compound α-cyclodextrin hydrate (commercially available from Aldrich Chemical Company) to the melt in progressively greater amounts, reduces the viscosity of the melts (Example 3, 4 and 5) to virtually the value of that of the melt that has no (SC-1).

Surface tension studies show that addition of α-cyclodextrin to water does not reduce its surface tension; i.e., it remains at about 72 mNm^{-1} as measured by the Wilhemy plate method.

In Fig. 2, it can be seen that the surface tension of SC-1 (consisting of 31% of SC-1 (a) and 69% of SC-1 (b)) decreases to about 43 dynes/cm for a $5x10^{-4}$ M SC-1 solution. The sharp break in the curve at about 5×10^{-5} M (log[SC-1]= -4.3) is the critical micellar concentration of SC-1. This behavior is typical of surfactant molecules and thus SC-1 is a surfactant (i.e., an amphiphile).

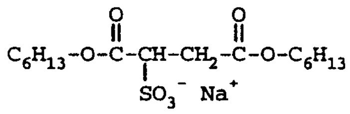
In Fig. 3, it can be seen that the addition of increasing amounts of SC-1 to an aqueous solution of α-cyclodextrin (10^{-3} M), results in a drop in surface tension only after the molar amount of SC-1 approaches the number of moles of α-cyclodextrin. Assuming a 1:1 type association, the binding constant is about 990 M^{-1}.

By comparing Fig. 2 and Fig. 3 it can be seen that the surface tension of a $5x10^{-4}$ M SC-1 in the absence of α-cyclodextrin is about 43 dynes/cm while it is significantly higher (69 dynes/cm) in the presence of 10^{-3} M α-cyclodextrin. Viewed another way, the data in Fig. 3 is also consistent with the conclusion that adding α-cyclodextrin to a solution of SC-1 would cause an increase in the surface tension of the solution as there would be less free SC-1.

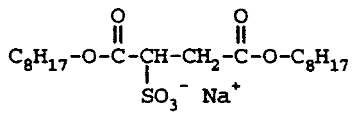
Claims

1. An aqueous photographic coating composition comprising an aqueous solution comprising gelatin and an anionically charged, hydrophobic group-containing compound that is (a) soluble in water or a mixture of water and a water-miscible organic solvent, and (b) which confers an undesirably high viscosity to aqueous gelatin solutions, wherein the composition further comprises a cyclodextrin in an amount sufficient to reduce the viscosity of the solution.

2. A photographic coating composition in accordance with claim 1, wherein the anionically charged, hydrophobic group-containing compound is sodium dodecyl sulfate, sodium octyl sulfate, sodium decyl sulfate, sodium tetradecyl sulfate, sodium or potassium salt of octadecyl hydroquinone sulfate, or a compound of the formula:

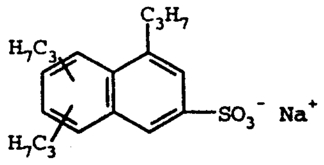


$$C_6H_{13}-O-\overset{\overset{O}{\|}}{C}-\underset{SO_3^-\ Na^+}{\underset{|}{CH}}-CH_2-\overset{\overset{O}{\|}}{C}-O-C_6H_{13}$$



$$C_8H_{17}-O-\overset{\overset{O}{\|}}{C}-\underset{SO_3^-\ Na^+}{\underset{|}{CH}}-CH_2-\overset{\overset{O}{\|}}{C}-O-C_8H_{17}$$

or



3. A photographic coating composition in accordance with claim 1, wherein the anionically charged, hydrophobic group-containing compound is a sulfonated alkyl hydroquinone.

4. A photographic coating composition in accordance with claim 1, wherein the cyclodextrin is α-cyclodextrin.

5. A method of reducing the viscosity of an aqueous gelatin solution containing an anionically charged, hydrophobic group-containing compound that is (a) soluble in water or a mixture of water and a water-miscible organic solvent,

and (b) which confers an undesirably high viscosity to aqueous gelatin solutions, which method comprises adding to said solution a cyclodextrin in an amount sufficient to reduce the viscosity of the solution.

6. A method of reducing the viscosity of an aqueous gelatin solution containing an anionically charged, hydrophobic group-containing compound that is (a) soluble in water or a mixture of water and a water-miscible organic solvent, and (b) which confers an undesirably high viscosity to aqueous gelatin solutions, which method comprises adding to said solution a cyclodextrin in an amount sufficient to reduce the viscosity of the solution without causing a reduction in the surface tension of the composition.

7. A photographic element comprising a support having thereon a layer comprising:

(i) gelatin,
(ii) an anionically charged, hydrophobic-group containing compound that is (a) soluble in water or a mixture of water and a water- miscible organic solvent, and (b) which confers an undesirably high viscosity to aqueous gelatin solutions, and
(iii) a cyclodextrin.

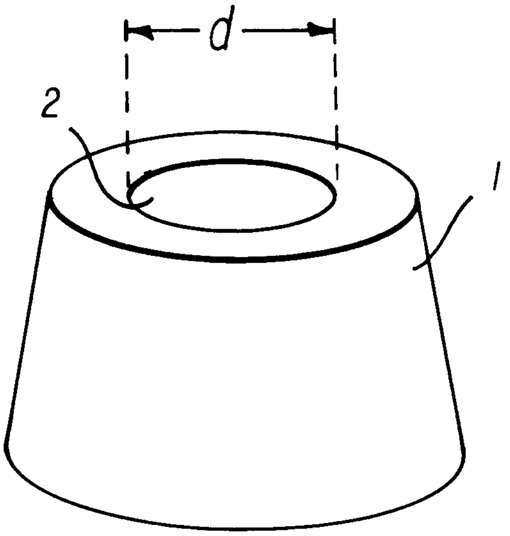


FIG. 1

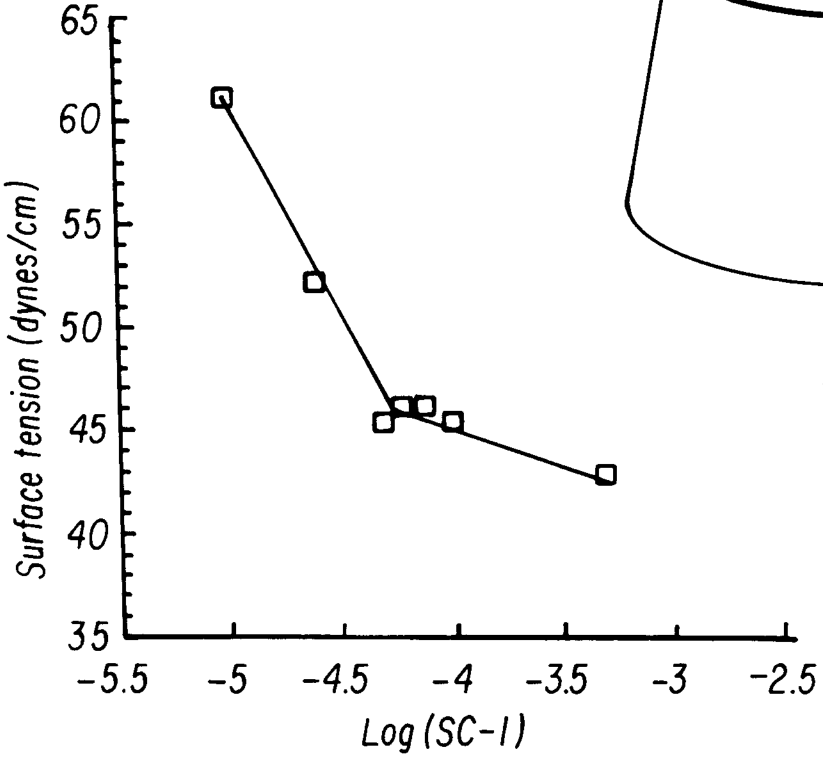


FIG. 2

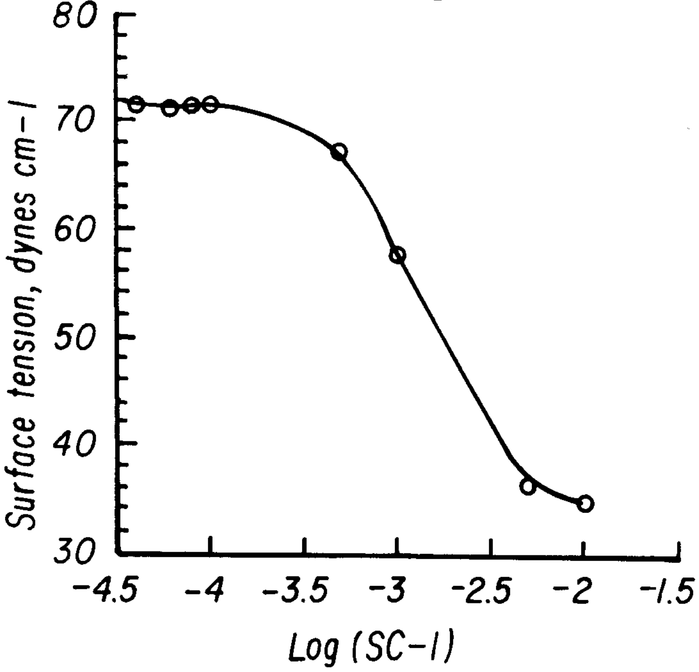


FIG. 3