

Oct. 24, 1950

J. A. H. HART ET AL
PHOTOGRAPHIC LAYERS CONTAINING GELATIN-ANION
SOAP COMPLEXES AND THEIR PREPARATION
Filed Oct. 19, 1945

2,527,262

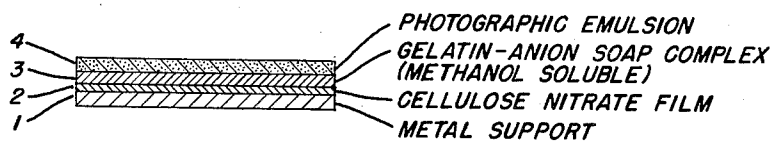


Fig. 1

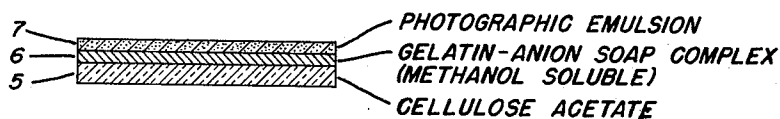


Fig. 2

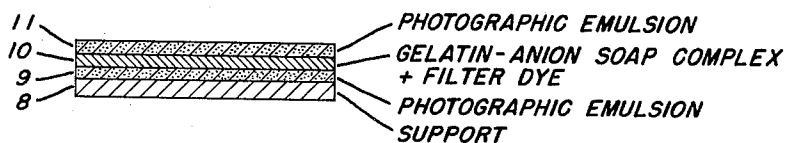


Fig. 3



Fig. 4

INVENTOR.
JOHN ALFRED HENRY HART
KENNETH GEORGE ALFRED PANKHURST
ROBERT CHARLES MORRIS SMITH
BY *Lynn Barratt Morris*

ATTORNEY

UNITED STATES PATENT OFFICE

2,527,262

PHOTOGRAPHIC LAYERS CONTAINING
GELATIN-ANION SOAP COMPLEXES
AND THEIR PREPARATION

John Alfred Henry Hart, Kenneth George Alfred Pankhurst, and Robert Charles Morris Smith, Ilford, England, assignors to Ilford Limited, Ilford, England, a company of Great Britain

Application October 19, 1945, Serial No. 623,446
In Great Britain October 30, 1944

9 Claims. (Cl. 95—8)

1

This invention relates to the production of photographic materials.

When an anion soap is added to a solution of gelatin at a low pH value or in the presence of an electrolyte (when the pH value need not necessarily be low), a complex is formed between the gelatin and anion soap and this separates out.

It has now been discovered that the gelatin/anion soap complexes thus formed, and also analogous complexes formed with a sulphonic acid containing a highly hydrophobic radicle in the anion, are readily dispersible in organic solvents, e. g. methyl alcohol, and that the dispersions thus formed are suitable for coating gelatin layers in the production of photographic materials containing such layers. According to this invention, therefore, a method for coating a gelatin layer in photographic materials comprises coating on a supporting surface forming an element of such material a dispersion in which the solvent medium is predominantly organic, formed by dispersing in an organic solvent medium a complex formed by precipitating gelatin from its aqueous dispersion by means of an anion soap, or by means of a sulphonic acid containing a highly hydrophobic radicle in the anion, the said aqueous dispersion being at a pH value below the isoelectric point of the gelatin, or at a higher pH value and containing an electrolyte. The precipitated complex may contain a small proportion of water and this be included in the organic solvent dispersion.

According to a further feature of the invention, there is included in an organic solvent dispersion so formed and so used a proportion of another colloid which is soluble in the solvent medium already present, or which is soluble in a solvent medium which is miscible with the solvent medium already present, to form a stable combination.

The gelatin/anion soap complexes and analogous complexes formed from sulphonic acids as defined above, may be prepared by the addition of the anion soap solution to a solution of the gelatin and allowing the resulting precipitate to sediment out. However, they can be prepared merely by allowing the gelatin to stand in a solution of the anion soap. The complexes may be dispersed in the organic solvent medium without washing, but it is preferred to wash the complex to remove unwanted ions. Instead of the anion soap itself, the corresponding free acid may be

2

employed. The technique of maintaining the original aqueous dispersion of the gelatin at a low pH value appears to be equivalent in effect to the use of the free acid, but the use of the free acid presents the advantage that the resulting complex is not contaminated with the cation of the anion soap. Complexes free from water-soluble salts are found to be more readily dispersible in some organic solvent media.

The invention will be described with particular reference to the use of anion soaps, but it is to be understood that sulphonic acids which, though not true anion soaps, contain a highly hydrophobic anion, can be used analogously.

It has been discovered that for each particular anion soap there is an optimum ratio of the soap to the gelatin which results in a complex of the highest solubility in organic solvents, and a method is available for determining such optimum ratio in each particular case.

If an anion soap is added in gradually increasing quantity to a gelatin solution at low pH, or at higher pH in the presence of electrolyte, a gelatin/anion soap complex forms and separates out. By measuring the amounts of the anion of the anion soap remaining in the supernatant liquid after the mixture has been allowed to stand for some hours, thus reaching equilibrium, and plotting these quantities as ordinates against the quantities of anion soap added as abscissae, using a logarithmic scale, a curve is obtained showing a straight line rising portion followed by a fall where the complex begins to separate. The curve falls to a minimum value and then rises again. It has been discovered that, generally speaking, this minimum value (referred to as the "inflexion point") represents the particular complex having the greatest hydrophobic character and the greatest solubility in organic solvents. The precise position of the inflexion point, however, depends on various factors, including the pH and the quantity of electrolyte present, if any.

A curve of this type can be obtained in respect of any particular anion soap which it is desired to use, and it may be said that, as a general proposition, where plain gelatin is concerned, the preferred conditions for obtaining the highest degree of solubility in organic solvents are that the anion of the anion soap used should be as strongly hydrophobic as possible, the pH of the

solution should be below the isoelectric point of the gelatin, the electrolyte concentration of the anion soap should be as low as possible, and the concentration of the anion soap should be as near the inflexion point as possible. The low pH value enables the use of the free acid of the anion soap. Generally speaking pH values of the order of 2.5 to 3.0 are suitable, but lower values, e. g. as low as 2.0 may be used.

Anion soaps are surface-active compounds in which the reduction in surface tension resultant on their addition to water is due to the anion. The classification of soaps is discussed in the book *Kolloidchemische Grundlagen der Textilveredlung* by Dr. E. Valko, 1937, at pages 519-522, to which reference is made for the meaning of the expression "anion soaps."

Specific classes of compounds falling within this generic expression are as follows:

(a) Soluble salts of long-chain-alkyl carboxylic acids, e. g. soluble salts of fatty acids containing 8 or more carbon atoms, as for example, oleic, ricinoleic, linoleic, stearic and palmitic acids.

These, however, are in general much less satisfactory for use 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 8 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 8 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 sulphated succinic acid.

Thus, it will be seen that anion soaps containing sulphonic or sulphuric acid groups are preferred to those containing carboxylic acid groups.

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

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

The expression "long-chain-alkyl" is intended to mean at least 8, and preferably at least 12, carbon atoms in the alkyl group.

Very many anion soaps are commercially marketed as detergents and these commercial products may conveniently be employed in the process of this invention. Thus suitable commercial products are the compounds sold under the trade names:

Agral N	Nekal BX
Aresklene 375	Permalin N
Dispersol	Santomer D
Gardinol	Sulphonated Lorol T. A.
Igepon T	Sulphonated Lorol N. H.
Lissapol A	Sulphonated Lorol C. Y.
Lissapol C	Sulphonated Ocenol
Lissatan A	Teepol X
Lohrinol	Tergitol 4
Nekal A	Tergitol 7

Agral N is the sodium salt of an alkyl naphthalene sulphonic acid.

Aresklene 375 is the sodium salt of an alkyloxydiphenyl disulphonic acid.

Dispersol is the sodium salt of dinaphthyl methane disulphonic acid.

Gardinol is an alkali metal sodium long-chain-alkyl sulphate of 10 to 18 carbon atoms.

Igepon T is the sodium salt of oleyl-methylamino-ethane sulphonic acid.

Lissapol A is sodium hexadecyl sulphate.

Lissapol C is sodium hexadecyl sulphate.

Lissatan A is a condensation product of sodium hexadecyl sulphate and formaldehyde.

Lohrinol is a sulphonated fatty acid.

Nekal A, Nekal BX, and Permalin N are all sodium salts of alkyl naphthalene sulphonic acids.

Santomer D is the sodium salt of an alkyl benzene sulphonic acid.

Sulphonated Lorol T. A. is triethanolamine dodecyl sulphate.

Sulphonated Lorol N. H. is ammonium dodecyl sulphate.

Sulphonated Lorol C. Y. is cyclohexylamine dodecyl sulphate.

Sulphonated Ocenol is a sulphonated mixture of aliphatic unsaturated alcohols of 16 to 18 carbon atoms, predominating in the latter.

Teepol X is a mixture of sodium alkyl sulphates. Tergitol 4 and Tergitol 7 are sodium secondary-alkyl sulphates.

Such commercial detergents and still more the pure anion soaps contained in them, are much preferred to the ordinary alkali-metal soaps of fatty acids referred to under (a) above. As already indicated, there may be used, instead of the anion soap itself, the free acid derived from such soap.

As indicated above, instead of true anion soaps, certain sulphonic acids of which the anion is highly hydrophobic may be employed. These may be simple acids, for example 2-naphthol-1-sulphonic acid, 1-naphthol-4-sulphonic acid or anthraquinone-2-sulphonic acid, or may be more complex, for example dyestuffs such as Kiton Fast Yellow 3G (Colour Index No. 645) which contains a sulphonyl-pyrazolone radicle, and Naphthalene Orange GS (Imperial Chemical Industries Ltd.).

Generally speaking the most suitable organic solvents for dispersing the complexes are those containing hydroxy groups, e. g. methyl and ethyl alcohols, ethylene glycol mono methyl ether, ethyl lactate and diacetone alcohol. Organic solvents not containing hydroxy groups are generally only useful together with some water or some hydroxy solvent, e. g. acetone, methyl ethyl ketone, dioxane, methylene chloride, chloroform and mesityl oxide are preferably used in admixture with water or methyl alcohol. Small quantities of esters, e. g. methyl acetate, butyl acetate, ethers, e. g. diethyl ether, and hydrocarbons, e. g. benzene and toluene, may also be included in the solvent medium.

The choice of solvent will depend on the particular nature of the complex. Complexes formed at low pH and containing a relatively low proportion of the anion soap (or corresponding acid) are generally more easily soluble in polar solvents or in solvents containing some water, whilst those formed at higher pH values and containing more anion soap (or corresponding acid) are generally soluble in non-polar solvents, e. g. toluene. The complexes may be swollen in the organic solvent medium and dis-

5

person is usually facilitated by gentle warming.

The following table shows examples of the preferred conditions, as represented by the inflexion points of the curves, for precipitating a gelatin/anion soap complex using various pure and commercial anion soaps:

Anion Soap	Quantity added per liter of gelatin solution	pH	Added electrolyte (normality)
	Grams		
a. Santomerse D	1.6	3.0	none
b. Santomerse D	2.4	5.5	0.5
c. Teepol X	10	3.0	none
d. Teepol X	22.5	5.5	0.5
e. Dodecyl sodium sulphate	1.5	3.0	none
f. Dodecyl sodium sulphate	2.3	3.0	0.5
g. Dodecyl sodium sulphate	11.5	4.8	0.5
h. Agral N	4.2	3.0	none
i. Agral N	5.8	3.0	0.5
j. Permalin N	3.2	3.0	none
k. Permalin N	12	5.5	0.5
l. Aresklene 375	3.7	3.0	none
m. Aresklene 375	5.8	5.5	0.5
n. Nekal A	4	3.0	0.5
o. Igepon T	6	3.0	none

It will be understood that many of the commercial anion soaps mentioned in the above table are adulterated with electrolytes so that the absence of added electrolyte does not necessarily mean that no electrolyte is present. In the tests referred to in this table the gelatin concentration was 0.67% and the temperature was 50° C. in each case:

Those complexes formed in the presence of electrolyte generally speaking contain more water, and if containing too much are insoluble in the lower alcohols. Solubility in xylene and chloroform appears to improve the greater the quantity of anion soap relative to gelatin, up to the inflexion point, and this condition can generally be favoured by increasing the pH value or adding electrolyte.

As already indicated, an important feature of this invention is the formation of dispersions which comprise a gelatin anion/soap complex dispersed in an organic solvent medium, together with a proportion of another colloid soluble in such organic solvent medium or in an organic solvent medium miscible therewith. Such other colloids may be, for example, cellulose esters, e. g. cellulose nitrate, cellulose acetate, far-hydrolysed cellulose esters (e. g. cellulose acetate having an acetyl content of 20 to 30%), polyvinyl acetates, polyvinyl acetals, methyl methacrylate polymers, and the partial hydrolysis products thereof, alkyd resins, and mixed interpolymers such as the interpolymers of maleic acid or anhydride with styrene or methyl methacrylate.

The coating solutions obtained by the process of this invention may be employed for the formation of all types of colloid layers commonly present in photographic materials. They are of particular value in the formation of substrata serving to anchor a photographic emulsion layer to a hydrophobic colloid support such as cellulose nitrate or cellulose acetate film base. However, they may also be employed in the formation of anti-halation layers, in which case the solutions may contain a dye or pigment which absorbs light of the wavelength to which the photographic emulsion employed is sensitive; in the formation of filter layers, for example in the production of multi-layer materials for colour photography, in which case they should contain a colouring matter of the appropriate hue;

6

in the formation of anti-abrasion super-coats, serving as an outer protection for the emulsion, in the formation of anti-static layers, and in the formation of colloid layers containing colour-former substances to be coated adjacent to photographic silver halide emulsion layers.

Where the coating solutions are to contain dyes, pigments (including colloidal silver), colour-formers and the like, these may in some cases be present in the original aqueous gelatin dispersion from which the gelatin/anion soap complex is separated, since many of these substances, particularly pigments and particulate colour-formers, will separate with the complex. Alternatively they may be added at any subsequent stage in the preparation of the coating solution.

The following examples illustrate specific applications of the solutions of the complexes according to this invention:

EXAMPLE 1

Subcoat solution for application to cellulose nitrate base

50 grams of gelatin were melted in 4 litres of water to form a dispersion. To this was added 150 grams of the commercial anion soap Agral N (an alkyl naphthalene sodium sulphonate) dissolved in 800 cc. of water, and this was followed by 40 cc. of 2N hydrochloric acid. The gelatin/anion soap complex separated as a rubbery mass and the supernatant liquid was decanted off. The complex was then washed in 4 litres of water and then dissolved in 300 cc. of hot methyl alcohol. The complex was re-precipitated by the addition of 300 cc. water and then re-dissolved in 500 cc. methyl alcohol. This solution was diluted to 1 litre with methyl alcohol and 10 grams of cellulose nitrate was added. This final solution, coated on a cellulose nitrate lacquered film carried on a metal support, allowed to dry, and then coated with emulsion, was found to give excellent anchorage between the cellulose nitrate surface and the emulsion, and this strong adhesion was not adversely affected by the usual processing operations. The resulting element is shown in Fig. 1 of the drawing wherein metal support 1 is provided with a coating of cellulose nitrate 2 which carries layer 3 composed of the gelatin anion soap complex which in turn carries photographic emulsion layer 4.

EXAMPLE 2

Subcoat solutions for application to cellulose acetate film base

(a) The following solution was prepared:

Gelatin 10% solution	cc.	50
Methyl alcohol	cc.	50
Salicylic acid	gm.	3

To this was added 50 cc. of a 10% solution of Permalin N. The resulting precipitate was washed with 100 cc. water, drained and dissolved in 50 cc. hot methyl alcohol. It was reprecipitated by adding 50 cc. water and re-dissolved in 50 cc. methyl alcohol. This solution was diluted with 150 cc. methyl alcohol and 300 cc. acetone, and was suitable for coating on cellulose acetate film base. A gelatin photographic emulsion subsequently applied adhered firmly to the subcoat base so prepared.

(b) 200 cc. of a 3% solution of gelatin purified by the method described in British Specification No. 558,262 was prepared and to this was

added 25 cc. of a 15% solution of the free acid obtained by the extraction with ether of an acidified solution of Permal N. The resulting precipitated complex was drained, dissolved in 100 cc. warm methyl alcohol and reprecipitated by adding 200 cc. water. The precipitate was further washed and re-dissolved in 150 cc. warm methyl alcohol. This solution was diluted with 350 cc. acetone and applied to cellulose acetate film base 5 as shown in Fig. 2 of the drawing. It formed a good substratum 6 to which a gelatin photographic emulsion 7, subsequently coated, adhered strongly.

(c) To 100 cc. of a 0.67% solution of gelatin was added 8.3 cc. of normal hydrochloric acid solution and 11 cc. of Teepol X. The resulting precipitated complex was dissolved in methyl alcohol, reprecipitated, taken up in 150 cc. methyl alcohol and diluted with 350 cc. acetone, as in the previous example, to form an equally satisfactory subcoat solution.

(d) To 100 cc. of a 5% solution of gelatin was added 15 cc. of a 10% solution of naphthalene-2-sulphonic acid. The resulting precipitated complex was dissolved in 50 cc. of hot methyl alcohol, diluted with 110 cc. of methyl alcohol and 325 cc. acetone. Finally 0.25 cc. of 40% formaldehyde solution was added and the solution coated on cellulose acetate film base to form a satisfactory substratum as before.

EXAMPLE 3

Coloured filter layers

(a) This example illustrates the use of a sulphonic acid dyestuff in the formation of the complex.

To 100 cc. of a 4% solution of gelatin purified by the process of British Specification No. 558,262 was added 200 cc. of a 1% solution of Kiton Fast Yellow 3G. The precipitated complex was dissolved in 100 cc. of methyl alcohol and coated over a dried gelatin photographic emulsion layer. The dye did not penetrate the emulsion and could be removed by washing in water before or after processing the emulsion.

This technique is also of value in the formation of filter layers which lie between emulsion layers in multilayer photographic elements intended for colour photography. The resulting element as shown in Fig. 3 of the drawing wherein support 8 is coated with photographic emulsion 9 which carries filter layer 10 which in turn supports emulsion layer 11.

(b) This example illustrates the separate addition of a dye to a gelatin/anion soap complex.

To 1 litre of a 0.67% solution of gelatin was added 40 gms. of ammonium nitrate and 25 cc. of Teepol X. The solution was allowed to stand for four hours and the supernatant liquid was then decanted. The residual complex was stirred with 30 cc. of xylene and boiled until all the water contained in it had been removed. The solution of the complex in xylene was then made up to 300 cc. with xylene, to replace evaporation losses, and diluted with 300 cc. toluene containing 1.5 gms. of Cellaquer Red 75079 dye (Williams & Co.).

This solution was coated over a dried emulsion layer. It did not penetrate into the emulsion layer and could be completely removed by gentle swabbing with water.

EXAMPLE 4

Anti-static layer

1.5 cc. of a solution of the complex in xylene, 75

prepared as in Example 3 (b), was diluted with 98.5 cc. of benzene and coated on cellulose nitrate film 12 to form antistatic layer 13 as shown in Fig. 4 of the drawing. It was found to impart good anti-static properties, and also had the effect of reducing surface friction so that the film was less easily scratched.

EXAMPLE 5

Solution for substrata and other uses

50 grams of gelatin were melted in 2 litres of water to form a dispersion. To this was added 150 grams of the commercial anion soap Agral N followed by 40 cc. of 2N hydrochloric acid. The supernatant liquid was decanted off and the precipitated complex washed in 4 litres of water. The complex was then dissolved in 600 cc. of hot methyl alcohol, re-precipitated by the addition of 1 litre of water, re-dissolved in 300 cc. of hot methyl alcohol, re-precipitated by the addition of 300 cc. of water, pressed free of liquid and finally dissolved in 500 cc. of hot methyl alcohol. This solution was then diluted with 1½ litres of cold methyl alcohol and 3 litres of acetone.

The resulting solution, coated on cellulose acetate film base, dried, and then supercoated with an ordinary gelatin silver halide emulsion, afforded strong adhesion between the base and the emulsion both in the dry condition and during the processing of the emulsion.

By adding a suitable dye to it, e. g. a small quantity of Acid Green G, it was suitable for coating as an anti-halation layer on one side of cellulose acetate film base, carrying on the other side a panchromatic emulsion. It was also suitable for coating on the surface of a photographic emulsion to form an anti-abrasion or "non-stress" layer. By adding baryta to it the solution was suitable for forming a baryta coat on paper base intended to be subsequently coated with photographic emulsion. By diluting 1 part of the coating solution with 20 parts of 95% ethyl alcohol, a solution was obtained which, when coated on cellulose nitrate base, had good anti-static properties.

The invention provides dispersions having a gelatin basis dispersed in organic solvent and the dispersions are therefore of value in a number of special applications. For example, they are of particular value for spray coating. Normal gelatin dispersions present considerable difficulties in spray coating since it is usually necessary to maintain the dispersion warm in the spray-gun to prevent it setting therein. Moreover, the ordinary gelatin dispersions will not adhere firmly if sprayed on to lacquered metal sheet. By the present invention, however, dispersions may be obtained which have little tendency to set in the spray-gun. Moreover, the organic solvent usually has a slight solvent action on lacquered surfaces and thus facilitates adhesion between such surfaces and the gelatin dispersion thereon. The spray-coating of lacquered metal sheets with photographic emulsion is of particular value in the production of photo-templates and the preliminary spray coating of such metal sheets with a gelatin dispersion according to this invention enable a strongly adherent subcoat to be obtained.

Another use to which the dispersions of this invention may be put is in the production of printing paper to be used for printing from wet negatives. The dispersions of this invention have a good resistance to water, though they are readily permeable by ordinary alkaline developing

solutions. Paper coated with emulsion and supercoat with a gelatin dispersion according to this invention may be used for printing from wet negatives, though it is usually preferable to employ a dispersion containing a proportion of other colloids, e. g. cellulose nitrate and a methyl methacrylate-methacrylic acid co-polymer. Such dispersions not only have a good resistance to water, but also a good resistance to hypo which may be carried by the wet negative. Advantageously, in the production of wet-printing paper using the dispersions of this invention the emulsion itself should be a dispersion of a gelatin/silver halide/anion soap complex in organic solvent, as described in our co-pending U. S. application Ser. No. 623,445, filed October 19, 1945, now Patent No. 2,527,261.

What we claim is:

1. A photographic element comprising a support bearing a sublayer consisting essentially of a complex of gelatin with an anion soap, which complex is soluble in a solution composed of methyl alcohol, said element having a light-sensitive silver halide emulsion layer contiguous with said sublayer.

2. A photographic element comprising a support bearing a sublayer consisting essentially of a complex of gelatin and an anion soap containing a sulfur acid grouping, which complex is soluble in a solution composed of methyl alcohol, said element having a light-sensitive silver halide emulsion layer contiguous with said sublayer.

3. A photographic element comprising a support bearing a sublayer consisting essentially of a complex of gelatin and water-soluble salt of a sulfated higher alcohol, which complex is soluble in a solution composed of methyl alcohol, said element having a light-sensitive silver halide emulsion layer contiguous with said sublayer.

4. A photographic element comprising a support bearing a sublayer consisting essentially of a complex of gelatin and an anion soap, which complex is soluble in a solution composed of methyl alcohol and a compatible hydrophobic colloid, said element having a light-sensitive silver halide emulsion layer contiguous with said sublayer.

5. A photographic element comprising a support bearing a sublayer consisting essentially of a complex of gelatin and an anion soap, which complex is soluble in a solution composed of methyl alcohol and cellulose nitrate, said element having a light-sensitive silver halide emulsion layer contiguous with said sublayer.

6. A photographic element comprising a support bearing a sublayer consisting essentially of a complex of gelatin and an anion soap, which com-

plex is soluble in a solution composed of methyl alcohol, cellulose nitrate and a hydrophobic acid colloid, said element having a light-sensitive silver halide emulsion layer contiguous with said sublayer.

7. A photographic element comprising a support bearing in order a sublayer consisting essentially of a complex of gelatin and an anion soap, which complex is soluble in a solution composed of methyl alcohol, light-sensitive silver halide emulsion layer and a protective layer composed of the said complex.

8. A photographic element comprising a support bearing a sublayer composed essentially of a complex of gelatin and an anion soap, which complex is soluble in a solution composed of methyl alcohol, a contiguous light-sensitive silver halide emulsion layer, said element also bearing a layer consisting essentially of said complex which contains an antihalation dye.

9. A photographic element comprising a support bearing a sublayer consisting essentially of a complex of gelatin and an anion soap, which complex is soluble in a solution composed of methyl alcohol, a contiguous light-sensitive silver halide emulsion layer, a filter layer consisting essentially of said complex containing a filter dye and a gelatino silver halide emulsion layer contiguous with said filter layer.

JOHN ALFRED HENRY HART.

KENNETH GEORGE ALFRED PANKHURST.

ROBERT CHARLES MORRIS SMITH.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,290,794	Sheppard	Jan. 7, 1919
2,118,059	Slack et al.	May 24, 1938
2,182,794	Dawson	Dec. 12, 1939
2,282,001	Russell et al.	May 5, 1942
2,290,239	McQueen	July 21, 1942
2,304,940	Mannes et al.	Dec. 15, 1942
2,338,664	Nadeau et al.	Jan. 4, 1944

FOREIGN PATENTS

Number	Country	Date
537,256	Great Britain	Sept. 13, 1939
556,360	Great Britain	Oct. 1, 1943

OTHER REFERENCES

Journal of the American Chemical Society, Dec., 1943, pp. 2187-2190 and May, 1944, pp. 692-697.