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PHOTOGRAPHIC ELEMENT AND METHOD
OF MAKING IT

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This invention relates to surface-active materials which serve as wetting, dispersing and emulsifying agents and particularly to the use of such materials in the production and treatment of materials containing colloid layers such as photographic films, plates, papers, baryta coated papers and similar materials.

In recent years there have been produced large numbers of organic surface-active compounds. Such compounds normally ionise in aqueous solution and according to whether the wetting function is due to the anion or the kation are referred to as anion-active or "anionic" and kation-active or "kationic" agents respectively.

It has now been discovered, and this forms the basis of the present invention, that when anion-active and kation-active substances are employed in combination the resulting wetting power is very much greater than is obtained by the use of either of such substances separately in comparable concentration. Anion-active and kation-active substances when mixed in aqueous solution react together to produce a relatively insoluble complex of which both the anion and the kation are surface-active and it is believed that the remarkable increase in wetting obtained by the use of a combination of such wetting agents is due to the formation of this complex, since if the complex so formed is isolated and used as a wetting agent it exerts a wetting power comparable to that exerted by the mixture of anion-active and kation-active agents from which it was isolated.

The complex wetting agents may be isolated by mixing together the anionic and kationic agents, preferably in substantially chemically equivalent proportions, and isolating the complex formed which contains both an active anion and an active kation by mechanical means if it is relatively insoluble in the reaction solution, e. g. by centrifuging or by extraction with an organic solvent, e. g. ethyl ether.

According to the present invention, therefore, in a process wherein a surface is desired to be wetted, the wetting operation is effected in the presence of a combination of anion-active and kation-active wetting agents.

The expression "combination" of anion-active and kation-active wetting agents is intended to include both mixtures of the agents and the isolated complex wetting agents referred to above.

The combination of wetting agents may be present in the layer whose surface it is desired to wet (and this is preferred) or in the wetting fluid, or one of the said wetting agents may be present in said surface and the other in said fluid.

As already indicated, the combinations of wetting agents characteristic of this invention are of particular value in the production and treatment of photographic materials.

In the production of photographic films, plates and papers, a support, e. g. of cellulose nitrate, cellulose acetate, glass or paper is provided on one or both surfaces with one or more superposed layers of photographic emulsion, usually gelatino-silver halide emulsion, and such layer or layers may be present with other layers of colloid material acting as substrata, intermediate layers, filter layers, antihalation or backing layers or supercoating layers. For example, a support of cellulose derivative film may be provided with a substratum layer having a basis of gelatin, or of a mixture of gelatin and a cellulose derivative, and a gelatino silver halide emulsion layer may be coated on the substratum layer. In the case of photographic elements to be used for multi-colour photography a plurality of emulsion layers may be coated on the support and such emulsion layers may be coated in direct contact with one another or may be separated by plain or coloured gelatin layers as desired. Further, the outermost emulsion layer in a photographic element may be supercoated with a further colloid layer in order to prevent damage to the emulsion surface.

Although for some purposes the coating layers employed may be water-insoluble, it is far more frequent that the coating layers are of water-soluble or water-dispersible colloids, such as gelatin. It will be appreciated, therefore, that it is a matter of considerable importance in the manufacture of photographic elements where the support or any colloid layer already present is to be provided with a superposed layer of another colloid by coating it with an aqueous dispersion of such colloid that the support or colloid layer already present should be readily wetted by aqueous solutions. Only in this way can it be ensured that the superposed coating may be readily formed as a uniform continuous layer. Furthermore, it is a matter of considerable importance in the processing treatment of photographic films, plates and

papers, e. g., with developing and fixing baths, that the elements should be readily wetted by aqueous solutions.

In order to facilitate such wetting, it is well known to include saponin or an anion-active wetting agent such as a sulphonated oil or soap, or both, as ingredients of the colloid layers.

According, therefore, to a further feature of this invention, in the production of materials containing colloid layers and particularly photographic films, plates, papers, colour filters and similar products, wherein coating compositions consisting essentially of dispersions of colloids are applied to film, plate, paper or other supports or to set or dried colloid layers already present on such supports, there is present either in the colloid dispersion or in the support or colloid layer to which it is to be applied, or in both, taken together or separately, a combination of anion-active and kation-active wetting agents.

The invention further provides photographic elements in which the outermost layer contains a combination of anion-active and kation-active wetting agents and which are therefore very readily wetted by aqueous processing solutions.

The degree of wetting obtained by the combination of wetting agents of this invention is greater than that obtainable by either of the two agents separately in comparable concentration. Where the agents are used in the coating of colloid layers the concentration of the anion-active and kation-active agents required to give a marked increase in wettability may be as low as 1 part of each compound in 100,000 parts of aqueous colloid dispersion compared with one part in 5,000 parts of aqueous colloid dispersion for the separate wetting agents.

If the ratio of anion-active to kation-active agent is substantially maintained the ease of wetting increases progressively as the concentrations of the two components are raised.

Anion-active wetting agents which may be employed are, for example, aliphatic alcohol sulphates, aliphatic sulphonates, aromatic sulphonates, sulphonated taurine derivatives, soaps and sulphonated castor oils. As specific examples there may be mentioned dodecyl triethanolamine sulphate, dodecyl sodium sulphate, Turkey red oils and the materials sold under the trade names Igepon T (believed to be the sodium salt of oleyl amino ethane sulphonic acid), Aresklene 375 (believed to be the sodium salt of dibutyl phenyl phenol disulphonic acid), Lissapol C (believed to be a sulphated fatty alcohol) and Santomerse D (believed to be an alkylated aryl sulphonate).

Kation-active wetting 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, hexadecyl pyridinium bromide and the materials sold under the trade names Fixanol (believed to be a quaternary ammonium compound) and Sapamine MS (believed to be a diethyl aminoethyl long-chain alkyl amide ester). One or more anion-active agents may be used in combination with one or more kation-active agents, if desired.

It is found that the wetting power of the combinations of anion-active and kation-active agents of this invention increases progressively as the amounts of such agents are brought more closely to the point of chemical equivalence and that in the neighbourhood of this point the wet-

ting power is increased to a surprisingly high degree, a phenomenon which is believed to be due to the formation of the complex type of wetting agent referred to above. Apart from chemical combination between the agents, it is possible that either or both may be adsorbed by or may react with the materials which are being wetted. For example, where the agents are being used to effect the wetting of colloid layers they may be adsorbed by or may react with the colloid layer or layers, or materials contained in such layers. It is to be understood that in such a case the term "chemical equivalence" refers to the free agents unadsorbed and uncombined with such other materials.

In the coating of a support or colloid layer carried thereby with a dispersion of a colloid, the anion-active and kation-active wetting agents may both be incorporated in the support or colloid layer already present (as the case may be), both in the colloid dispersion which is being applied, or one in the support or colloid layer already present (as the case may be) and one in the colloid dispersion. However, it is generally preferable that both the anion-active and kation-active wetting agents should be present in the support or layer to which the colloid dispersion is to be applied. The colloid layer to which the dispersion of colloid is applied may be a dried layer or may be in the form of a set jelly from which surplus solvent has not been removed.

Whereas, as indicated above, a mixture of anion-active and kation-active wetting agents may be present in an underlayer of colloid, e. g. a sensitive gelatino photographic emulsion to which it is desired to apply a colloid layer or a further gelatino photographic emulsion in liquid form, this mixture of wetting agents may also with advantage be present in the outermost colloid layer or layers of the final photographic element in which case a considerable advance in ease of wetting by photographic processing solutions is obtained.

Where a mixture of anion-active and kation-active agents is employed in the production of photographic materials carrying light sensitive emulsions, it is generally desirable that if the agents are not present in equivalent proportions, any excess of one over the other should be in favour of the anion-active agent since an excess of kation-active agent in some cases tends to affect the properties of the light-sensitive emulsions deleteriously. Moreover, if the mixture of agents is added to a light-sensitive colloid emulsion it is usually desirable to add the anion-active agent first and then add the kation-active agent, for the same reason.

Although the invention is of particular value in facilitating ease of wetting in gelatin layers in photographic plates, films or papers, it can be applied to the manufacture and treatment of any materials which consist of a support coated with plain, dyed or pigmented gelatin or other colloid layer or layers, e. g. light filters. Moreover, the combinations of wetting agents of the invention may be usefully employed in connection with other water-dispersible colloid layers, e. g. agar-agar, casein, albumin, alginates and synthetic water-dispersible colloids. The combinations of wetting agents are unaffected by ethyl alcohol and other agents commonly present in photographic layers, such as the alums used as hardening agents.

The following examples illustrate the invention

but are not to be regarded as limiting it in any way:

In these examples the wetting power of the combinations of wetting agents was assessed by the maximum speed at which it proved possible to apply successfully a coating of colloid in the presence of the combination of wetting agents, in a continuous coating operation.

Example I

A layer of gelatin is applied to a support by coating the support with a solution of the following composition at 95° F.:

"Fixanol"	grams..	0.2
Dodecyl triethanolamine sulphate.....	do.....	0.2
Gelatin	do.....	80.0
Water to.....	litre..	1

The resulting layer is then set at 60° F. A supercoating solution of the following composition is then applied:

Gelatin	grams..	40
Water to.....	litre..	1

It is found that the supercoating solution spreads smoothly and easily on the underlying gelatin coating so that it may readily be coated on a continuous coating machine.

By increasing the amounts of Fixanol and dodecyl triethanolamine sulphate to 1 gram each, an even greater degree of ease of wetting is obtained.

Example II

To a 6% solution of gelatin were added 10 cc. of a 0.5% aqueous solution of dodecyl pyridinium sulphate per litre of the gelatin solution. The solution was divided into a number of portions and to each portion one of a range of quantities of 0.5% aqueous solution of sodium dodecyl sulphate was added. The several solutions so prepared were coated upon strips of photographic film base, set at room temperature and supercoated with a 4% solution of gelatin containing no wetting agent. The supercoating solution spread smoothly on all the gelatin subcoats, but with the greatest facility upon that in which the addition of sodium dodecyl sulphate was at the rate of 5 cc. of 0.5% aqueous solution per litre.

It was established by direct titration of the two wetting agents against one another in the absence of gelatin employing the method of G. S. Hartley and D. F. Runnicles (Proc. Roy. Soc. A. vol. 168, pp. 420-440, Nov. 1938) that 10 cc. of the 0.5% aqueous solution of dodecyl pyridinium sulphate was chemically equivalent to 4 cc. of the 0.5% aqueous solution of sodium dodecyl sulphate. The slight difference between this quantity (4 cc.) of sodium dodecyl sulphate solution and that found to give greatest ease of wetting in the present example (5 cc.) is probably due to adsorption of wetting agent to gelatin.

Example III

To a photographic gelatino silver bromide emulsion was added 25 cc. of a 0.5% aqueous solution of dodecyl pyridinium sulphate per litre of the emulsion. The treated emulsion was divided into a number of portions and to each portion one of a range of quantities of 0.5% aqueous solution of sodium dodecyl sulphate was added. The several emulsions so prepared were coated upon glass, the layers obtained were set to jelly at room temperature and coatings of an aqueous 2.2% solution of gelatin were applied

to them. It was found that in all cases the gelatin solution readily wetted the underlying emulsion coatings, a maximum wetting effect being obtained when the quantity of sodium dodecyl sulphate solution employed was 5 cc. per litre of emulsion.

By the titration method mentioned in Example II 25 cc. of the dodecyl pyridinium sulphate solution were found to be chemically equivalent to 12.5 ccs. of the sodium dodecyl sulphate solution. The difference (between 5 cc. and 12.5 cc.) is probably due to adsorption of wetting agent to constituents of the emulsion.

Example IV

A layer of gelatin was applied to a support by coating the support with a solution of the following composition at 95° F.:

Dodecyl triethanolamine sulphate.....	gms..	0.2
Gelatin	do.....	80.0
Water to.....	litre..	1

The resulting layer was then set at 70° F. A supercoating solution of the following composition was then applied:

"Fixanol"	grams..	0.2
Gelatin	do.....	40.0
Water to.....	litre..	1

In this example the anionic and kationic wetting agents were present separately and it was found that the supercoating solution spread smoothly and evenly on the underlying gelatin layer.

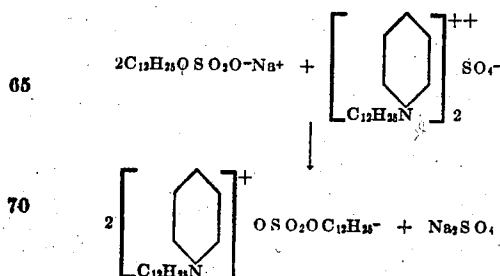
A similar result was obtained by employing Fixanol in the under layer of gelatin and dodecyl triethanolamine sulphate in the supercoating layer, in the same amounts.

Example V

63.2 ccs. of a 5% aqueous solution of dodecyl pyridinium sulphate were thoroughly mixed with 36.6 ccs. of a 5% aqueous solution of a proprietary wetting agent known to contain sodium dodecyl sulphate as the active ingredient, these relative quantities being found by prior test to give maximum coagulation. The reaction mixture consisted of a semi-gelatinous cloudy mixture and this was centrifuged for about 6 hours. The product thus separated consisted of a curd-like substance which contained about 30% of solid matter which was recovered as a wax-like substance.

The product was freely soluble in ethyl alcohol and in benzene though it is to be noted that sodium dodecyl sulphate is insoluble in ethyl alcohol and that neither sodium dodecyl sulphate nor dodecyl pyridinium sulphate is appreciably soluble in benzene.

It is believed that the reaction proceeds according to the equation:



Photographic film base carrying a layer of gelatin was coated with a light-sensitive emul-

sion to which had been added a 5% solution in ethyl alcohol of the complex wetting agent prepared as above, 1 cc. of the solution being added per litre of emulsion. The emulsion layer was set to gel form and was found to be very readily wetted by a supercoat solution consisting of a 4% solution of gelatin in water.

Similar results were obtained using the complex wetting agents obtained by reacting dodecyl pyridinium sulphate with Santomerse D (a commercial wetting agent of the anion-active class, the word Santomerse being a registered trade-mark) or with the sodium salt of oleyl amino ethane sulphonic acid (sold under the name Igepon T, the word Igepon being a registered trade-mark).

Example VI

100 ccs. of a 20% aqueous solution of a proprietary wetting agent containing hexadecyl pyridinium bromide was mixed with 74 cc. of a 20% aqueous solution of a proprietary wetting agent of the alkylated benzene sulphonate class, these quantities being found by test to give maximum coagulation. The coagulated product was separated from the reaction solution by extracting with 500 cc. of diethyl ether and evaporating the ether extract. The product which was a waxy solid was found to be freely soluble in ethyl alcohol.

The complex prepared as above was used as in Example V and gave similar satisfactory results.

Although the uses of the combination of wetting agents characteristic of this invention have been described with particular reference to the manufacture of photographic materials they may be used in other connections where a wetting action is desired. For example, they may be included in photographic developers or in textile treating baths.

What I claim is:

1. A process for the production of photographic materials containing colloid layers wherein a coating composition consisting essentially of an aqueous dispersion of a water-dispersible colloid is applied to a support, which comprises facilitating the coating of said composition on said support by means of a combination of anion-active and kation-active wetting agents present, during the coating operation, at the common surface of said support and said coating composition, the proportions of free anion-active and kation-active agents present being substantially chemically equivalent.

2. A process for the production of photographic materials containing colloid layers wherein a coating composition consisting essentially of an aqueous dispersion of a water-dispersible colloid is applied to the surface of a support which already carries a coating of a set water-dispersible colloid, which comprises facilitating the coating of such composition on said surface by means of a combination of anion-active and kation-active wetting agents present, during the coating operation, at the common surface of said set water-dispersible colloid and said coating composition, the proportions of free anion-active and kation-active agents present being substantially chemically equivalent.

3. A process for the production of photographic materials containing gelatin layers wherein a coating composition consisting essentially of an aqueous dispersion of gelatin is applied to the gelatin surface of a support already carrying a gelatin layer, which comprises facilitating the

coating of such composition on said gelatin surface by means of a combination of anion-active and kation-active wetting agents present, during the coating operation, at the common surface of said gelatin layer and said coating composition, the proportions of free anion-active and kation-active agents present being substantially chemically equivalent.

4. A process for the production of photographic materials containing gelatin layers wherein a coating composition consisting essentially of an aqueous dispersion of gelatin is applied to the gelatin surface of a support already carrying a gelatin layer, which comprises facilitating the coating of such composition on said gelatin surface by means of a combination of anion-active and kation-active wetting agents present in said gelatin layer, the proportions of free anion-active and kation-active agents present being substantially chemically equivalent.

5. A process for the production of photographic materials containing gelatin layers wherein a coating composition consisting essentially of an aqueous dispersion of gelatin is applied to a gelatin light-sensitive emulsion layer which comprises facilitating the coating of such composition on said emulsion layer by means of a combination of anion-active and kation-active wetting agents present in said emulsion layer, the proportions of free anion-active and kation-active agents present being substantially chemically equivalent.

6. A photographic element containing a support and at least one layer of a water-dispersible colloid, said layer having in intimate contact therewith a combination of anion-active and kation-active wetting agents in substantially chemically equivalent proportions.

7. A photographic element containing a support and at least two superposed layers of water-dispersible colloid, said superposed layers containing, when considered together, a combination of anion-active and kation-active wetting agents in substantially chemically equivalent proportions.

8. A photographic element containing a support and at least two superposed layers of water-dispersible colloid, the layer adjacent the support containing a combination of anion-active and kation-active wetting agents in substantially chemically equivalent proportions.

9. A photographic element containing a support and at least two superposed layers of water-dispersible colloid wherein the colloid consists essentially of gelatin, said superposed layers containing, when considered together, a combination of anion-active and kation-active wetting agents in substantially chemically equivalent proportions.

10. A photographic element containing a support and at least two superposed layers of water-dispersible colloid wherein the colloid consists essentially of gelatin, the layer adjacent to the support containing a combination of anion-active and kation-active wetting agents in substantially chemically equivalent proportions.

11. A photographic element containing a support and an outer layer of a water-dispersible colloid, said outer layer containing a combination of anion-active and kation-active wetting agents in substantially chemically equivalent proportions.

12. A photographic element containing a support, and an outer layer consisting essentially of gelatin, said outer layer containing a combina-

tion of anion-active and kation-active wetting agents in substantially chemically equivalent proportions.

13. A photographic element comprising a support and at least one layer of a water-dispersible colloid, said layer having in intimate contact therewith a small amount of a combination of dodecyl triethanolamine sulphate and a kation-active wetting agent in substantially chemically equivalent proportions.

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14. A photographic element comprising a support and at least one layer of a water-dispersible colloid, said layer having in intimate contact therewith a combination of an anion-active wetting agent and hexadecyl pyridinium bromide in substantially chemically equivalent proportions.

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