Patented Feb. 13, 1945 2,369,469

UNITED STATES PATENT OFFICE

2,369,469

PHOTOGRAPHIC MATERIALS

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No Drawing. Application January 23, 1943, Serial No. 473,389. In Great Britain February 11, 1942

4 Claims. (Cl. 95—7)

This invention relates to improvements in light-sensitive photographic materials. The invention is particularly applicable to the manufacture of photographic materials for color photography having two or more light-sensitive emulsions on one or more supports.

In light-sensitive photographic materials, more especially those for use in colour photography it is, as is known, often desirable to incorporate pigments, dyes, dye-derivatives or dye-forming substances in photographic silver salt emulsions having water-soluble or water-insoluble colloid binders or in non-sensitive layers having water-soluble colloid binders such as gelatine. I use the term "dye body" herein to designate any pigment, dye, dye-derivative or dye-forming substance which it may be desired to incorporate in light-sensitive or non-sensitive layers. I use the term "non-sensitive" herein to designate any layer not adapted to give rise to image formation therein on exposure of the sensitive emulsion or emulsions associated therewith. I use the term "dye derivative" herein to designate any derivative of a dye from which the dye can be formed in the emulsion or other colloid binder e. g. by oxidation or reduction. Examples of dye-forming substances are leuco dyes and color couplers.

Non-sensitive layers having colloid binders containing dye bodies may be required for various purposes, e. g. to reduce halation or to exert a filtering action on the exposure light whether this is the light received in the camera or received during printing or employed for fogging residual silver halide in reversal.

Sensitive layers having colloid binders are often required to contain sensitizing dyes to modify their spectral sensitivity or to contain other dye bodies for the production of colored images, e. g. in color photography. Such layers may consist of or contain silver salt emulsions such as gelatino-silver halide emulsions or silver halide collodion emulsions with which it may be desired to associate dye bodies. Such dye bodies may be used for the subsequent production of coloured separation images by an imagewise bleach out process. If dye derivatives or dye-forming substances are used there may be treated for the imagewise production of dyestuffs or for the diffuse production of dyestuff for subsequent imagewise bleaching. If dye-forming substances are used, these may be color couplers serving for the production of colored separation images by color development. I use the term "color coupler" herein to designate any body which is capable of combining with the oxidation products of the developing agent used for developing the exposed silver salt to metallic silver with the production of coloring matter in the region where the silver is developed. Subsequent removal of metallic silver without removal of coloring matter leaves a substantially clear, transparent dye image.

In making photographic materials containing sensitive or non-sensitive colloid layers, it has been customary to incorporate dye bodies directly in the colloid medium where its presence is required, such colloid medium being gelatine in most cases. Serious difficulties are often encountered in doing this particularly when the colloid medium is water-soluble. Thus when the dye body has a low solubility in the colloid medium it may not be possible to incorporate the desired quantity or the dye body may separate out in large crystals or aggregates in the process of coating and drying the colloid. Another trouble frequently met is the tendency of the dye body to diffuse out of the layer or emulsion in which it is incorporated into an adjacent layer or layers or emulsion or emulsions. I use the term "adjacent" herein to designate a layer or emulsion not separated from the layer or emulsion containing the dye body by any water-impermeable layer such as the support although it may be separated by a water-soluble colloid such as gelatine. This is the case when layers, one or more of which contain dye bodies, are cast one upon another, with or without intermediate plain colloid layers or where emulsions are disposed in the form of differentially sensitized grains in a single body of binder such as gelatine. British Patent specification No. 503,752 describes various arrangements of three differentially color sensitized emulsions on a single support wherein the difficulty of wandering of dye-bodies may be encountered. If some dye bodies wander from a non-sensitive layer into a sensitive layer they may have a deleterious action such as a fogging or desensitizing action. If they wander from one sensitive emulsion to another and such emulsions are destined to record different color sensations, the true color rendering may be detrimentally affected. Such wandering may take place during coating or drying or during processing.

Numerous proposals have been made to produce color couplers which will not wander or diffuse from the emulsions in which they are incorporated. In some of these proposals attempts were made so to alter the color couplers that they would have an affinity for gelatine, e. g. by the introduction of groups said to be "substantive." In other, groups of high molecular weight were introduced into the color couplers.

Although it has been proposed to cause color couplers to be absorbed on to the silver halide grains with the object of avoiding diffusion, most of the methods proposed have involved chemical synthesis of a more complex color coupler from a simpler color coupler. When this is done there is usually an undesirable tendency for the absorption range to become wider and the absorption curve to become flatter, resulting in less pure dye images. The use of colour couplers having a very low solubility in water or alkaline coupling developers is of advantage in that they show little or no tendency to wander from the emulsion layer or the emulsion grain in which they are incorporated but their insolubility in water frequently makes it difficult for them to be dispersed in adequate amounts and to an adequately fine degree on the emulsion. If they are not adequately dispersed then the dye which is formed tends to be produced in localized spots resulting in a granular appearance which impairs the photographic reproduction.

The use of an auxiliary carrier, such as a water-insoluble water-permeable cellulose derivative, natural resin or synthetic resin having the dye body dissolved or dispersed therein has been proposed as a means of preventing or minimising diffusion. It sometimes happens that when diffusion of a color coupler or other dye body is retarded in this way, the further difficulty is sometimes encountered that the processing baths employed do not act to a sufficient extent or sufficient rapidity upon the colour coupler or other dye body. It occasionally happens, for example, that when an emulsion containing an insoluble coupling component or one associated with a water-insoluble water-permeable binder has been exposed in the usual manner and developed with the customary type of color coupling developer, a very weak color or even no color at all is produced.

It is also sometimes difficult, when a colour coupler or other dye body is associated with a water-insoluble water-permeable binder, to find a binder which has the necessary solvent action for the color coupler or other dye body which is also sufficiently permeable to aqueous processing solutions. If the water-insoluble water-permeable binder has insufficient solvent action for the dye body, there is a tendency for the dye body or the dye formed from it or both to separate as a crystalline deposit on ageing of the finished emulsions.

One object of my invention is a method of incorporating a dye body in a colloid medium in which it has only low solubility which method prevents or minimises the risk of the dye body separating in large crystals or aggregates.

Another object of my invention is to incorporate a dye body in a colloid medium so that diffusion therefrom is prevented or minimised during coating or photographic processing.

Another object is to incorporate dye bodies non-diffusibly in colloid media while retaining sharp light absorption characteristics in the dye bodies or dyes formed therefrom.

Another object is to assist the dispersion in a colloid medium of a relatively insoluble dye body.

Another object is to enable dye bodies to be non-diffusibly incorporated in colloid media so that processing baths may nevertheless act on them to a sufficient extent and sufficiently rapidly.

Another object is to provide a water-insoluble, water-permeable binder having a good solvent action on dye bodies and with which dye bodies may be incorporated in colloid media.

The present invention in its broadest aspects comprises incorporating dye bodies in photographic colloid binders, for example in silver salt emulsions or light-screening layers, in the presence of hydrolysed natural resins or of resin esters or ethers or ether esters formed with organic or inorganic acids or alcohols. The hydrolysed natural resins can be used in the form of their salts, either water-soluble or water-insoluble, or their esters, ethers or ether esters. The invention does not, however, include the use of salts of hydrolysed lac.

I have found that by the use of hydrolyzed natural resins or resin derivatives as described above in conjunction with dye bodies, better results can often be obtained than by the use of the resins themselves or salts of resins themselves. Among the advantages secured by the use of hydrolysed natural resins or resin derivatives as described above are that, as a rule,

1. They form a finer dispersion than the parent resin.

2. They have an increased capacity for dissolving the dye body.

3. By adjusting the degree of hydrolysis in the case of hydrolysed resins, or by using suitable acids or alcohols for esterification or etherification in the case of resin derivatives, products of the same refractive index as gelatin can be obtained thus eliminating light scatter and matte surfaces when gelatine is employed as the carrier.

The hydrolysed resins are all oils or plastic at normal room temperatures and have higher acid values than the parent resin.

The principal difference between hydrolysed resins and the resin derivatives referred to is that the former are completely soluble in or removed by alkaline solutions such as developers in a short time while the latter can be made completely insoluble in alkaline liquids such as developers if required by complete esterfication of the ethers. Whether the hydrolysed resins or the resin derivatives are employed in any particular case will be determined by whether insolubility in alkali or solubility in alkali is the more favourable condition for the use to which the photographic material will be put.

The photographic material of the present invention has one or more layers on one or more supports and at least one layer has a colloid binder, especially a water-soluble colloid binder such as gelatine, containing a dye body as herein defined and a hydrolysed natural resin or a salt thereof or an ester or ether or ether ester of a natural resin or of a hydrolyzed natural resin. More specifically, the photographic material of the present invention may have one or more light-sensitive emulsions of silver salt colloid binder on one or more supports and have at least one non-sensitive layer having a water-soluble binder, such as gelatine, containing a dye body as herein defined and a hydrolyzed natural resin or a salt thereof or an ester or ether or ether-ester of a natural resin or of a hydrolysed natural resin. Alternatively, the photographic material of the present invention may have one or more light-sensitive emulsions of silver salt in colloid binder on one or more supports at least one of the emulsions containing at least one dye body as herein defined and

a hydrolysed natural resin or a salt thereof or an ester or ether or ether-ester of a natural resin or of a hydrolysed natural resin Such dye body may comprise a color coupler or a sensitizing dye or both.

The colloid binder of the emulsion or emulsions containing the color coupler, sensitizing dye or other dye body may be a water-soluble colloid such as gelatine.

The material may be one in which two or more emulsions are coated in superimposed layers on a single support, preferably all on one side of the support. There may be three differentially color sensitized emulsions on the same side of the support, preferably in superimposed layers.

When a non-sensitized layer contains the dye body, this may serve as a light screening layer e. g. an anti-halation layer on the back of a support which has a silver salt emulsion or silver salt emulsions on its front, or a light-filter layer arranged over a silver salt emulsion or emulsions or between two silver salt emulsions.

Anti-halation layers, as is known, most desirably have a water-insoluble but alkali soluble binder so that they will strip off and dissolve in the usual alkaline developing baths.

The method of the present invention for incorporating a dye body as herein defined in a photographic layer consists in dissolving or dispersing the dye body in a hydrolysed natural resin or a salt thereof or in an ester, ether or ether-ester of a natural resin and then mixing such solution or dispersion with the colloid binder or the photographic layer. This method is suitable for incorporating a color coupler or sensitizing dye or both in a silver salt emulsion.

The resins which can be used in carrying out the present invention include lacs, colophony and certain fractions of copals, damar, mastic and sandarach. These are bleached and dewaxed (in the case of the lacs) and hydrolysed to any desired degree with caustic soda. The products of higher acid values than those of the natural resins are more readily soluble in alkaline processing solutions, and also better solvents for the dye bodies. Their refractive indices can also be brought nearer to that of gelatin thus eliminating light scatter. They are precipitated as resinous oils on pouring from thin water miscible solvents into gelatin or water-wetting agent solutions. One can also add the dye body and resin separately but results obtained by this method are inferior to that already mentioned.

To get good resin dispersion the resin solutions should preferably be less than 10 per cent unless homogenization is undertaken after precipitation. The addition of a wetting agent to the resin solution, e. g. Lubrol W. improves the ease of dispersion.

If non-solubility in processing solutions is desirable the alkali-solubility of the resin carrier can be reduced by forming esters or ethers or ether-esters with organic or inorganic acids or alcohols. Oily products are formed in many cases. Hydrolysed resins can also be esterified or etherified.

The following derivatives illustrate the compounds used:

Hydrolysed lac	Hydrolysed sandarach
Hydrolysed soft lac	Hydrolysed copals
Hydrolysed hard lac	Hydrolysed damar
Hydrolysed colophony	
Hydrolysed mastic	

Acetic-acid lac esters	See London Shellac Research Bureau Technical Paper No. 15
Butyric acid-lac esters	
Lauric acid-lac esters	
Stearic acid-lac esters	
Rosin lac esters	
Oleic acid lac esters	
Linseed oil lac esters	
Phosphoric acid-lac esters	

Fatty acid—lac glycerol esters—see above No. 12 and No. 14.

Glycol ether-crotonic and cinnamic esters of lac—No. 17 and No. 19.

Esters and ethers of the other resins can be prepared in a similar way. The ethers and esters of the hydrolysed resins are also formed in the same way.

As already stated, the hydrolysis of natural resins can be carried out with caustic soda and bleaching can if desired be carried out simultaneously, e. g. with sodium hypochlorite. The hydrolysis products generally have lower softening-melting ranges and higher acid values than the original resins. They tend, therefore, to be precipitated as oily particles on addition to solutions of gelatine or other water-soluble binder (of which agar-agar is an example) and, as already pointed out, are more readily attacked and dissolved by alkaline processing solutions. The hydrolysis products have an increased capacity for dissolving dye bodies, especially color couplers so that on precipitation in a water-soluble binder which may be a photographic emulsion the dye body does not tend so readily to crystallize out. Furthermore hydrolysis products of many resins, e. g. soft lac, have refractive indices which are the same as that of gelatin so that even if the resin is not removed during processing as the sodium salt the free resin acid formed in the acid fixer is invisible where the layer dries.

One important use of the invention is in anti-halation layers particularly for roll film. Such roll film may have one or more emulsion layers on one side of the support and the anti-halation layer on the other. It is important that the dye present in the anti-halation layer shall not wander because (*a*) it should not stain the film support, and (*b*) when the film is rolled up the anti-halation layer is in contact with the emulsion layer.

Another important use of the invention is in filter layers present between different emulsion layers in a multilayer color photographic element such as the "double layer" and "triple layer" elements described in British Patent specification No. 503,752. Such an element have successively coated on one side of a single support a red sensitized emu sion, a green sensitized emulsion and a not-specially color-sensitized emulsion. Between this latter emulsion and the green sensitized emulsion there may be a yellow colored filter layer which can advantageously be made with the aid of the present invention. There may also be a yellow or red colored filter layer between the red-sensitized emulsion and the green sensitized emulsion which can also be made with the aid of the present invention.

A further important use of the invention is in a color-photographic material having three differentially color sensitized silver salt emulsions on a single support. As already stated the emulsions may be arranged in many ways as set forth in British Patent specification No. 503,752. One important example of such a material is that just described above having three superimposed emul-

sion layers. The red sensitive emulsion may have particles containing blue-green dye therein, the green sensitive emulsion particles containing magenta dye such as Oil Red O (Schultz, Farbstofftabelen No. 92) or Alcol Fast Red 4 BL and the not specially color sensitized emulsion particles containing a yellow dye such as benzene-azo-resorcinol. Alternatively, the emulsions may respectively contain color couplers adapted to give rise to blue-green, magenta and yellow dyes.

Many of the color couplers known in the art may be used in practicing the invention, such as those described in British Patent specifications Nos. 458,664, 458,665, 478,942, 478,983, 478,989, 478,990, 493,952, 496,196, 496,245, 519,695, 524,040, 525,874, 525,875, 527,493, 531,246, 531,312, 536,939, 538,914, 537,921, 537,696 and 541,589.

Dyes suitable for use in silver salt emulsions include azo dyes capable of being bleached in the region of a silver image and soluble in organic solvents such as *n*-butyl alcohol. Vat dyes such as anthraquinone dyes soluble in organic solvents may be used.

Dyes suitable for use in filter layers or anti-halation layers are described in British Patent specification No. 540,365.

Example 1

0.1 gram Methyl Red, 0.1 gram Lubrol W and 1.0 gram hydrolysed colophony in 10 cc. alcohol and 10 cc. acetone are added with stirring to 100 cc. of gelatin solution. The resulting mixture is coated as a filter layer, e. g. between a red-sensitized emulsion layer and a green-sensitized emulsion layer.

The colophony is hydrolysed by dissolving 25 grams thereof in 200 cc. alcohol and boiling for ½ hour with a solution of 8 grams of caustic soda in 300 cc. water. It is precipitated with dilute acid, extracted with butyl alcohol, dried and the alcohol driven off by warming, if desired under reduced pressure.

Example 2

0.2 gram Magenta P. 120 (water-soluble) (sold by I. C. I. Dyestuffs Ltd), 1 gram hydrolysed soft lac resin and 0.1 gram Lubrol W, in 20 cc. alcohol are poured into 100 cc. of a 7 per cent gelatin solution. The resulting mixture is coated for use as an anti-halation layer. The dye, although water-soluble dye, is so fixed that it is difficult or even impossible to remove it by washing with water. An alkaline photographic developer will, however dissolve the resin and bleach the dye. The lac is hydrolysed by dissolving 25 grams soft lac (bleached and dewaxed) in 50 cc. spirit and standing for 1 hour at 20° C. with 200 cc. of a 4% aqueous solution of caustic soda.

Example 3

0.2 gram Malachite Green, 1 gram hydrolysed gum mastic and 0.1 gram Lubrol W, in 15 cc. acetone and 5 cc. industrial spirit (alcohol) are stirred into 100 cc. of a 7 per cent gelatin solution. The solution can be coated for use as an anti-halation layer, the water-soluble dye being firmly fixed until the resin has been acted upon by alkali. The hydrolysed mastic is prepared by dissolving 25 grams mastic in 200 cc. acetone and boiling for 1 hour with 200 cc. of a 5 per cent aqueous solution of caustic soda.

Example 4

0.2 gram 2-hydroxy-5-methoxy-azobenzene and 1 gram butyric acid-lac ester in 10 cc. methyl alcohol and 5 cc. acetone are precipitated by stirring into 100 cc. of a 7 per cent gelatin solution. The resulting mixture can be coated to form a filter layer. The preparation of the lac ester can be found on page 6 of the above mentioned Technical Paper No. 15.

Example 5

0.2 gram 2:4-dihydroxyazobenzene and 2 grams ethylene glycol-lac-ester dissolved in 20 cc. spirit and 5 cc. toluene are poured into 100 cc. of a 7 per cent gelatin solution. This can be coated for use as a filter layer. The preparation of the lac-ether is described in the above-mentioned Technical Paper No. 17 p. 6.

Water-soluble salts, such as the sodium salts or water-insoluble salts or alcohol-soluble salts or alcohol-insoluble salts of the hydrolysed resin or resin esters or ethers can be used in a like manner.

Example 6

0.2 gram 2:4-dihydroxyazobenzene and 2 grams of the sodium salt of hydrolysed colophony (see Example 1) in 30 cc. industrial spirit (alcohol) are stirred into 150 cc. 7 per cent gelatin solution. A layer coated from this mixture contains the dye well dispersed and can be used as a light filter.

Example 7

0.2 gram Ink Blue and 2 grams of the calcium salt (alcohol soluble) of hydrolysed hard lac are dissolved in 35 cc. spirit then stirred into 200 cc. 7 per cent gelatin solution. The Ink Blue is firmly fixed and the mixture can be coated for use as anti-halation layer.

Example 8

To 800 cc. of a contrasty bromide emulsion containing the equivalent of 20 grams silver nitrate is added a solution of .003 gram 5-[-2(2-ethyl-1-benzoxazolylidene)-ethylidene]-3-ethyl-1-phenyl-2-thiohydantoin (British Patent specification No. 450,958 Example 43) in 10 cc. acetone. After 10 minutes, 20 cc. of a 1 per cent solution of hydrolysed hard lac resin (acid value 200) is added. This emulsion is then mixed at 30° C. with 800 cc. of a soft bromide emulsion containing the equivalent of 20 grams silver nitrate to which has been added 20 cc. of a 1 per cent solution of hydrolysed hard lac resin. The mixture is kept 60 minutes and coated on paper. Wandering of the dye on processing the coating is very much less than in the case of an emulsion containing no hydrolysed resin but otherwise similar.

Example 9

To 800 cc. of a contrasty chloride emulsion containing the equivalent of 20 grams silver nitrate is added a solution of 0.003 grams dye (as in Example 8) 0.03 gram hydrolysed colophony in 10 cc. alcohol. After 10 minutes 20 cc. of a 1 per cent solution of a lac-acetic acid condensate is added. The emulsion is then mixed with 30° C. with 800 cc. of a soft chloride emulsion containing the equivalent of 20 grams silver nitrate to which has been added 20 cc. of a 1 per cent solution of the same lac-acetic acid condensate.

When the emulsion is coated as a layer, a marked decrease of dye wandering is noticeable as compared with an emulsion not containing hydrolysed resin but otherwise similar. The

hydrolysed colophony is obtained by cooking a solution of 25 grams colophony in 300 cc. alcohol with 8 grams caustic soda dissolved in 50 cc. water for an hour then precipitating with acid.

Example 10

2.5 g. P-nitrobenzylcyanide, 25 grams hydrolysed soft lac resin (see Example 2) and 0.5 gram Lubrol W are dissolved in a mixture of 250 cc. spirit and 250 cc. acetone and the whole stirred into 2,500 cc. of silver bromide emulsion containing 80 grams silver nitrate. A layer which has been coated and dried gives on exposure and development with a developing solution containing p-diethylamino aniline as the developing agent a brilliant magenta image which shows little evidence of any dye wandering.

Example 11

5 gram o-phenylphenol (see specification No. 458,665) 25 grams hydrolysed colophony (see Example 1) and 0.5 gram N:N'-ethylene dioxy methyl pyridine perchlorate (dispersing agent) are dissolved in 500 cc. alcohol and the solution stirred into 2,500 cc. of an emulsion containing 80 grams silver nitrate. The emulsion is coated on a support.

Example 12

5 grams 1-phenyl-3-methyl-5-pyrazolone, 30 grams ethyleneglycol-lac ether are dissolved in 500 cc. industrial spirit (alcohol) and added to 2,500 cc. of a silver bromide emulsion containing 150 grams silver nitrate. The emulsion is coated on a support.

The emulsions of Examples 11 and 12 give well dispersed dye images (blue and magenta respectively) on exposure and colour development. The coupler does not noticeably wander into adjacent layers.

I declare that what I claim is:

1. A photographic material having on a support at least one light-sensitive emulsion of silver salt containing color coupler and an auxiliary agent selected from the group which consists of hydrolysed natural resins, esters, ethers and ether esters of natural resins and esters, ethers and ether esters of hydrolysed natural resins.

2. A gelatino-silver halide emulsion containing a color coupler and an auxiliary agent selected from the group which consists of hydrolysed natural resins, esters, ethers and ether esters of natural resins and esters, ethers and ether esters of hydrolysed natural resins.

3. A gelatino-silver halide emulsion containing color coupler and hydrolysed soft lac resin.

4. A gelatino-silver halide emulsion containing color coupler and ethyleneglycol-lac ether.

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