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INCORPORATING PROCESS FOR INTRODUCING ADDITIVES INTO PHOTOGRAPHIC LAYERS

Fritz Nittel, Cologne-Stammheim, and Karl Lohmer, Leverkusen, Germany, assignors to Agfa-Gevaert Aktiengesellschaft, Leverkusen, Germany

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Int. Cl. G03c 1/40
U.S. Cl. 96—100 4 Claims

ABSTRACT OF THE DISCLOSURE

Improved oil formers for incorporating additives into photographic layers containing gelatin as binder, are aliphatic substituted succinic acid half amides, the amide also being substituted.

This invention relates to a process for introducing photographic additives into materials that form photographic layers and auxiliary layers.

It is known that emulsifiable compounds, for example color couplers, UV-absorbers, brightening agents and similar additives, can be introduced into gelatin solutions by means of so-called oil formers. According to U.S. Patents 2,322,027 and 2,533,514, for example, color couplers are incorporated in water-soluble photographic colloids by dissolving the color coupler in a water-insoluble organic liquid of relatively high boiling point and emulsifying or dispersing the resulting solution in the photographic emulsion. The disadvantage of this process is that hydrophilic developers in particular, for example of the N-butyl-N-ω-sulfobutyl-p-phenylene diamine type, have little or no penetration into the oil droplets. This results in a loss of sensitivity, in a flattening of gradation and in reduced image density. On the other hand, residues of hydrophobic developers can be retained in the droplets and can give rise to fogging when the photographic material is treated in oxidizing bleaching baths.

Hydrophilic substances, for example color couplers containing a carboxyl group, are introduced into the gelatin in the form of their sodium salts. Since the gelatin solutions are subsequently adjusted to a pH-value of from 6.2 to 6.5, these compounds are generally present in microcrystalline distribution. In many instances, the protective colloid effect of the gelatin is inadequate, so that recrystallization occurs. This gives rise to the formation of intermediate states which uncontrollably influences sensitivity, gradation and color brilliancy.

Although hydrophilic substances, for example color couplers, containing —SO_3H groups generally show greater compatibility with gelatin than the aforementioned compounds, recrystallization phenomena do nevertheless occur in many instances during digestion, above all with compounds having an enolate form which promotes solubility in alkaline media. At pH-values of from 6.2 to 6.5, which are shown by most emulsions, the recrystallization-inhibiting effect of the —SO_3Na group is no longer sufficient. This is again manifested in a loss of sensitivity,

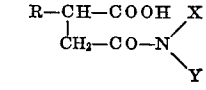
in a reduction in color brilliancy and in decrease of gradation.

Even the use of lithium salts and increased additions of wetting agents has not brought about any appreciable improvement.

In addition, a number of the aforementioned hydrophilic substances have the property of increasing the viscosity of the casting composition, in some instances to such a considerable extent that it is no longer possible to process compositions of this kind.

The object of the present invention is to develop an incorporation process which does not have any of the disadvantages referred to above.

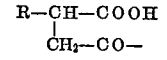
We now have found a process for the production of photographic layers containing photographic additives in heterogeneous distribution, these additives being emulsified in the form of a solution into the casting composition for the layer, and the resulting mixture being cast onto a substrate. The process is characterized in that the additives are emulsified together with compounds of the following general formula



in which

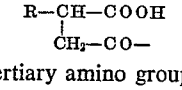
R represents a saturated or unsaturated linear or branched aliphatic radical having 6 to 18 carbon atoms;

X (optionally together with Y) represents a group which, through an intermediate grouping having at least 1 carbon atom, contains at least one other N-atom that either carries another radical of the following formula



or is part of a tertiary amino group or of an aromatic ring; and

Y represents hydrogen or alkyl, or (optionally together with X) represents a group which, through an intermediate grouping having at least 1 carbon atom, contains at least one other N-atom that either carries another radical of the following formula



or is part of a tertiary amino group or of an aromatic ring.

The following compounds have proved to be suitable:

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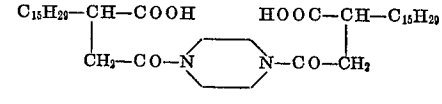

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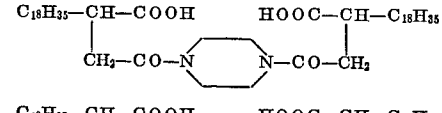

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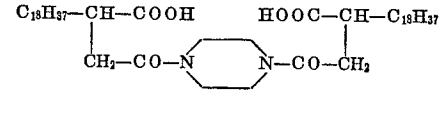

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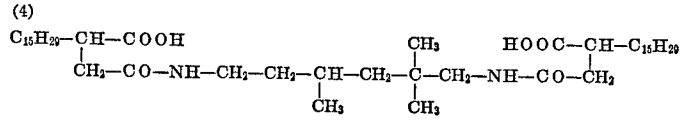

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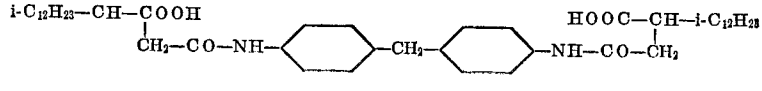

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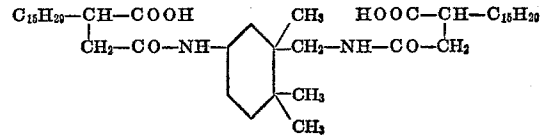

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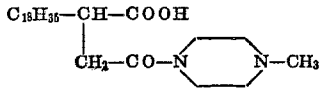

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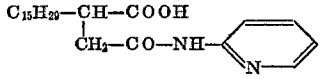

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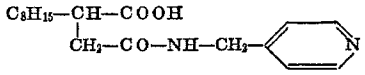

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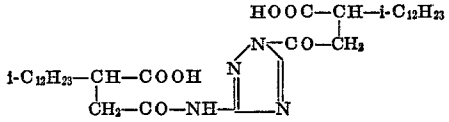

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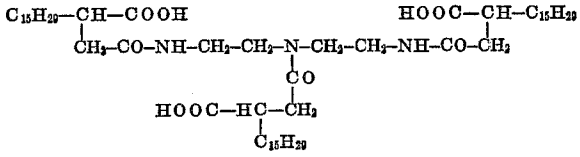

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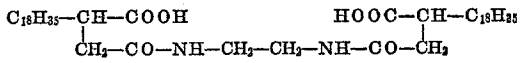

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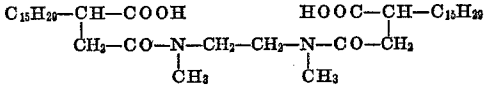

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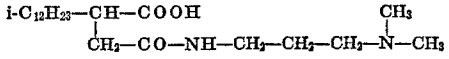

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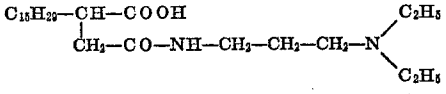

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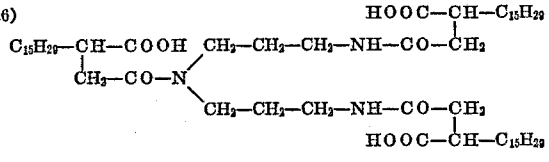

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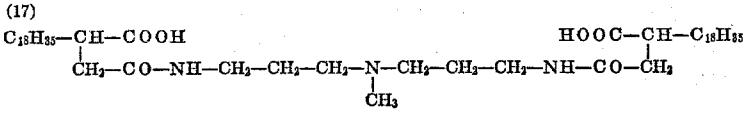

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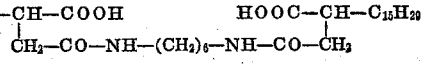

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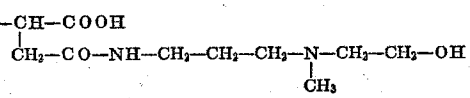

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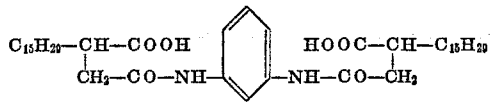

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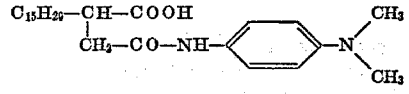

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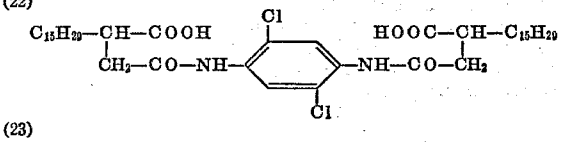

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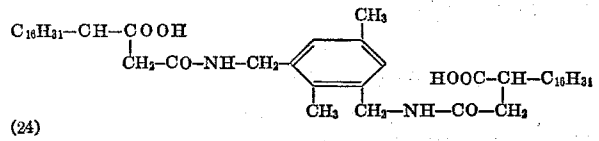

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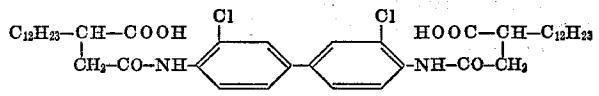

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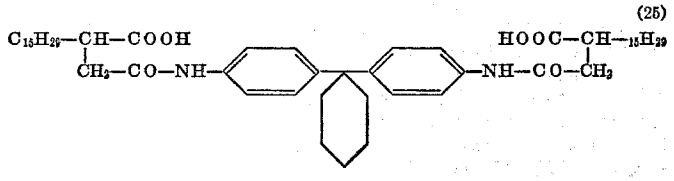

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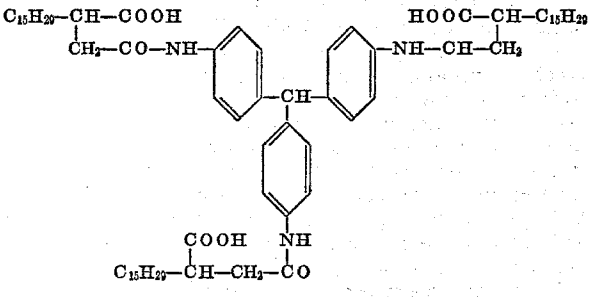

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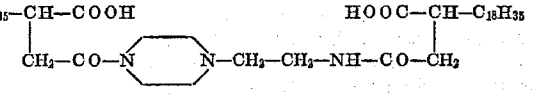

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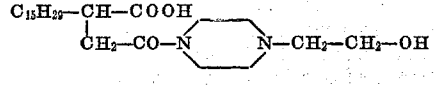

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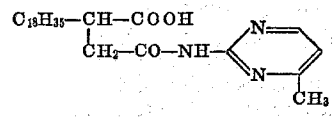

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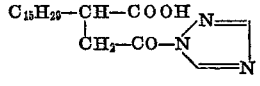

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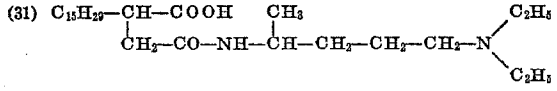
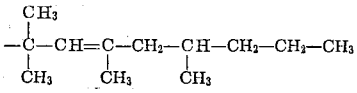


The radical i-$C_{12}H_{23}$ appearing in a number of compounds in the above list stands for the group 1,1,3,5-tetramethyl-oct-2-en-yl whose structural formula is



The other fatty radicals mentioned are all isomer mixtures. In addition to the unsaturated fatty radicals, the hydrogenated fatty radicals can also be used.

The preparation of the compounds of the present invention is generally known. The starting materials normally used are suitable amino compounds which contain at least two nitrogen atoms separated by an intermediate grouping having at least one carbon atom, and are reacted with a long-chain substituted succinic acid anhydride. The succinic acid anhydride ring is opened to form an amide group and a carboxyl group. Products in which the long-chain radical is in the α-position to the carboxyl group and products in which it is in the β-position to the carboxyl group, are simultaneously formed. In the interests of simplicity, only one form is shown in the general formula and in the examples. However, this is not intended in any way to limit the invention to this particular form.

When the compounds of the present invention contain several substituted succinic acid radicals, the radicals in question are preferably the same radicals. In principle, however, it is also possible to react the amino compounds with mixtures of different substituted succinic acid anhydrides in order in this way to obtain compounds containing different succinic acid radicals in statistical distribution.

The process of the present invention is generally carried out as follows:

The photographic additives such as color couplers, UV-absorbers, brightening agents, stabilizers or developers, are dissolved with the compounds to be used in accordance with the invention, in a water-immiscible organic solvent, and the resulting solution is emulsified into the casting composition for the photographic layer. The casting solutions contain the binding agent and other ingredients, if any, in the ratio corresponding to the required concentration of the additives and the emulsification is effected by means of an emulsifying apparatus. Suitable examples of which include high-speed stirrers, so-called mixing sirens, Ultraturrax or ultrasonic devices.

Hydrophilic substances, for example the aforementioned color couplers containing carboxyl groups or —SO_3H groups, are incorporated in another way. In this alternative process, the compounds of the present invention, preferably those containing a tertiary amino group, are dissolved in an alkaline liquid, together with the additives present in alkali-soluble form optionally with a wetting agent, and the resulting solution is added to an acidified casting solution with intensive stirring, as previously explained. As a result, the pH-value of the casting solution changes to from 6.2 to 6.5. Certain couplers without SO_3—H or COOH-groups, but which form alkali-soluble enolates, can also be similarly incorporated.

The advantage of the oil former compounds of the present invention, in addition to a very pronounced crystallization-inhibiting effect, especially on co-emulsified color couplers, is that they do not interfere with the coupling of oxidized color developers. The oil former compounds form soaps under alkaline conditions, e.g. during development. Unlike lower carboxylic acids or those containing only a short fatty radical, the oil former compounds of the present invention cannot be rinsed out in alkaline medium. As a result, they also prevent precipitation of the dye formed during color development and the occurrence of irregular color surfaces. The dye components are also prevented from crystallizing out, in some instances even as early as during digestion. In addition, the compounds of the present invention, unlike conventional hydrophobic oil formers, do not cause flattening of the gradation curve or any reduction in the image density. In addition, they largely prevent the increase in viscosity during digestion caused by many color couplers containing COOH or SO_3H groups.

The compounds of the present invention have the following advantages over the compounds described in Belgian patent specification No. 731,288:

The tendency towards crystallization of the emulsifying substances is even more effectively suppressed by the compounds of the present invention, so that it is possible for even highly crystallizable substances to be emulsified without the occurrence of recrystallization. The refractive index of the compounds of the present invention is virtually the same as that of dried gelatin, so that there are no signs of opalescence. The light stability of color couplers in the emulsion is considerably improved by the present invention. Finally, the plane position (stability toward curling) of the photographic materials are improved by virtue of the compounds of the present invention.

The compounds described here are generally used in a ratio of 0.1 to 10 parts by weight per part by weight of the substance to be incorporated, the preferred range being from 0.3 to 1 part by weight. The higher concentrations up to 10 parts by weight are interesting when it is only intended to introduce small quantities of an additive, for example a stabilizer, into the casting solution.

Examples of suitable water-immiscible organic solvents include chlorinated short-chain aliphatic compounds, for example methylene chloride, and also ethyl acetate and diethyl carbonate.

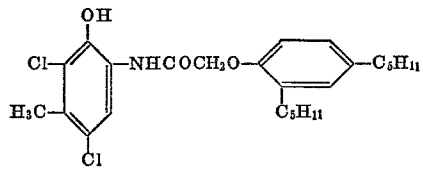
Although gelatin is preferably used as binding agent for the photographic layers, it can be partly replaced by other film-forming natural or synthetic polymers, for example alginic acid and derivatives thereof such as salts, esters or amides; carboxymethyl cellulose; alkyl cellulose; starch and derivatives thereof; polyvinyl alcohol; copolymers with vinyl alcohol and vinyl acetate units; polyvinyl pyrrolidone and the like; and anionic polyurethanes and other latices, for example, copolymers of acrylic esters, acrylonitrile and acrylamide, etc.

The photosensitive emulsions can be chemically sensitized by carrying out ripening in the presence of small quantities of sulfur—containing compounds, for example allyl isothiocyanate, allyl thiourea or sodium thiosulfate, etc. The photosensitive emulsions can also be sensitized by the tin compounds described in Belgian patent specifications No. 493,464 and 568,687; by the iminoaminomethane sulfinic acid compounds described in Belgian patent specification No. 547,323; or by small quantities of noble metal compounds, such as compounds of gold, platinum, palladium, iridium, ruthenium and rhodium. It is also possible for the emulsions to be sensitized with polyalkylene oxide derivatives, for example polyethylene oxide having a molecular weight of from 1,000 to 20,000; and with condensation products of alkylene oxides and aliphatic alcohols, glycols, cyclic dehydration products of hexitols, with alkyl-substituted phenols, alpihatic carboxylic acids, aliphatic amines, aliphatic diamines and amides. The condensation products have a molecular weight of at least 700 and preferably of more than 1,000. To obtain special effects, these sensitizers can of course be used in combined form, as described in Belgian patent specification No. 537,278 and in British patent specification No. 727,982.

In the following examples the gelatin used is ordinary photographic gelatin.

EXAMPLE 1

A solution of 40 g. of the cyan coupler of the formula



and 40 g. of Compound 1, is emulsified together with 4 g. of sulfosuccinic acid-bis-(2-ethyl-hexyl)ester, dissolved in 160 cc. of ethyl acetate, into 1 kg. of a 10% by weight aqueous gelatin solution at a temperature of 50° C. Following removal of the ethyl acetate solvent in a thin-film evaporator, the emulsified product is added to 1 kg. of a red-sensitized silver halide gelatin emulsion containing, per kilogram, 0.15 mol of silver chloride, 0.04 mol of silver bromide and 100 g. of gelatin.

The mixture thus prepared is used in the usual way as a red-sensitive layer containing a cyan coupler in a multilayer color photographic material.

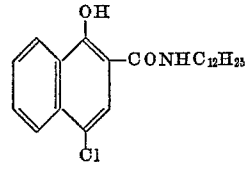
In the absence of the compound of the present invention crystallization occurs even during brief digestion. The same effect occurs in the dried layer during storage.

After exposure, the material is developed in a bath containing N-butyl-N-ω-sulfobutyl-p-phenylene diamine as the developer substance.

There is no evidence here of flattening of gradation or of a reduction in image density such as normally produced by conventional hydrophilic developers in the absence of the compounds according to the invention.

EXAMPLE 2

As in Example 1, 40 g. of the cyan coupler of the formula

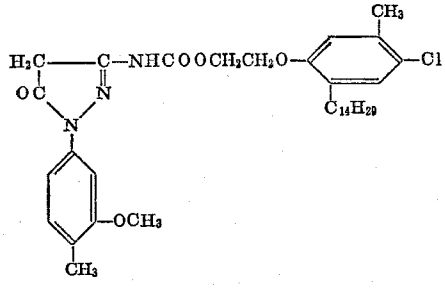


together with 20 g. of Compound 13 and 4 g. of sulfosuccinic acid-bis-(2-ethyl-hexyl) ester, are emulsified into 1 kg. of a 10% by weight aqueous gelatin solution. The product of emulsification is added to 1 kg. of the red-sensitized silver halide gelatin emulsion described in Example 1.

The same results described in Example 1 are obtained after the mixture has been processed.

EXAMPLE 3

As in Example 1, 25 g. of the magenta coupler of the formula

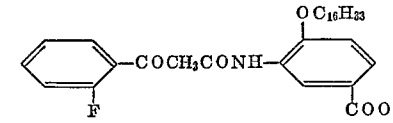


together with 12.5 g. of compound 27 are emulsified into 1 kg. of a 10% by weight aqueous gelatin solution and the product is added to 1 kg. of a green-sensitized silver-halide gelatin emulsion containing, per kilogram, 0.15 mol of silver chloride, 0.04 mol of silver bromide and 100 g. of gelatin.

The mixture is processed as in Example 1. The green-sensitive layer shows the properties described in Example 1.

EXAMPLE 4

36 g. of the yellow coupler of the formula



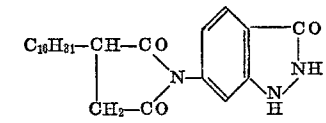
are dissolved together with 18 g. of Compound 15 in 360 ml. of water, 40 ml. of 5 N NaOH and 75 ml. of methanol, and the resulting solution is emulsified at 40° C. into 1 litre of a 10% by weight aqueous gelatin solution containing 90 ml. of a 21% by weight solution of monosodium citrate. The emulsion has a pH value of 6.1.

The product of emulsification is added to 1 kg. of a blue-sensitive silver halide gelatin emulsion containing 0.22 mol of silver bromide and 100 g. of gelatin per kilogram.

The mixture is worked up as described in Example 1. The blue-sensitive layer containing the yellow coupler shows the properties described in Example 1. In the absence of Compound 15, the coupler component soon crystallizes out.

EXAMPLE 5

22.5 g. of the magenta coupler of the formula

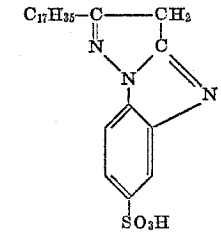


are dissolved together with 18 g. of Compound 14 and 1 g. of sulfosuccinic acid-bis-(2-ethyl-hexyl)ester as wetting agent in 230 ml. of water, 30 ml. of 5 N NaOH and 75 ml. of methanol, and the resulting solution is emulsified at 40°C. into 1 litre of a 10% by weight aqueous gelatin solution containing 40 ml. of 21% by weight monosodium citrate solution. The emulsification product is added to 1 kg. of a green-sensitized silver halide gelatin emulsion containing, per kilogram, 0.15 mol of silver chloride, 0.04 mol of silver bromide and 100 g. of gelatin.

The same results as in Example 4 are obtained after the mixture has been processed as described before.

EXAMPLE 6

25 g. of the magenta coupler of the formula

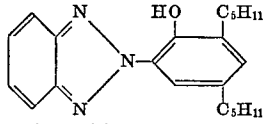


are dissolved together with 15 g. of Compound 14 and 1 g. of sulfosuccinic acid-bis-(2-ethyl-hexyl)ester as wetting agent, in 250 ml. of water, 50 ml. of 1 N lithium hydroxide solution and 75 ml. of methanol, and the resulting solution is emulsified at 40° C. into 1 litre of a 10% by weight aqueous gelatin solution containing 40 ml. of a 21% by weight monosodium citrate solution.

The emulsification product is added to 1 kg. of a green-sensitized silver-halide gelatin emulsion containing, per kilogram, 0.15 mol of silver chloride, 0.04 mol of silver bromide and 100 g. of gelatin. The mixture is processed as before. In the absence of Compound 14, the component crystallizes out during digestion.

EXAMPLE 7

30 g. of the UV-absorber of the formula



are dissolved together with 15 g. of Compound 1 and 3 g. of sulfosuccinic acid-bis-(2-ethyl-hexyl)ester in ethyl acetate and the resulting solution is emulsified into 1 kg. of a 10% by weight aqueous solution. The product of emulsification is cast as UV-protective layer over a color photographic material.

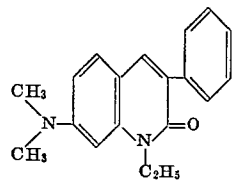
The protective layer produced by the process according to the invention is clear, whilst a layer produced without Compound 1 shows excessive wet turbidity and high opalescence when dry. Accordingly, the protective layer produced by the process of the present invention can be employed as the uppermost protective layer over a color photographic material.

EXAMPLE 8

30 g. of the UV-absorber used for Example 7 are dissolved in ethyl acetate together with 15 g. of Compound 2 and 3 g. of sulfosuccinic acid-bis-(2-ethyl-hexyl)ester, and the resulting solution is emulsified into 1 litre of a 10% by weight aqueous gelatin solution to which 50 ml. of a 40% by weight aqueous suspension of an anionic polyurethane have previously been added. The emulsification product is cast as UV-protective layer over a color photographic material. The result corresponds to that of Example 7.

EXAMPLE 9

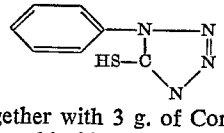
0.5 g. of the brightening agent of the formula



and 2.5 g. of Compound 21 are dissolved in 10 ml. of ethanol and 10 ml. of methylene chloride, and the resulting solution is emulsified into 1 kg. of a 10% by weight aqueous gelatin solution. The emulsification product is cast as uppermost protective layer over a color-photographic material in which one of the lower protective layers is designed to act as UV-protective layer. The fluorescence of the brightening agent is in no way impaired.

EXAMPLE 10

100 mg. of a stabilizer of the formula

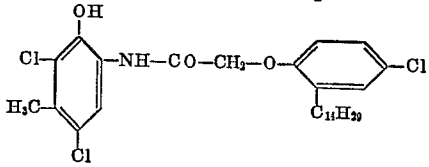


are dissolved, together with 3 g. of Compound 30, in 10 ml. of methylene chloride and the resulting solution is emulsified into 1 kg. of a 10% by weight aqueous gelatin solution. The emulsification product is used as a protective layer for a color photographic material.

The presence of Compound 30 prevents the stabilizer from diffusing into the adjacent layers.

EXAMPLE 11

A solution of 40 g. of the cyan coupler of the formula



and 40 g. of Compound 15 in 80 ml. of diethyl carbonate is emulsified at 50° C. into 1 kg. of a 10% by weight aqueous gelatin solution. The emulsification product is added to 1 kg. of a red-sensitized silver halide emulsion containing 0.15 mol of silver chloride, 0.04 mol of silver bromide and 100 g. of gelatin.

When hydrophilic color developers are used, for example N-butyl-N-ω-sulfobutyl-p-phenylene diamine, the aforementioned blue-green component shows hardly any coupling in the absence of the compound of the present invention. For the same silver covering and for the same exposure, the following final densities are obtained:

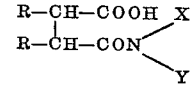
without the compound of the invention $d=0.67$
with the compound of the invention $d=2.52$

A similar effect is also shown by the dicarboxylic acids described in Belgian patent specification No. 731,288, such as pentadecylene succinic acid. However, the light stability of the dyes in combination with the compounds of the present invention is considerably better. The following results are obtained for an exposure time of 7.5×10^6 lux hours:

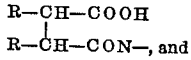
Original dye density	Percentage residual dye content, percent: Dye plus pentadecylene succinic acid	Dye plus Compound 15
$d=0.7$	38	78
$d=1.3$	51	81
$d=2.5$	56	92

What is claimed is:

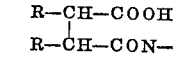
1. In a photographic layer containing a gelatin binder in which is heterogeneously dispersed a photographic additive dissolved in an oil former, the improvement according to which the oil former has the formula



where
one R is hydrogen
the other R is a saturated or unsaturated aliphatic hydrocarbon radical having 6 to 18 carbons
X is a group that (a) is connected to the N through a carbon, and (b) has a tertiary amino group or a nitrogen heterocycle or another



Y is I hydrogen, II alkyl, III a part of X, or XI a group that (a) is connected to the first-mentioned N through a carbon and (b) has a tertiary amino group or a nitrogen heterocycle or another



2. The combination of claim 1 in which the oil former is present in a concentration from 0.1 to 10 parts by weight for every part by weight of the additive.

3. The combination of claim 1 in which the additive is a color coupler.

4. The combination of claim 1 in which the additive is a hydrophilic color coupler.

References Cited

FOREIGN PATENTS

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J. TRAVIS BROWN, Primary Examiner

U.S. Cl. X.R.

96—67, 82, 84, 114.5