

[54] **PROCESS OF INCORPORATING
ADDITIVES INTO PHOTOGRAPHIC
EMULSIONS**

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96/114.5

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[56] **References Cited**

UNITED STATES PATENTS

3,689,271 9/1972 Nittel et al..... 96/100

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Assistant Examiner—Richard L. Schilling

Attorney—Arthur G. Connolly et al.

[57] **ABSTRACT**

The emulsification of additives into a photographic emulsion is stabilized by combining the additive with mono aryl esters or mono cycloalkyl esters of a succinic acid that has a long chained aliphatic substituent.

10 Claims, No Drawings

PROCESS OF INCORPORATING ADDITIVES INTO PHOTOGRAPHIC EMULSIONS

The present invention relates to a process for incorporating substances in materials which are used to form photographic layers and auxiliary layers.

It is already known that emulsifiable compounds such as color couplers, UV absorbers, white toners and similar additives may be incorporated in gelatin solutions by using so-called oil forming agents. According to U.S. Pat. Nos. 2,322,027 and 2,533,514, for example, color couplers used in the production of photographic products are incorporated in emulsions by dissolving the color coupler in an organic liquid of relatively high boiling point which is insoluble in water, and emulsifying or dispersing the solution in the emulsions. This process has the disadvantage that hydrophilic developers, e.g., N-butyl-N- ω -sulphobutyl-phenylenediamine, penetrate the oil droplets only to a slight extent, if at all. This causes loss in sensitivity, flattening of the gradation and a reduced image density. Also residues of hydrophobic developer may be retained in the droplets and cause fogging when the photographic material is treated in oxidizing bleaching baths.

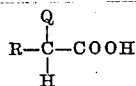
Hydrophilic substances such as color couplers which carry a carboxyl group are incorporated in gelatin in the form of their sodium salts. Since the gelatine solutions are subsequently adjusted to a pH of 6.2 to 6.5, these compounds are generally present in microcrystalline distribution. The protective colloidal action of gelatin is in many cases insufficient, so that recrystallization occurs influencing sensitivity, gradation and color brilliance in an uncontrollable manner.

Although hydrophilic substances such as color couplers which carry SO_3H groups are generally more compatible with gelatin than the above mentioned compounds, recrystallization still occurs in many cases during digestion of the gelatine, especially in the case of compounds that have an enolate form which promotes solubility in an alkaline medium. At the pH values of 6.2 - 6.5 to which most emulsions are adjusted, the action of the SO_3Na group in preventing recrystallization is no longer sufficient. This again leads to a loss in sensitivity, reduction in the color brilliance and loss in gradation. The use of lithium salts and increased amounts of wetting agents has been found to also bring no significant improvements.

Numerous hydrophilic substances of the above mentioned types, moreover, have the property of increasing the viscosity of the casting solution, in some cases to such an extent that such solutions can no longer be worked up.

It is an object of the present invention to provide an incorporation process which does not have the above mentioned disadvantages.

In our patent application Ser. No. 814,808, now U.S. Pat. No. 3,689,271, filed Apr. 9, 1969 there have been described compounds of the general formula

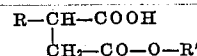


wherein R means a saturated or unsaturated alkyl radical of at least five carbon atoms and Q possibly con-

tains the group COX, with X having various meanings.

These compounds are said to prevent crystallization and to favor the coupling of oxidized color developers, especially of hydrophilic oxidized color developers. I now have found new compounds which are even more useful in emulsifying additional substances such as color couplers, UV absorbers, white toners or stabilizers in hydrophilic binders for photographic layers.

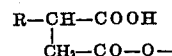
The compounds according to the present invention correspond to the formula:





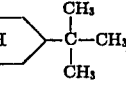


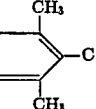
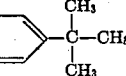
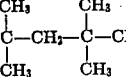
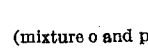
wherein

R = a saturated or unsaturated straight chained or branched aliphatic radical having six to 18 carbon atoms, and

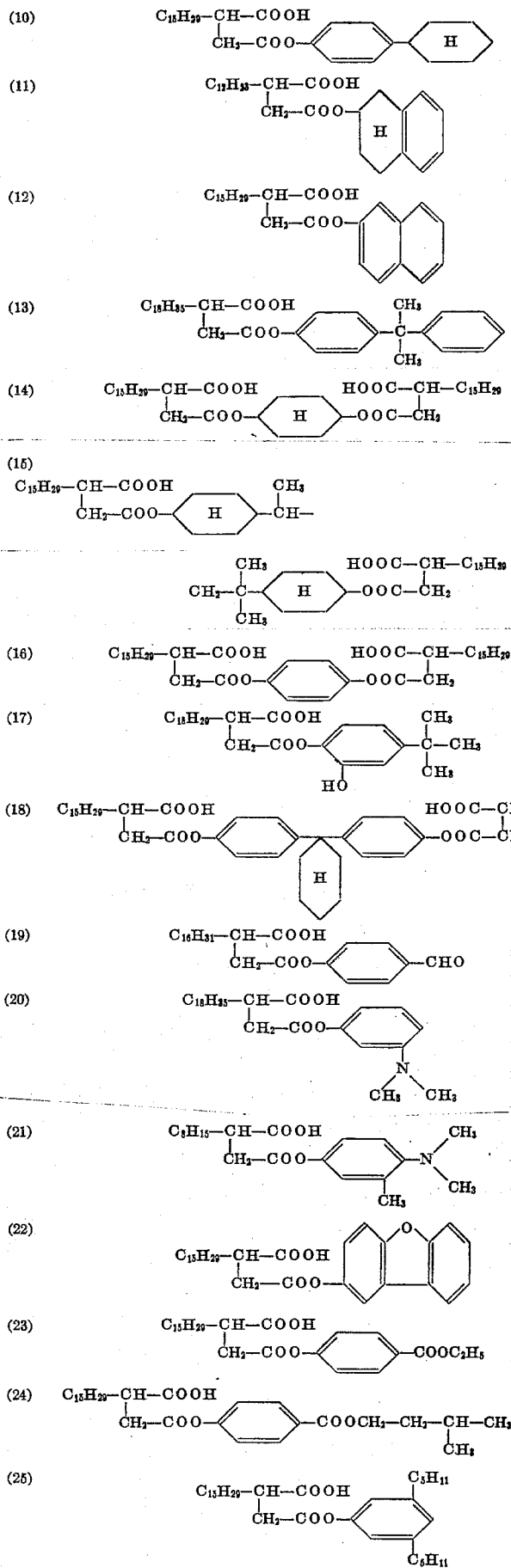
R' = a cycloalkyl group, e.g., a cyclohexyl group, an aryl group, e.g., a phenyl group, or a heterocyclic aromatic group. The said groups may themselves be suitably substituted, e.g., with halogen atoms such as chlorine or with alkyl, hydroxyl, alkoxy, acyloxy, aldehyde, carboxyl, carbalkoxy and/or amino groups, and they may contain condensed rings; if desired the cycloalkyl or aryl group represented by R' may carry an additional radical of the following formula:



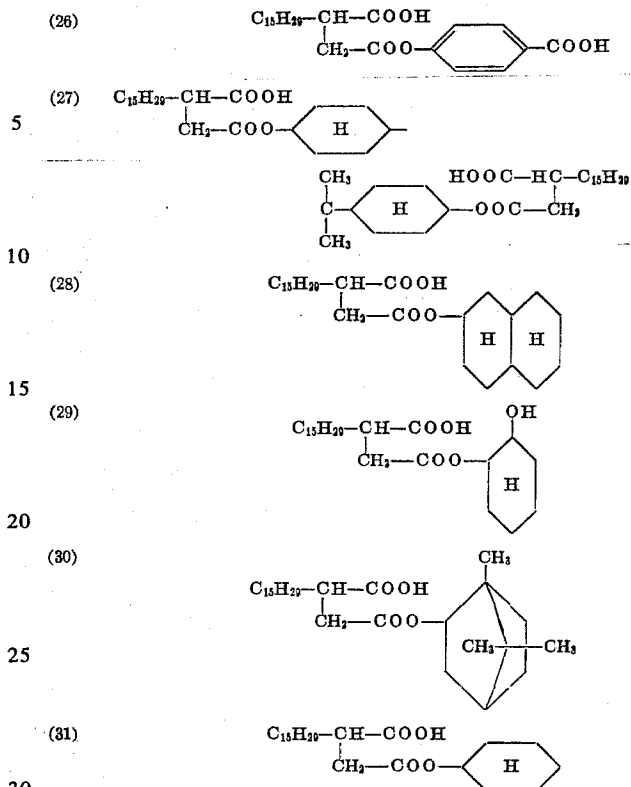
The following compounds have proved to be especially suitable:

- (1) $\text{C}_{15}\text{H}_{31}-\text{CH}-\text{COOH}$
|
 $\text{CH}_2-\text{COO}-$ 
- (2) $\text{C}_{15}\text{H}_{31}-\text{CH}-\text{COOH}$
|
 $\text{CH}_2-\text{COO}-$ 
- (3) $\text{C}_{15}\text{H}_{31}-\text{CH}-\text{COOH}$
|
 $\text{CH}_2-\text{COO}-$ 
- (4) $\text{C}_{15}\text{H}_{31}-\text{CH}-\text{COOH}$
|
 $\text{CH}_2-\text{COO}-$ 
- (5) $\text{C}_{15}\text{H}_{31}-\text{CH}-\text{COOH}$
|
 $\text{CH}_2-\text{COO}-$ 
- (6) $\text{C}_{12}\text{H}_{25}-\text{CH}-\text{COOH}$
|
 $\text{CH}_2-\text{COO}-$ 
- (7) $\text{C}_{15}\text{H}_{31}-\text{CH}-\text{COOH}$
|
 $\text{CH}_2-\text{COO}-$ 
- (8) $\text{C}_{15}\text{H}_{31}-\text{CH}-\text{COOR}$
|
 $\text{CH}_2-\text{COO}-$ 
- (9) $\text{C}_{15}\text{H}_{31}-\text{CH}-\text{COOH}$
|
 $\text{CH}_2-\text{COO}-$  (mixture o and p)

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The above long chained aliphatic radicals are generally isomeric mixtures. In addition to the alkyl radicals represented in the examples, which in most cases contain one unsaturated bond, hydrogenated alkyl radicals

may be used in the same way.

40 The compounds according to the invention are prepared by reacting suitable phenols or cyclohexyl alcohols with long chained substituted succinic acid anhydride in a known manner, preferably in the presence of acid or basic catalysts, such as sulfuric acid or pyridine.

45 In this reaction, the succinic acid anhydride ring is opened with formation of an ester bond and a carboxyl group. Products in which the long chained radical is in the α -position to the carboxyl group and those in which it is in the β -position to the carboxyl group are formed side by side. For the sake of simplicity, only one of these forms is represented in the general formula and in the examples, but the invention is not thus limited to this one form.

55 In cases where the compounds according to the invention contain several substituted succinic acid radicals, these are preferably the same radicals although in principle the cyclohexyl or aryl alcohols could be reacted with mixtures of variously substituted succinic acid anhydrides to yield compounds which contain various succinic acid radicals statistically distributed.

The process according to the invention is generally carried out as follows:

65 Substances which are capable of being emulsified, e.g., color couplers, UV absorbers, white toners, stabilizers or developers, are dissolved in an organic solvent which is immiscible with water, together with the compounds which are to be used according to the invention, and the resulting solution is emulsified in the cast-

ing solution for the photographic layer by means of an emulsifying apparatus in the proportion required to obtain the desired concentration of the substance which is to be incorporated, the said photographic layer containing the binder and optionally other ingredients. Suitable emulsifying apparatus for this purpose are, e.g., high speed stirrers, so-called mixing sirens, ultraturrax apparatus or ultrasound apparatus.

The compounds used according to the invention have the advantage not only of strongly inhibiting crystallization particularly the crystallization of color couplers which have been emulsified with them, but also of not preventing the coupling of oxidized color developers. The compounds form soaps in alkaline pH ranges, in other words, in the course of development. In contrast to lower carboxylic acids or those which have only a short fatty acid radical, the compounds described here are not washed out in an alkaline medium. They, therefore, prevent precipitation of the dye which is formed in the coupling reaction, and the occurrence of uneven colour surfaces. The crystallization of color couplers, which may otherwise already occur during the process of digestion, is also prevented. Furthermore, in contrast to the known hydrophobic oil-forming agents, the compounds used according to the invention cause neither flattening of the gradation nor a reduction in the image density. They also largely prevent the increase in viscosity which many color couplers containing COOH or SO₃H groups cause in the process of digestion.

The compounds according to the invention have the following advantages over the compounds described in patent application Ser. No. 814,808.

The tendency to crystallization of the substances which are to be emulsified is even more effectively suppressed so that even substances which have a very high tendency to crystallize may be emulsified without recrystallization taking place. When compounds to be emulsified are emulsified in the presence of the compounds according to the invention, only slight clouding of the wet layers is observed. The refractive index is practically the same as that of dry gelatin so that no opalescence occurs. This is particularly important when UV absorbents, e.g. those of the benzotriazole type, are used in the protective layer over color photographic materials. If the auxiliary substances according to the invention are not used, the opalescence is so severe that the black parts of the image have a bluish appearance.

The compounds described here are generally used in the proportion of 0.1 to 10 parts by weight for each part by weight of the substance which is to be incorporated, the proportion being preferably within the range of 0.3 to 1 part by weight. The higher concentrations of up to 10 parts by weight are useful for those cases in which only small quantities of additive, e.g., a stabilizer, should be introduced into the casting solution. Examples of particularly suitable organic solvents which are not miscible with water are chlorinated short chained aliphatic compounds, e.g., methylene chloride, as well as ethyl acetate and diethyl carbonate.

The binder used for the photographic layers is preferably gelatin although this may be partly replaced by other film-forming natural or synthetic polymers, e.g., alginic acid and its derivatives such as its salts, esters or amides, carboxymethyl cellulose, alkyl cellulose, starch and its derivatives, polyvinyl alcohol, copolymers containing vinyl alcohol and vinyl acetate units, polyvinyl

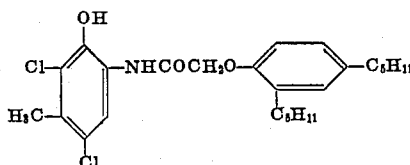
pyrrolidone and the like, anionic polyurethanes and other latices, e.g., copolymers of acrylic acid esters, acrylonitrile or acrylamide.

The photographic layers may contain all the known additives such as anti-fog agents, stabilizers, hardeners, plasticizers and wetting agents. Furthermore, they may be both chemically and spectrally sensitized.

The light-sensitive emulsions may be chemically sensitized by carrying out the ripening process in the presence of small quantities of compounds which contain sulfur, for example allyl isothiocyanate, allyl thiourea or sodium thiosulfate, or they may be sensitized by means of the compounds described in Belgian Pat. specifications Nos. 493,464 and 568,687, the iminoaminomethane sulfinic acid compounds described in Belgian Pat. specification No. 547,323, or small quantities of noble metal compounds such as compounds of gold, platinum, palladium, iridium, ruthenium and rhodium. The emulsions may also be sensitized with polyalkylene oxide derivatives, e.g., polyethylene oxide having a molecular weight of between 1,000 and 20,000, condensation products of alkylene oxides and aliphatic alcohols, glycols, cyclic dehydration products of hexitols, alkyl-substituted phenols, aliphatic carboxylic acids, aliphatic amines, aliphatic diamines and amides. The condensation products have a molecular weight of at least 700, and preferably more than 1,000. These sensitizers may, of course, be combined in order to obtain special effects, as described in Belgian Pat. specification No. 537,278 and in British Pat. specification No. 727,982.

EXAMPLE 1

A solution of 40 g of the following cyan-forming coupler:



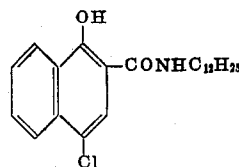
and 20 g of Compound 7 dissolved in 160 cc of ethyl acetate are emulsified in 1 kg of a 10 percent gelatine solution at 50°C. After removal of the solvent in a thin layer evaporator, the emulsion is added to 1 kg of a red sensitized silver halide gelatine emulsion which contains 0.33 mol of silver bromide, 0.0075 of silver iodide and 90 g of gelatine per kg.

The resulting mixture is used within a colour photographic multilayered material in the usual manner as a red-sensitive layer which contains cyan-forming coupler.

Flattening of the gradation and reduction in the image density which are caused by the known hydrophilic developers do not occur in this case.

EXAMPLE 2

40 g of the following cyan-forming coupler:

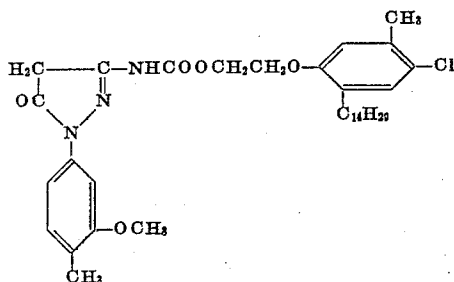


and 20 g of Compound 12 are together emulsified in 1 kg of a 10 percent gelatin solution as described in Example 1. The emulsion is added to 1 kg of a red sensitized silver halide gelatine emulsion described in Example 1.

The same results are obtained after the mixture has been worked up as described in Example 1.

EXAMPLE 3

25 g of the following magenta-forming coupler:

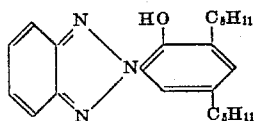


and 12.5 g of Compound 9 are together emulsified in 1 kg of a 10 percent gelatin solution as described in Example 1 and added to 1 kg of a green sensitized silver halide gelatin emulsion.

The mixture is worked up as in Example 1. The green-sensitive layer with regard to gradation and density shows the properties described in Example 1.

EXAMPLE 4

30 g of the following UV absorbent:



and 10 g of Compound 25 are dissolved in ethyl acetate and emulsified in 1 kg of a 10 percent gelatin solution. The emulsion is cast as a UV protective layer over a color photographic material.

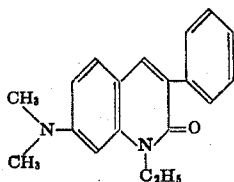
The protective layer prepared by the process according to the invention is clear, whereas a layer which has been prepared without Compound 25 remains cloudy.

EXAMPLE 5

30 g of the UV absorbent used for Example 4 and 15 g of Compound 8 are dissolved in ethyl acetate and emulsified in 1 kg of a 10 percent gelatin solution. The emulsion is cast as a UV protective layer over a color photographic material. The result is similar to that obtained in Example 4.

EXAMPLE 6

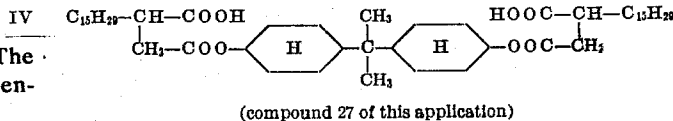
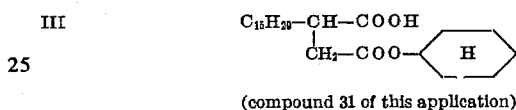
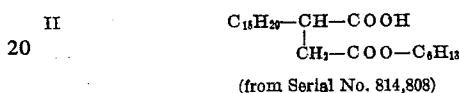
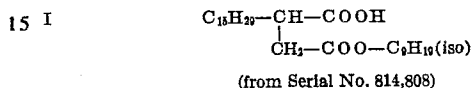
0.5 g of the following white toner:



and 2.5 g of Compound 20 are dissolved in 10 ml of ethanol and 10 ml of methyl chloride and emulsified in 1 kg of a 10 percent gelatin solution. The emulsion is cast as the uppermost protective layer over a color photographic material in which one of the lower protective layers is a UV protective layer. The fluorescence of the white toner is in no way impaired and no crystallization occurs.

EXAMPLE 7

The UV absorbent of Example 4 is dissolved in ethyl acetate and portions of this solution separately mixed with the following oilformers:



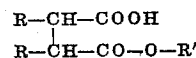
Each solution is poured on a glass plate and the solvent is evaporated. The Table indicates when crystallization of the UV absorbent occurs.

TABLE

oil-former added to 1 part of UV absorbent	crystallization observed after
no addition	5 minutes
1.5 parts of I	45 minutes
2 parts of I	2 hours
1.5 parts of II	1 hour
2 parts of II	2 hours
1.5 parts of III	no crystallization after 24 hours
2 parts of III	no crystallization after 24 hours
1.5 parts of IV	no crystallization after 24 hours
2 parts of IV	no crystallization after 24 hours

I claim:

1. In the process of emulsifying materials into an aqueous dispersion of a hydrophilic photographic binder with an oil former that stabilizes the emulsion, the improvement according to which the oil former has the formula:



wherein

one R is hydrogen and the other is a saturated or unsaturated straight chained or branched aliphatic radical having six to 18 carbon atoms, and R' = a cycloalkyl group, an aryl group or a heterocyclic aromatic group.

2. The combination of claim 1 in which the binder is

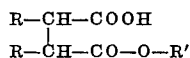
gelatin and the material to be emulsified is first dissolved in a volatile water-immiscible short chain aliphatic solvent along with the oil former, and the solution thus formed is emulsified into the gelatin emulsion.

3. The combination of claim 2 in which the organic solvent is methylene chloride.

4. The combination of claim 2 in which the organic solvent is diethyl carbonate.

5. The combination of claim 1 in which the binder is gelatin, the material to be emulsified is soluble in aqueous alkali, and is dissolved in an aqueous alkaline solution along with the oil former and the resulting solution emulsified into the gelatin emulsion.

6. In a photographic gelatin emulsion containing emulsified photographic additive particles and an oil former that stabilizes the emulsion, the improvement according to which the oil former has the formula:

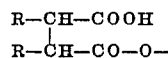


wherein

one R is hydrogen and the other a saturated or unsaturated straight chained or branched aliphatic radical having six to 18 carbon atoms, and

R' = a cycloalkyl group, an aryl group or a heterocyclic aromatic group.

7. The combination of claim 6 in which R' is substituted with another radical of the formula:



wherein

R is hydrogen or a saturated straight chain aliphatic radical having six to 18 carbon atoms.

8. The combination of claim 6 in which the photographic additive is a color coupler.

9. The combination of claim 6 in which the photographic additive is a UV absorber.

10. The combination of claim 6 in which the photographic additive is a white toner.

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