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Matsuo et al.

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[45] **Jan. 14, 1975**

[54] **QUICK-PROCESSABLE LIGHT-SENSITIVE COLOR PHOTOGRAPHIC MATERIAL**

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[30] **Foreign Application Priority Data**

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[51] **Int. Cl.** **G03c 1/78**

[58] **Field of Search** ..... 96/48 QP, 87 R, 100

[56] **References Cited**

UNITED STATES PATENTS

1,660,826	2/1928	Winogradoff	96/114.6
3,201,250	8/1965	Owen	96/87
3,328,167	6/1967	Owen	96/114.6
3,411,908	11/1968	Crawford et al.	96/87
3,630,742	12/1971	Crawford	96/87
3,697,305	10/1972	Tatsuta et al.	96/87

Primary Examiner—J. Travis Brown

Attorney, Agent, or Firm—Waters, Roditi, Schwartz & Nissen

[57] **ABSTRACT**

A light-sensitive silver halide photographic material which comprises a polyethylene film base which has been subjected to a corona discharge treatment having coated thereon a coupler-containing gelatin emulsion layer having a coupler-to-gelatin ratio in parts by weight of from about 1:3 to 1:5.

1 Claim, No Drawings

QUICK-PROCESSABLE LIGHT-SENSITIVE COLOR PHOTOGRAPHIC MATERIAL

This invention relates to a light-sensitive color photographic material for quick processing which does not form opaque due to blushing.

In recent years, quick processing of color photographic materials has been required. In order to make the quick processing possible, however, all the layers constituting the photographic materials, regardless of photosensitive layers and inter layers, are required to be made thinner, and thus should necessarily be reduced in amount of gelatin used. However, the reduction in amount of gelatin used results in such great disadvantages that the emulsions before and after coating are extremely deteriorated in stability and the resulting films are not uniform in thickness. This tendency is more marked in the case where an oil protect type coupler is used than in the case where an alkali dispersion type (Fischer's type) or bucket type coupler is used. When the amount of gelatin is reduced in the case where an oil protect type coupler is used, the surface of film formed after coating and drying of the emulsion is gradually covered with deposits to bring about a fogging phenomenon. This phenomenon is particularly marked when quick processing is carried out at an elevated temperature of 27°C. or more. The said phenomenon is not or scarcely brought about in case a Fischer's type or bucket type coupler is used. In the case where an oil protect type coupler is used to carry out oil protect dispersion (which comprises dissolving a coupler in a high boiling solvent and then dispersing the resulting solution in a gelatin emulsion), therefore, it is preferable that the amount of gelatin used is increased to overcome the above-mentioned disadvantages. However, if the amount of gelatin is increased, the resulting photographic material is naturally degraded in quick processability.

In the present invention, a polyolefin laminate paper or a polyolefin or polyester film base, which has been subjected to corona discharge treatment, is used as a support to make it possible to obtain a light-sensitive color photographic material reduced in amount of gelatin used which not only can be prevented from the above-mentioned fogging phenomenon but also can be subjected to quick processing.

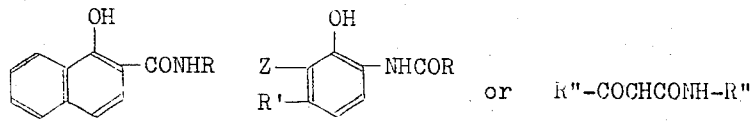
That is, the present invention provides a light-sensitive silver halide color photographic material which not only is protected from the above-mentioned fogging phenomenon but also is well permeated with processing solutions to make the quick processing thereof possible, is scarcely curled, and can be quickly dried.

According to the present invention, the amount of gelatin used may be reduced to such an extent that the ratio of coupler to gelatin is in the range from 1:5 to 1:3. In case the coupler to gelatin ratio becomes less than 1:3, there are some cases where fog is formed.

The oil protect type coupler used in the present invention is represented by the general formula,

$$A—X$$

wherein X is hydrogen, a halogen or a group splitting off at the time of coupling; and A is a coupler residue having, for example, the formula,



(I) (II) (III)

wherein R is an aryl group, an aralkyl group, or a straight chain or branched chain aliphatic hydrocarbon residue having 1 to 18 carbon atoms; R' is hydrogen atom or a straight chain or branched chain aliphatic hydrocarbon residue; R'' is a straight chain or branched chain aliphatic hydrocarbon residue having 1 to 32 carbon atoms, or a phenyl group; R''' is a phenyl group; and Z is hydrogen or a halogen.

Typical examples of the coupler used in the present invention are as shown below, though these are not limitative.

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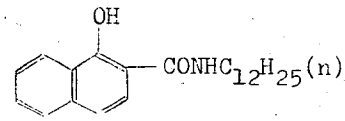

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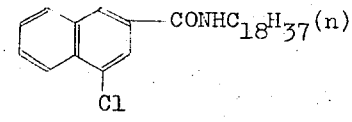

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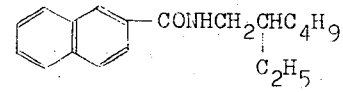

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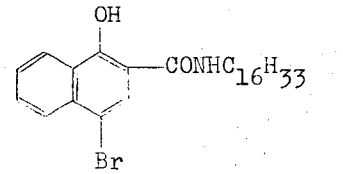

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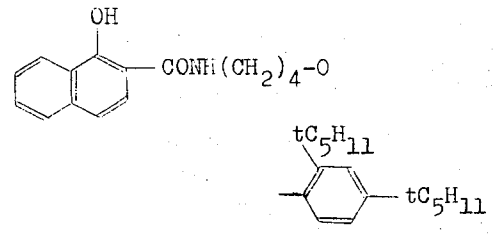

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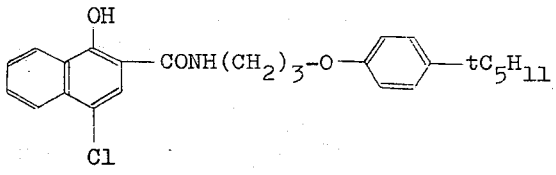

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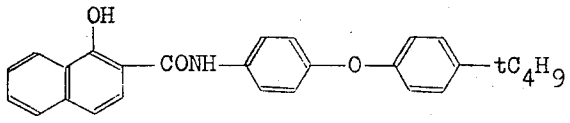

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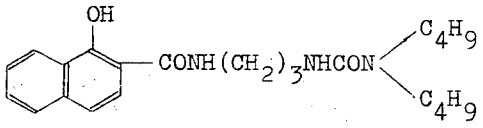

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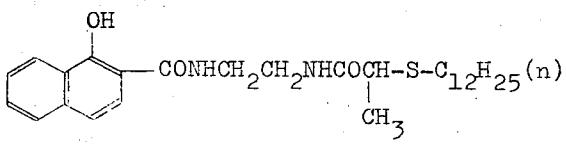

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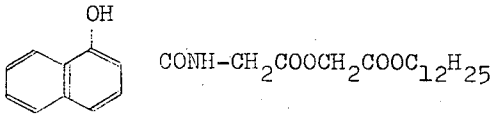

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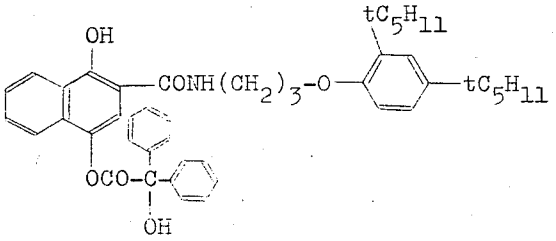

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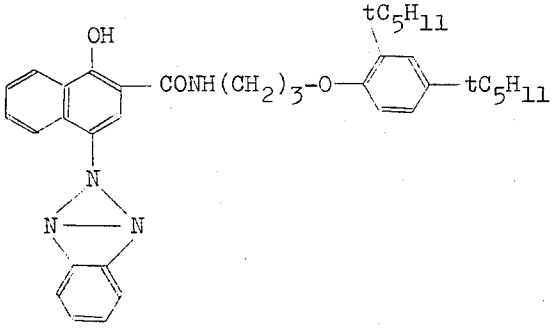

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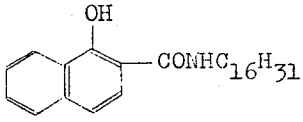
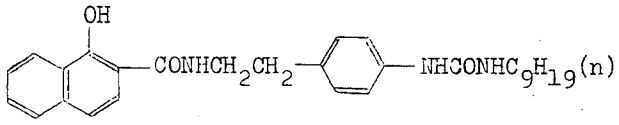
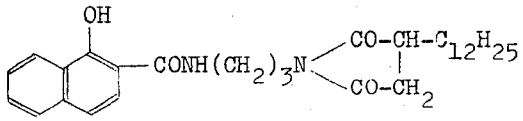
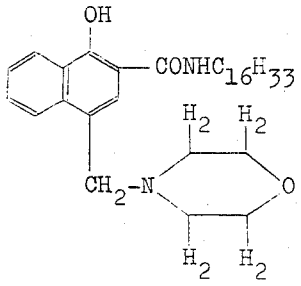
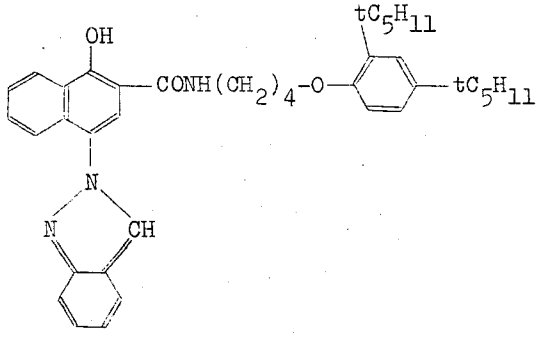
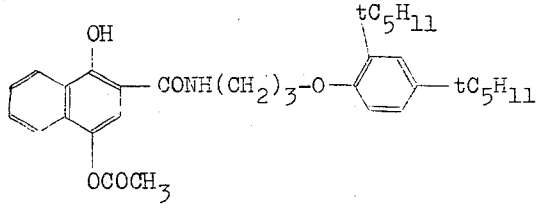


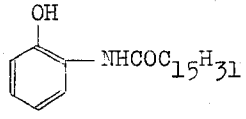
(14) 

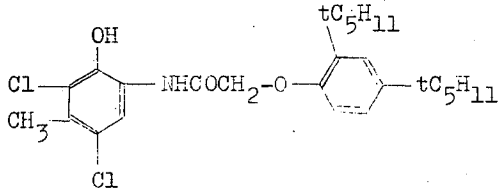
(15) 

(16) 

(17) 

(18) 

(19) 

(20) 

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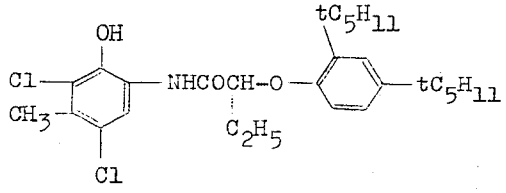

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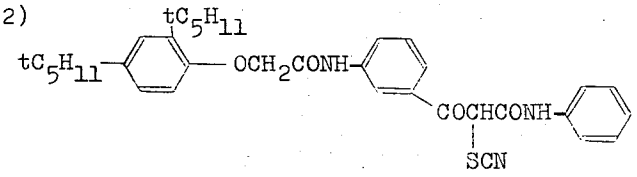

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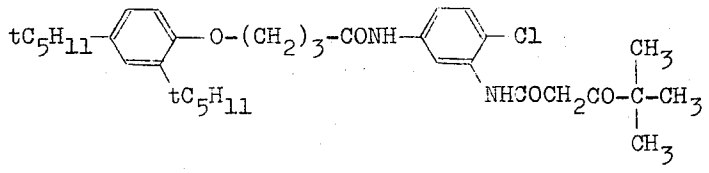

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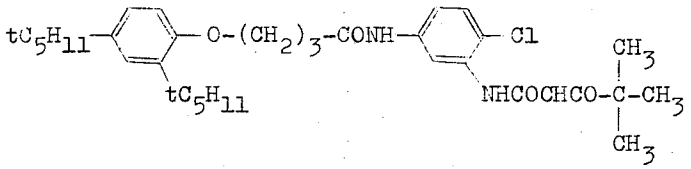

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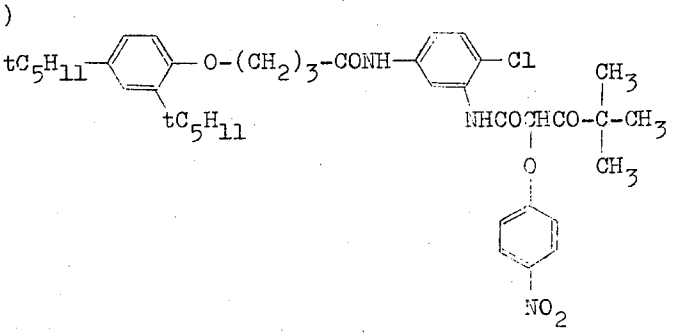

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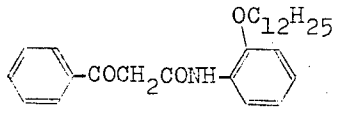

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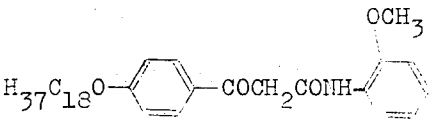

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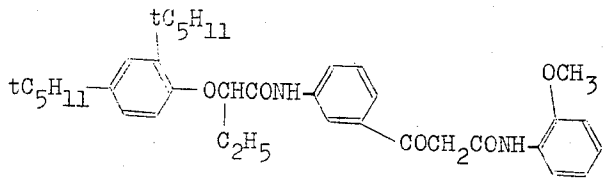

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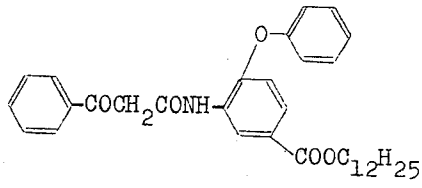

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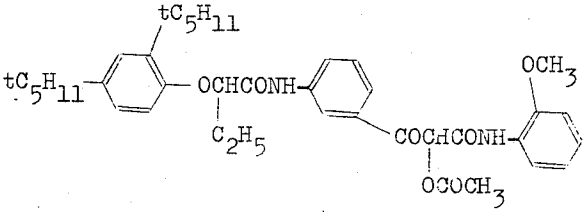

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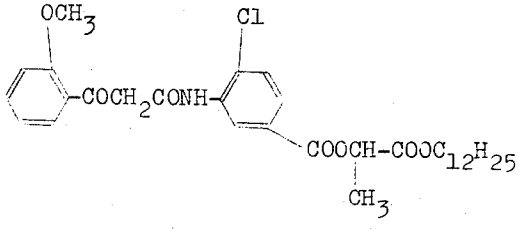

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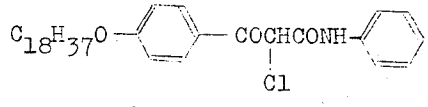

The corona discharge treatment of the support used in the present invention may be carried out in such a manner that the support is moved at a rate of 10 m/min., while applying a current of 0.75 A at an electric power 275 W, for example.

The present invention is illustrated below with reference to examples.

EXAMPLE 1

2 Grams of the exemplified coupler (27) was dissolved in a mixed solvent comprising 2 ml. of dibutyl phthalate and 6 ml. of ethyl acetate. The resulting solution was mixed with 6 ml. of a 5 percent aqueous solution of Alkanol B (a surface active agent produced by Du Pont) and 30 ml. of a 5 percent inert gelatin solution, and the mixed solution was dispersed by means of a colloid mill to obtain a coupler dispersion. The thus obtained coupler dispersion was added to an emulsion prepared by use of 6 g. of silver nitrate and 6.5 g. of gelatin. Subsequently, the emulsion was coated to a thickness of 3 μ on such support as shown in Table 1, and was then dried to prepare a sample. The sample was developed for 5 minutes, bleach-fixed for 2 minutes and water-washed for 2 minutes at 30°C., and was then dried. The developer and bleach-fixer used in this case were as follows:

Developer:

N-Ethyl-N-β-methanesulfonamideothyl-3-methyl-4-aminoaniline sulfate	5.0 g.
Anhydrous sodium sulfite	2.0 g.
Benzyl alcohol	3.8 g.
Sodium carbonate (monohydrate)	50.0 g.
Potassium bromide	1.0 g.
Sodium hydroxide	0.55 g.
Pure water to make	1 liter

Bleach-fixer:

Ethylenediaminetetraacetate sodium iron salt	45 g.
Ammonium thiocyanate	10 g.
Anhydrous sodium sulfite	10 g.
Ammonium thiosulfite	60 g.
Ethylenediaminetetraacetate tetrasodium salt	5 g.
Pure water to make	1 liter

The thus treated sample was subjected for 144 hours to heat and humidity resistance test while alternately allowing the sample to stand every 24 hours in an atmosphere kept at a temperature of 50°C. and a relative humidity of 50 percent and in an atmosphere kept at a temperature of 50°C. and a relative humidity of 80 percent. The results obtained were as set forth in Table 1.

Table 1

Sample	Support	After heat and humidity resistance test
1	Baryta paper (coupler: gelatin=1:4)	Fogged
2	Polyethylene laminate paper (subjected to corona discharge treatment)	Not fogged
3	Polyethylene sheet (subjected to corona discharge treatment)	Not fogged
4	Baryta paper (coupler: gelatin=1:8)	Somewhat fogged

As is clear from Table 1, the samples 2 and 3 according to the present invention formed no fog, whereas the control samples 1 and 4 formed fog.

EXAMPLE 2

The exemplified coupler (25) was added in the same manner as in Example 1 to a blue-sensitive emulsion in such a proportion that the coupler to gelatin ratio became 1:3. On the other hand, the exemplified coupler (1) was added in the same manner as in Example 1 to a red-sensitive emulsion in such a proportion that the coupler to gelatin ratio became 1:3. Subsequently, these two emulsions were successively coated on each of such supports as shown in Table 2 to prepare a sample. The coating was effected while forming an extremely thin gelatin layer between the resulting two layers and on the upper-most layer. The thus prepared sample was subjected to the same test as in Example 1. The results obtained were as set forth in Table 2.

Table 2

Sample	Support	After heat and humidity resistance test
1	Baryta paper	Fogged
2	Polyethylene laminate paper (subjected to corona discharge treatment)	Not fogged
3	Polyethylene sheet (subjected to corona discharge treatment)	Not fogged

EXAMPLE 3

The samples prepared in Example 1 were subjected to development, stop-fixing, bleaching, fixing and water-washing treatments in this order, and then subjected to the same test as in Example 1 to obtain the same results as in Example 1.

What we claim is:

1. A light-sensitive silver halide color photographic material suitable for quick processing, which comprises a support and, coated on said support, a coupler-containing photographic gelatin emulsion layer having a coupler-to-gelatin ratio in parts by weight of from about 1:3 to 1:5, said support having a polyethylene film base which has been subjected to a corona discharge treatment.

* * * * *