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(54) **Photographic emulsions containing scavengers for gelatin hardeners.**

(57) A method of hardening a silver halide photographic emulsion comprising providing a silver halide photographic emulsion comprising a negatively charged hydrophobic coupler dispersion containing a hydrophobic hardener scavenger and contacting the silver halide emulsion with a hydrophobic or positively charged hardener for a period of time sufficient to harden the emulsion.

EP 0 575 910 A2

Technical Field

This invention relates to a method of hardening gelatin, particularly in color silver halide photographic emulsions. It further relates to a hardened silver halide photographic emulsion.

Prior Art

Many color photographic emulsions are comprised of gelatin in which hydrophobic addenda such as couplers are dispersed. Commonly, the couplers are dispersed in small droplets of high boiling, hydrophobic solvent and the droplets of coupler and solvent are stabilized (prevented from coalescing) by use of a negatively charged surfactant. The negatively charged surfactant resides at the surface of the dispersion particle, resulting in a negatively charged, hydrophobic dispersion particle. Often such emulsions are hardened with a gelatin crosslinking agent to impart a variety of desirable physical properties to the emulsion, such as increased melting point, reduced swell, and increased physical toughness in aqueous processing solutions.

When the hardener is a relatively hydrophobic molecule, a significant portion of the hardener partitions into the hydrophobic droplets that contain coupler where the hardener might react with the coupler. When the hardener is positively charged, initially the hardener may be attracted to the negatively charged droplets that contain coupler.

When the hardener that has diffused into the dispersion particle reacts with the coupler it destroys both the hardener and coupler. This can cause deleterious physical and sensitometric properties such as a lessening of hardening capability and color-forming capability. In some cases the hardener can react with the coupler to produce a colored product, which can cause stain in the photographic material. Therefore, it is desirable to prevent the reaction of hardener with coupler.

US-A-4,904,579 describes the use of certain non-color forming, diffusion resistant carboxylic acid compounds with certain two-equivalent 5-pyrazolone magenta couplers to improve color forming properties and increase sensitivity and stability of photographic materials. The carboxylic acid compounds are not utilized as hardener scavengers.

There have been several alternative approaches to preventing the reaction of a hardener with a coupler that is contained in a hydrophobic dispersion. US-A-4,618,573 provides that the reaction between hardener and coupler can be prevented by the use of pyrazolazole type magenta couplers. US-A-4,863,841 states that the reaction between hardener and coupler can be prevented by the use of two-equivalent 5-pyrazolone type magenta couplers as opposed to four-equivalent 5-pyrazolone type magenta couplers. US-A-4,877,724 provides that the reaction between hardener and coupler can be prevented by use of dication ether hardeners in which one or more of the substituents on the dication ether is anionic so as to form an intramolecular salt.

Assessment of the Art

All of the above alternatives are undesirable, since each alternative either limits the choice of couplers and hardeners to those which do not react with each other, or to hardeners which do not partition into the dispersion particle. Therefore, it is desirable to prevent the reaction of hardener with coupler without limiting the choice of either the hardener or the coupler.

Summary of the Invention

The present invention provides a method to prevent or reduce the reaction of hydrophobic or positively charged hardeners with couplers when those couplers are dispersed in the form of negatively charged, hydrophobic dispersion particles. This is accomplished by including in the coating a hydrophobic hardener scavenger that resides primarily in the coupler dispersion.

This invention provides a method of hardening a silver halide photographic emulsion comprising

(a) providing a silver halide photographic emulsion comprising a negatively charged hydrophobic coupler dispersion containing a hydrophobic hardener scavenger; and

(b) contacting the silver halide emulsion with a hydrophobic or positively charged hardener for a period of time sufficient to harden the emulsion.

In one embodiment the hardener is a carboxyl activating hardener and the hardener scavenger is a hydrophobic, carboxylic acid compound. In another embodiment the coupler is a four-equivalent coupler. In yet another embodiment, the negatively charged hydrophobic coupler dispersion is prepared separately and

then combined with the silver halide emulsion. The hydrophobic hardener scavenger is added to the negatively charged hydrophobic coupler dispersion before the dispersion is combined with the silver halide emulsion. This invention further provides a photographic emulsion prepared by the above methods.

This invention additionally provides a hardened silver halide photographic emulsion comprising a hydrophobic hardener scavenger and a coupler dispersed in the form of hydrophobic negatively charged dispersion particles. In one embodiment the hardener scavenger is a hydrophobic, carboxylic acid compound.

The advantage of the present invention is a reduction in the amount of reaction between a hardener and coupler in instances where a hardener partitions into a dispersion particle that contains the coupler. This reduces the amount of hardener and coupler that is destroyed and, if the reaction of the hardener and coupler produces a colored product, reduces the stain that is produced.

Detailed Description of the Invention

The hardener scavengers of this invention are compounds that react competitively with hardener that partitions into the coupler droplets. The reactivity of the scavengers with hardener is such that the scavenger destroys a significant amount of the hardener that partitions into the coupler droplets before the hardener reacts with coupler.

The hardener scavenger is a hydrophobic molecule having one or more suitable reactive groups. The hardener scavenger must be hydrophobic so that the scavenger resides primarily in the hydrophobic dispersion particles allowing it to target hardener which has partitioned into the coupler containing hydrophobic droplets. Preferably, at least 50 % of the scavenger should so reside.

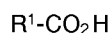
The scavenger must be compatible with photographic emulsions and elements. The scavenger should be substantially inert in the emulsion other than its reaction with the hardener. The scavenger should also be substantially inert during the processing of the photographic element.

The reactive group or groups of the scavenger must competitively react with the targeted hardener. Hardener scavengers include several classes of compounds which contain reactive groups which are specific for certain classes of hardeners. For instance, when hardeners of the carboxyl-activating type are used, preferred scavengers are hydrophobic, carboxylic acid compounds. When vinylsulfone or acrylate hardeners are used, preferred scavengers are hydrophobic amines or thiols.

The hardener scavenger can be added to the coupler dispersion during the preparation of the dispersion. Alternatively it can be added to the aqueous portion of the emulsion which contains the coupler dispersion. When the scavenger is added to the aqueous portion of the emulsion it may be added with or without a solvent. Suitable solvents are ketones or alcohols, with ethyl acetate being a preferred solvent. Preferably the scavenger is added to the coupler dispersion before it is combined with the silver halide emulsion. Most preferably it is added without any type of solvent to the oil portion of the dispersion ingredients prior to making the coupler dispersion.

The amount of scavenger added must be enough to effectively compete with the coupler. A preferable molar ratio of scavenger to coupler is from 1:1 to 1:100, and more preferably from 1:2 to 1:20. A mixture of scavengers from the same class can be utilized in the emulsion as long as each one is compatible with the hardener. If more than one class of hardener is used then more than one class of scavenger may be used.

Preferred compounds of the invention are described in further detail below. Useful hardener scavengers for carboxyl-activating hardeners are hydrophobic carboxylic acid compounds. These compounds may have one or more carboxyl groups. In a preferred embodiment the carboxylic compounds are represented by the formula.



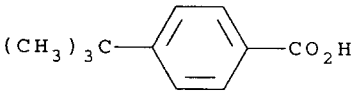
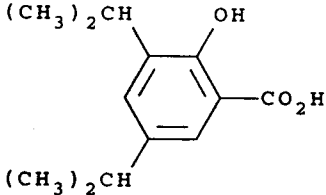
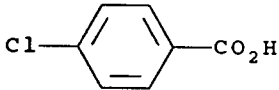
R^1 can be any hydrophobic group which meets the functional requirements of this invention, however, preferably R^1 represents a substituted or unsubstituted alkyl, aralkyl, aryl, alkenyl, or heterocyclic group.

More preferably, R^1 is an alkyl of 6 to 100 carbon atoms (for example, hexyl, dodecyl, 2-hexyldodecyl), an aralkyl of from 7 to 100 carbon atoms (for example, benzyl, phenethyl), an aryl of from 6 to 100 carbon atoms (for example, phenyl, naphthyl), an alkenyl of from 6 to 100 carbon atoms (for example, oleyl, linoleyl) or a heterocyclic ring of 6 to 100 carbon and heteroatoms. The preferred heteroatoms are N or O. More preferably R^1 is an alkyl group of 8 to 24 carbon atoms or an aryl group of 6 to 12 carbon atoms.

Useful substitutes of R^1 include halogen, alkoxy and alkyl groups of from 1 to 50 carbon atoms, and aryloxy and aryl groups of from 6 to 50 carbon atoms. Preferred substituents include alkyl groups of 1 to 24 carbon atoms, hydroxy groups and halogens, preferably chlorine.

Examples of preferred compounds are shown below in Table I.

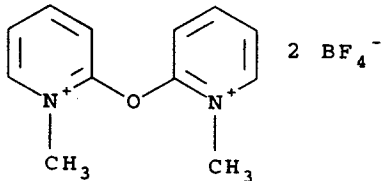
Table I

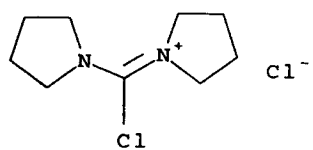
5		Compound
	$\text{CH}_3(\text{CH}_2)_{10}\text{-CO}_2\text{H}$	S-1
10	$\text{CH}_3(\text{CH}_2)_{16}\text{-CO}_2\text{H}$	S-2
15		S-3
20		S-4
25		
30		S-5

The compounds of the above formula can be made by techniques known to those skilled in the chemical synthesis art. Also, many of these compounds are commercially available.

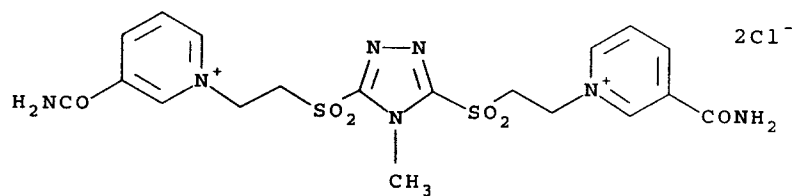
Hardeners included in the present invention include those which are hydrophobic or which have a positive charge on the central molecule. Examples of classes of hardeners which fall within this invention include those described in US-A-4,877,724; US-A-5,071,736 and US-A-4,863,841. Preferred hardeners are the carboxyl activated hardeners. More preferred hardeners are the dication ethers and more preferably the pyridylum ethers such as those described in US-A-4,877,724. The most preferred hardener is shown below as H-1 (bis (N-methyl-2-pyridylum tetrafluoroborate) ether). Examples of hardeners included in the present invention are shown in Table 2.

Table 2

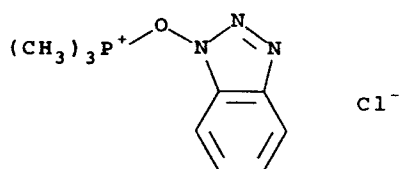
45		Compound
50		H-1



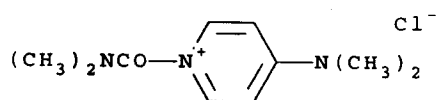
H-2



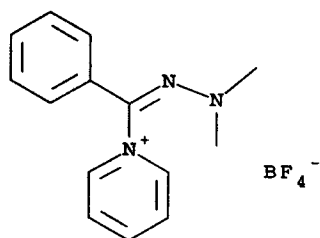
H-3



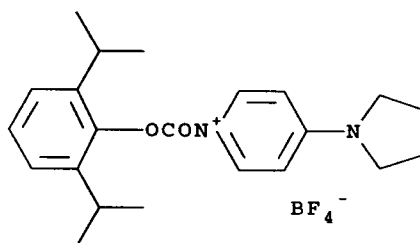
H-4



H-5

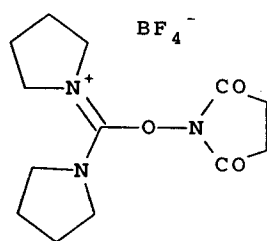


H-6



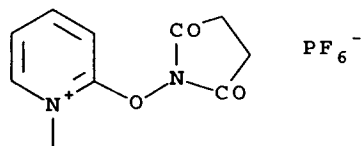
H-7

5



H-8

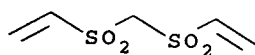
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H-9

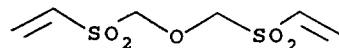
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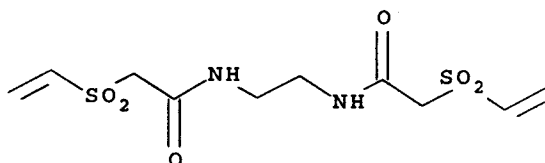
H-10

25



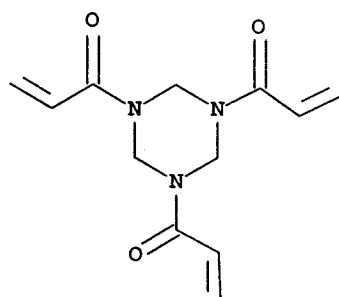
H-11

30



H-12

35



H-13

45

The hardeners of this invention are utilized as generally known in the art. The hardener may be added to the emulsion containing the negatively charged coupler dispersion or it may be added to another layer and migrate to the target emulsion layer. Examples of hardeners and their use are shown in Section X, Research Disclosure, December 1989, Item 308119, published by Kenneth Mason Publications, Ltd., Dudley Annex, 12a North Street, Emsworth, Hampshire PO10 7DQ, ENGLAND. This publication will be identified hereafter by the term "Research Disclosure".

The couplers of this invention can be any coupler which is suitable for use in a negatively charged hydrophobic dispersion in a silver halide emulsion. Examples of various couplers include but are not limited to those described in Research Disclosure Section VII, paragraphs D, E, F and G and the publications cited therein. These couplers can be incorporated in the elements and emulsions as described in Research Disclosure Section VII, paragraph C and the publications cited therein. This invention is particularly useful

with four-equivalent couplers which are more prone to react with hardeners, as discussed in US-A-4,863,841. More preferably the couplers of this invention are four-equivalent, 5-pyrazolone couplers. These couplers have a tendency to react with certain carboxyl activating hardeners to form a colored product which can cause staining.

5 The photographic elements used with this invention can be single color elements or multicolor elements. Multicolor elements typically contain dye image-forming units sensitive to each of the three primary regions of the visible spectrum. Each unit can be comprised of a single emulsion layer or of multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element, including the layers of the image-forming units, can be arranged in various orders as known in the art. In an
10 alternative format, the emulsions sensitive to each of the three primary regions of the spectrum can be disposed as a single segmented layer, for example, as by the use of microvessels as described in US-A-4,362,806. The element can contain additional layers such as filter layers, interlayers, overcoat layers, subbing layers and the like.

The silver halide emulsions employed in the elements of this invention can be either negative-working
15 or positive-working. Examples of suitable emulsions and their preparation are described in Research Disclosure Sections I and II and the publications cited therein. Some of the suitable vehicles for the emulsion layers and other layers of elements of this invention are described in Research Disclosure Section IX and the publications cited therein.

The silver halide emulsions can be chemically and spectrally sensitized in a variety of ways, examples
20 of which are described in Sections III and IV of the Research Disclosure.

The photographic elements of this invention or individual layers thereof can contain among other things brighteners (Examples in Research Disclosure Section V), antifoggants and stabilizers (Examples in Research Disclosure Section VI), antistain agents and image dye stabilizers (Examples in Research Disclosure Section VII, paragraphs I and J), light absorbing and scattering materials (Examples in Research
25 Disclosure Section VIII), plasticizers and lubricants (Examples in Research Disclosure Section XII), antistatic agents (Examples in Research Disclosure Section XIII), matting agents (Examples in Research Disclosure Section XVI) and development modifiers (Examples in Research Disclosure Section XXI).

The photographic elements can be coated on a variety of supports including but not limited to those described in Research Disclosure Section XVII and the references described therein.

30 Photographic elements can be exposed to actinic radiation, typically in the visible region of the spectrum, to form a latent image as described in Research Disclosure Section XVIII and then processed to form a visible dye image examples of which are described in Research Disclosure Section XIX. Processing to form a visible dye image includes the step of contacting the element with a color developing agent to reduce developable silver halide and oxidize the color developing agent. Oxidized color developing agent in
35 turn reacts with the coupler to yield a dye.

With negative working silver halide, the processing step described above gives a negative image. To obtain a positive (or reversal) image, this step can be preceded by development with a non-chromogenic developing agent to develop exposed silver halide, but not form dye, and then uniformly fogging the element to render unexposed silver halide developable. Alternatively, a direct positive emulsion can be
40 employed to obtain a positive image.

Development is followed by the conventional steps of bleaching, fixing, or bleach-fixing, to remove silver and silver halide, washing and drying.

The following examples are intended to illustrate, without limiting, this invention.

45 Example 1

A coupler dispersion containing Coupler-1 was prepared by conventional methods. An oil phase (see below) at 77 °C and an aqueous (see below) phase at 50 °C were mixed together with mild stirring. The mixture was then passed through a colloid mill five times. Most of the ethyl acetate was removed from the
50 dispersion using a rotary evaporator at 60 °C, using a water aspirator vacuum.

oil phase:	
addendum	grams
Coupler-1	60
dibutyl phthalate	30
ethyl acetate	120
DoxS-1	6
DST-1	26
scavenger (see Tables 3 and 4 for type and amount)	

aqueous phase:	
addendum	grams
gelatin	480
Alkanol TM XC	6
water to make	1000

Example 2

A comparative sample as well as samples of the present invention were coated on a polyethylene-coated paper support that had been previously coated with 3.23 g/m² of gelatin. Sample 1 was prepared for comparison with the present invention. Sample 1 contained 2.15 g/m² of Coupler-1, 7.53 g/m² of gelatin, and hardener H-1. Samples 2 through 9 were prepared as examples of the present invention in the same manner as Sample 1 except that a scavenger (See Table 3) was included in the dispersion.

Samples 1 through 8 were allowed to age in air at 25 C and 50% RH for several days. The reaction between Coupler-1 and H-1 causes a yellow stain which is evidenced by an increase in blue Dmin. If there is less reaction between Coupler-1 and H-1, that is if the hardener scavenger is effective, there should be a reduction in blue Dmin. Thereafter, blue Dmin was measured using a reflection densitometer equipped with a Status-A blue filter. The results are shown in Table 3.

Table 3

Sample	hardener	hardener level (g/m ²)	scavenger	scavenger level (g/m ²)	ctg age (days)	blue Dmin
1 ^c	H-1	0.607	none	----	7	0.254
2 ⁱ	H-1	0.607	S-1	0.1076	7	0.126
3 ⁱ	H-1	0.607	S-1	0.2153	7	0.094
4 ⁱ	H-1	0.607	S-1	0.4306	7	0.077
5 ⁱ	H-1	0.607	S-2	0.3057	7	0.108
6 ⁱ	H-1	0.607	S-3	0.1910	7	0.096
7 ⁱ	H-1	0.607	S-4	0.2382	7	0.094
8 ⁱ	H-1	0.607	S-5	0.1679	7	0.158

^ccomparison example

ⁱexample of the present invention

It is apparent from the results in Table 3 that the blue Dmin is greatly reduced in Sample 2 through 8 of the present invention, compared to Sample 1.

The chemical compound causing the yellow stain in Sample 1 was identified as D-1, the product of the reaction between hardener H-1 and Coupler-1, by extraction of Sample 1, followed by isolation of the colored reaction product by HPLC, and followed by determination of its structure by mass spectroscopy and NMR spectroscopy.

Example 3

Comparative samples as well as samples of the present invention were coated on a polyethylene-coated paper support that had previously been coated with 3.23 g/m² of gelatin. Sample 9 was prepared for comparison with the present invention. The first layer contained 0.269 g/m² of a AgCl emulsion, 0.420 g/m² of Coupler-1, and 1.722 g/m² of gelatin. The second layer contained 1.076 g/m² of gelatin and hardener H-1. Additional samples (Samples 10-12) were prepared as examples of the present invention. They were prepared in the same manner as Sample 9 except that a scavenger (See Table 4) was included in the preparation of the Coupler-1 dispersion.

Samples 9 through 12 were allowed to stand for 7 days in air at 25 °C and 50% RH and thereafter, exposed (S19 1B sensitometer, 3000 °K, 2.95 log lux, HA50 filter, 0.60 inconel filter, NP11 filter, 21 step 0-3.0 ND tablet, 1/10 second), and processed (Colenta automatic processor, RA4 processing, development for 45 seconds at 95 °F). Blue Dmin was measured using a reflection densitometer equipped with a Status-A blue filter. The results are shown in Table 4.

Table 4

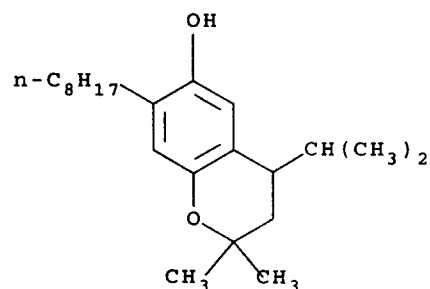
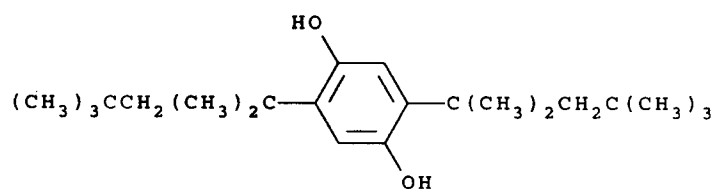
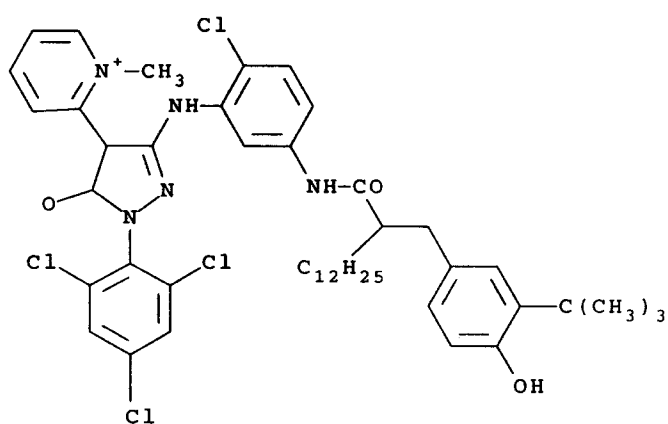
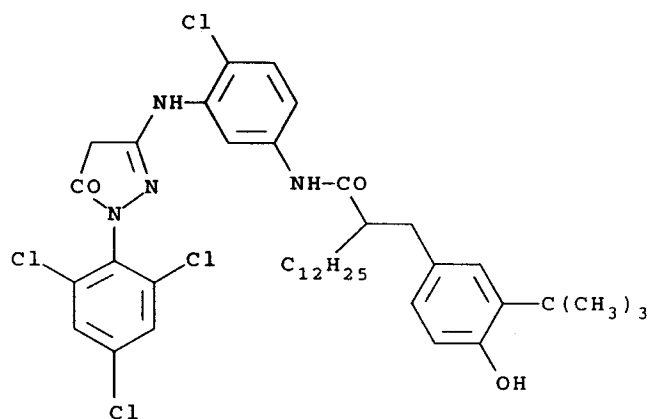
Sample	hardener	hardener level (g/m ²)	scavenger	scavenger level (g/m ²)	ctg age (days)	blue Dmin
9 ^c	H-1	0.3399	none	----	15	0.056
10 ⁱ	H-1	0.3399	S-1	0.04198	15	0.036
11 ⁱ	H-1	0.3399	S-3	0.03724	15	0.032
12 ⁱ	H-1	0.3399	S-4	0.04650	15	0.034

^ccomparison example

ⁱexample of the present invention

It is apparent from the results in Table 4 that the blue Dmin is greatly reduced in Samples 10 through 12 of the present invention, compared to Sample 9. In addition to the data displayed in Table 4, it was found that photographic sensitivity and contrast were unaffected by any level of any scavenger.

The structures of chemical compounds used in the Coupler Dispersion Example 1 are illustrated below.



Claims

- 55
1. A method of hardening a silver halide photographic emulsion comprising
 - (a) providing a silver halide photographic emulsion comprising a negatively charged hydrophobic coupler dispersion containing a hydrophobic hardener scavenger; and

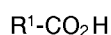
(b) contacting the silver halide emulsion with a hydrophobic or positively charged hardener for a period of time sufficient to harden the emulsion.

2. The method of claim 1 characterized in that the hardener is a positively charged hardener.

3. The method of claim 1 characterized in that the hardener is a carboxyl activating hardener.

4. The method of claim 3 characterized in that the hardener scavenger is a hydrophobic, carboxylic acid compound.

5. The method of claim 4 characterized in that the hardener scavenger is a hydrophobic, carboxylic acid compound represented by the formula:



wherein R^1 is a substituted or unsubstituted alkyl, aryl, or alkenyl group of 6 to 100 carbon atoms or a substituted or unsubstituted aralkyl of 7 to 100 carbon atoms or a substituted or unsubstituted heterocyclic ring of 6 to 100 carbon and heteroatoms wherein the heteroatoms are N or O.

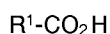
6. The method of claim 1 characterized in that the molar ratio of hardener scavenger to coupler contained in the silver halide photographic emulsion is 1:1 to 1:100.

7. The method of claim 1 characterized in that the coupler is a four-equivalent coupler.

8. A method of hardening a silver halide photographic emulsion comprising

(a) preparing a negatively charged hydrophobic coupler dispersion, wherein the coupler is a four-equivalent coupler;

(b) adding to the coupler dispersion at any point during its preparation a hydrophobic carboxylic acid compound hardener scavenger represented by the formula:



wherein R^1 is a substituted or unsubstituted alkyl, aryl, or alkenyl group of 6 to 100 carbon atoms or a substituted or unsubstituted aralkyl of 7 to 100 carbon atoms or a substituted or unsubstituted heterocyclic ring of 6 to 100 carbon and heteroatoms wherein the heteroatoms are N or O; and wherein the molar ratio of hardener scavenger to coupler is 1:1 to 1:100;

(c) combining the hardener scavenger/coupler dispersion with a silver halide emulsion to form a coupler containing silver halide emulsion; and

(d) contacting the coupler containing silver halide emulsion with a hydrophobic carboxyl activating hardener for a period of time sufficient to harden the emulsion.

9. A photographic emulsion prepared by any one of the methods described in claims 1 through 8.

10. A hardened silver halide photographic emulsion comprising the hydrophobic hardener scavenger of claims 1 through 9 and further comprising the coupler of claims 1 through 9 dispersed in the form of hydrophobic negatively charged dispersion particles.