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3,255,000
ACTIVATED HARDENING OF PHOTOGRAPHIC
EMULSIONS

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No Drawing. Filed Feb. 14, 1963, Ser. No. 258,599
8 Claims. (Cl. 96-111)

This invention relates to the activated hardening of
photographic emulsions in which a hardener having a
double bond in the alpha position to an oxygen contain-
ing group such as an acid, ester, amide, carbonyl or
sulfonyl group is incorporated in a gelatin photographic
emulsion which emulsion is then coated out onto a sup-
port in the form of a photosensitive layer and applied
thereover is a layer containing a volatile organic base.

Oftentimes photographic gelatin emulsions contain
hardeners whose action is prolonged over a considerable
period of time; hence, an emulsion layer having the de-
sired degree of hardness when freshly made may continue
to harden, upon keeping, to such a degree that it loses its
permeability to processing solutions. This may result in
undesirable sensitometric effects such as greatly de-
creased contrast after storage.

One object of our invention is to provide for the harden-
ing of photographic emulsion layers in which the desired
degree of hardness is attained in the fresh coating and
the full effect of the hardener is obtained initially rather
than continuing over a prolonged period. Another ob-
ject of our invention is to provide for a practical ap-
plication of a hardening accelerator to photographic emul-
sions containing hardeners which have a double bond in
the alpha position to an oxygen containing group such
as an acid, ester, amide, carbonyl or sulfonyl group
therein. A further object of our invention is to avoid the
deleterious effects obtained by adding hardening accel-
erators directly to photographic emulsions. Other objects
of our invention will appear herein.

We have found that the above objects are accomplished
by incorporating in a gelatin-silver halide photographic
emulsion as a hardener a compound having a double
bond in the alpha position to an oxygen containing group
such as an acid, ester, amide, carbonyl or sulfonyl group
and after this emulsion has been applied as a layer on a
suitable support it is then overcoated with a subsequent
layer containing a volatile organic base followed by dry-
ing which removes the organic base from the coated
layers. Examples of hardeners of the type described
which are useful in our invention are 1,3,5-triacryloyl-
hexahydro-s-triazine, divinyl sulfone, acryloxyethyl-
carbonyl-substituted gelatin, N-methylolacrylamide, 3,5-
cyclopentenedione, the copolymers of ethylene and beta-
vinylsulfonylethyl acid maleate and the copolymers of
vinylacryloxyethylurethane and vinyl acid succinate. Ex-
amples of volatile organic bases which may be employed
are any of the amines which have a boiling point of up
to about 125° C. so as to be readily removed in the dry-
ing operations in the manufacture of the photographic
film. Suitable examples of such amines are sec.-butyl-
amine, diethylamine, n-butylamine, n-pentylamine, di-iso-
propylamine, di-n-propylamine, N-ethylbutylamine, N-
methyl-di-propylamine, N-methylbutylamine and triethyl-
amine.

Any amount of the hardener incorporated in the photo-
graphic emulsion has some hardening effect but in prac-
tice ordinarily 0.25 to 25.0% of the hardener based on
the weight of the colloid is employed for optimum results.
The amount of volatile organic base employed in the
overcoating operations should be such that the layer has
a decided basicity such as a pH of 8-12 or more. The
emulsion is coated onto any one of the conventional types

of film supports such as cellulose triacetate or polyester
film base or paper it being understood that the support
may be subbed or otherwise coated in conventional man-
ner before the application of the emulsion layer. After
the emulsion layer is applied and preferably after drying,
it is then coated with an aqueous overcoat containing the
volatile organic base which is then dried in the usual
manner. The temporary contacting of the emulsion layer
with the alkaline overcoat is sufficient to cause accelerated
hardening even though the base is removed shortly after
the overcoating is applied during the normal drying
process.

The following examples illustrate our invention:

Example 1

A fast negative silver bromide-gelatin emulsion
containing as a hardener 2.0% of 1,3,5-triacryloylhexa-
hydro-s-triazine based on the weight of the gelatin was
coated onto a cellulose triacetate film support at the rate
of 840 mg. of gelatin per square foot. Hardeners of this
type are described in Belgian Patent No. 575,428. The
emulsion coating was then dried.

Another coating of emulsion was applied to like sup-
port in the same manner but immediately after drying
there was applied an overcoat comprising a 2% aqueous
solution of triethylamine which was applied at the rate
of 4 ccs. of triethylamine solution per square foot. The
coated product was then dried in the usual manner. The
films thus obtained were given equal exposures in a Kodak
1B sensitometer, processed for 5 minutes in Kodak DK-50
developer, fixed, washed and dried. Testing of the two
products indicated the following:

TABLE I

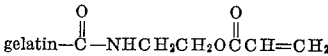
Ctg. No.	Fresh Tests			Optical Density		Vert. Swell	120° F. 1 week incubation γ
	Rel. Speed	γ	Fog	Wet	Dry		
1-----	100	1.20	0.01	2.12	1.98	177	0.90
2-----	91	1.05	0.02	1.76	1.75	88	0.87

The vertical swell in water was determined by im-
mersing the film in water and measuring the percent of
thickness increase of the coating on the film base. The
coating in which a triethylamine overcoating was used
showed a great increase in hardness as compared to the
coating without the triethylamine overcoat. This effect
is also demonstrated by the lower gamma of the second
coating as compared to that of the first coating and the
smaller change in gamma of former after storage for one
week at an elevated temperature.

A further important advantage arising from this type of
activated hardening is the considerable improvement in
the wet-dry density behavior of the treated emulsion. The
triethylamine-treated coating showed no density change
on drying, while the untreated coating loses 6.6% of its
wets density as it dries. Because of the effectiveness of
the accelerator in hardening the gelatin, use of hardener
in the fixing bath is unnecessary.

Example 2

A coating was applied to a support from the same kind
of emulsion as used in the preceding example except
that 15.0% of hardener based on the weight of the gela-
tin was used. The hardener employed was acryloxyethyl-
carbonyl-substituted gelatin having the structural for-
mula:



A second coating of the emulsion was made in like

manner and after drying it was overcoated with triethylamine as described in the preceding example. The films obtained were exposed, processed, fixed, washed and dried in the manner described in the preceding example. Two additional coatings were made using emulsion containing no hardener and emulsion with no hardener but overcoated with aqueous triethylamine. The resulting products were designated A, B, C and D, respectively. The results obtained on testing these 4 film samples were as follows:

TABLE II

Ctg. No.	Fresh Tests			Optical Density		Vert. Swell	120° F. 1 week incubation γ
	Rel. Speed	γ	Fog	Wet	Dry		
A-----	100	1.20	0.01	2.20	2.01	247	0.98
B-----	100	1.01	0.01	1.84	1.77	133	0.94
C-----	100	1.51	0.02	2.97	2.54	782	1.37
D-----	100	1.49	0.02	2.98	2.56	623	1.34

It is apparent that the triethylamine overcoat alone (Ctg. No. D) caused no more than a relatively insignificant reduction of the very large vertical swell in the case of the unhardened coating (Ctg. No. C). Also it is apparent that the triethylamine treatment causes no deleterious photographic effects on the film (Ctg. No. B) which is treated therewith.

While particular reference has been made to gelatin as the colloid in the photographic silver halide emulsion, any vehicle which contains amino groups and which is compatible with the silver halide may be used.

The photographic emulsions of our invention may contain, if desired, the usual coating aids, sensitizers, stabilizers, etc. as are known in the art.

If desired, the photographic emulsion and the fluid containing the volatile organic base may be applied simultaneously by the method described in T. A. Russell U.S. Patent 2,761,418.

We claim:

1. A method for the activated hardening of photographic emulsion layers which comprises incorporating in a silver halide-gelatin photographic emulsion a hardening amount of 1,3,5-triacryloylhexahydro-s-triazine, applying the emulsion to a support therefor and after drying the resulting layer applying thereover a layer containing triethylamine.

2. A method for the activated hardening of photographic emulsion layers which comprises incorporating in a silver halide-gelatin photographic emulsion a hardening amount of acryloxyethylcarbonyl-substituted gelatin, coating the emulsion onto a support and after drying the resulting layer applying thereover a layer of triethylamine.

3. A method for the activated hardening of photographic emulsion layers which comprises incorporating in the emulsion to be coated onto a support a hardener for the vehicle thereof comprising a compound characterized by the presence of a double bond alpha to a carbonyl or a sulfonyl of an acid, ester or amide radical which contains a carbonyl, a sulfonyl or both and after the emulsion has been applied to the support and the resulting layer has been dried applying thereover a layer containing an organic base having a boiling point of no more than approximately 125° C.

4. A method for the activated hardening of photographic emulsion layers which comprises incorporating in the emulsion to be coated onto a support a hardener for the vehicle thereof comprising a compound characterized by the presence of a double bond alpha to a carbonyl or a sulfonyl of an acid, ester or amide radical which contains a carbonyl, a sulfonyl or both and after the emulsion has been applied to the support and the resulting layer has been dried applying thereover a layer containing triethylamine.

5. A method for the activated hardening of photographic emulsion layers which comprises incorporating in a silver halide-gelatin emulsion a gelatin hardener characterized by the presence therein of a double bond alpha to a carbonyl or a sulfonyl of an acid, ester or amide radical which contains a carbonyl, a sulfonyl or both, applying the emulsion to a support and after drying the resulting layer applying thereover a layer containing an organic base having a boiling point of no more than approximately 125° C.

6. A method for the activated hardening of photographic emulsion layers which comprises incorporating in a silver halide-gelatin emulsion a gelatin hardener characterized by the presence therein of a double bond alpha to a carbonyl or a sulfonyl of an acid, ester or amide radical which contains a carbonyl, a sulfonyl or both, applying the emulsion to a support and after drying the resulting layer applying thereover a layer containing triethylamine.

7. In the preparation of photographic products in which a photographic emulsion containing a hardener for the vehicle thereof is a compound characterized by the presence of a double bond alpha to a carbonyl or a sulfonyl of an acid, ester or amide radical which contains a carbonyl, a sulfonyl or both is coated out onto a support and dried, the step which comprises applying over the dry photographic emulsion layer a layer of an organic base having a boiling point of no more than 125° C.

8. A method of preparing photographic products in which a gelatin-silver halide photographic emulsion contains a gelatin hardener which is a compound characterized by the presence of a double bond alpha to a carbonyl or a sulfonyl of an acid, ester or amide radical which contains a carbonyl, a sulfonyl or both, is applied to a support and dried, the step which comprises applying over the dry photographic emulsion layer a layer of triethylamine.

References Cited by the Examiner

UNITED STATES PATENTS

2,973,285	2/1961	Berke et al.	117—62.2
2,994,611	8/1961	Heyna et al.	96—111
3,061,436	10/1962	Himmelmann et al.	96—111
3,085,897	4/1963	Priest et al.	117—62.2

FOREIGN PATENTS

1,090,427	10/1960	Germany.
860,323	2/1961	Great Britain.

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