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PLASTICIZERS FOR RADIATION SENSITIVE SYSTEMS

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This invention broadly relates to improvements in radiation sensitive systems and more specifically involves the discovery of improved polymeric plasticizers for the gelatin vehicles thereof.

These radiation sensitive systems which may be coated onto photographic film base materials or other supports are essentially comprised of a radiation sensitive component such as one or more of the silver halides dispersed throughout a dispersion medium or vehicle comprised of any of a number of photographic gelatins or blends thereof. Such systems are generally known as emulsions and may contain as additives, optical sensitizers, chemical sensitizers, spreading agents, anti-foggants, surfactants, dyes, couplers, and the like well known to the photographic art to perform certain specific functions in black-and-white and color photography. These emulsions after their application to supports are generally hardened by means of chemicals which may actually crosslink the gelatin and prevent accidental disruption or removal thereof.

Though the emulsion of the as-purchased film appears to be perfectly dry, it is actually in a somewhat swelled though lubricated condition resulting from water gained during its manufacture. Consequently, should the film be stored under low relative humidity conditions for extended periods of time, the outer portions of the emulsion layer adjacent the atmosphere will dry out at a faster rate than the inner portions. The attendant contraction of the outer portions which now have lost their aqueous lubricant may cause them to split or craze in much the same manner as wet lumber does when rapidly dried from the outside in. This problem also exists perhaps even to a greater degree in the storage of negatives, transparencies and prints under low relative humidity conditions, and in a still broader sense exists wherever continuous gelatin coatings are employed.

Cracks of 1/64 of an inch or more have been observed in the emulsion layers, but the size of the cracks of course vary depending upon the thickness of the layers and the ambient atmosphere. Cracks of any dimension in the emulsion layer, however, will impair the quality of the photographic reproduction of the scene image and where fine detail must be scrupulously recorded as, for example, in X-rays and detail map making, cracks of any size are intolerable.

Heretofore, various types of polymeric plasticizers have been incorporated in varying amounts into photographic emulsions, but while improving the flexibility and resistance of the emulsions to cracking and crazing, they also operate to cause hazing of emulsions wet by aqueous solutions. When this hazing occurs, for example, during film processing, proper visual observation of the degree of development, the completeness of the wash, imperfections, and so forth, is rendered difficult, if not impossible. Moreover, even after the finished negative or transparency has been obtained, water may be inopportunely splashed onto the emulsion to again cause the hazing and give the appearance that the processed film is somehow defective.

While the hazing phenomenon is not completely understood, it is thought to result from the differences in the indices of refraction of the wet gelatin and the wet plasticizer, and also from the incompatibility of these materials in the wet condition. Whatever the cause, however,

this hazing renders proper processing of the film difficult and detracts from the appearance of finished negatives and transparencies which may inadvertently become wetted.

A principal object of the invention therefore is to provide an improved photographic film emulsion which is resistant to cracking and crazing under conditions tending to dry the same, and which does not become hazy when wetted, particularly with aqueous solutions.

Another object is to provide polymeric plasticizers which may be readily incorporated into photographic film emulsions to impart the desired flexibility and non-hazing characteristics thereto without adversely affecting critical characteristics of the emulsion such as speed, sensitivity, contrast, gamma, fog level and the like.

A further object is to provide, according to the preceding objects, a plasticized gelatin vehicle for radiation sensitive systems in general.

It would seem that many types of polymeric materials could accomplish these objects, however, as will hereinafter become evident, the materials shown by applicants to actually perform satisfactorily are severely limited to a few specific copolymers or mixtures thereof formed as hydrosols and adapted to be mixed with the gelatin to provide an aqueous system applicable to film base materials by present film coating apparatus. These copolymers are comprised of acrylic acid and/or methacrylic acid copolymerized with one or more of n-butyl acrylate, tertiary butyl acrylate, n-amyl acrylate, and n-hexyl acrylate in an aqueous medium to form the hydrosols. The most satisfactory plasticizers developed are the copolymers of acrylic acid or methacrylic acid and n-butyl acrylate. It will also become evident that the proportions of the monomer components of these copolymers are limited to a well defined range outside of which either haze is produced in the wet emulsion or excessive and unworkable viscosity of the plasticizer hydrosol results.

Further objects, advantages and novel aspects of the invention will become apparent from the detailed description of the invention set forth in the following example and tests.

EXAMPLE A

Preparation and testing of a typical binary copolymer hydrosol of the present invention

The following mixture, which represents approximately 17 mole percent acrylic acid in the copolymer was placed in a 370 ml. bottle, swept with nitrogen, capped, and allowed to tumble at 40° C. for 16 hours:

0.30 g.	Potassium persulfate.
3.00 ml.	Triton 770 (concentrated to a 40% solution).
200.00 ml.	Distilled water.
54.00 g.	n-Butyl acrylate.
6.00 g.	Acrylic acid.
0.15 g.	Potassium metabisulfite dissolved in 40 ml. of additional distilled water.

At the end of this period the resulting hydrosol was filtered through cloth to remove any coagulum formed and the filtrate adjusted to a pH of 6.0 using a 10% by weight aqueous sodium hydroxide solution. A portion of the hydrosol was then diluted with distilled water to 10% total solids and mixed with a sufficient amount of a warm (40° C.) 7% by weight aqueous solution of "photographic gelatin" to obtain a copolymer-gelatin solids ratio of 1:1. The term "photographic gelatin" designates high molecular weight dehydro-amino acid polymers well known to the photographic art. The resulting warm mixture was coated on a glass plate and permitted to dry overnight at room temperature. A perfectly clear film resulted which on wetting with water developed a slight haze over a period

of several hours which is a satisfactory performance for most purposes.

In the above formulation, the potassium persulfate, Triton 770 (an anionic aryl alkyl ether sulfate dispersing agent), and potassium metabisulfite perform their designed fuctions of catalysis, polymer dispersion, and catalysis promotion respectively. In the operation of the catalyst system, the formation of the polymerization free radical catalyst $\cdot SO_4$- from $K_2S_2O_8$ is promoted at a relatively low temperature by the $K_2S_2O_5$ which allows the more desirable higher molecular weight copolymers to be formed. The Triton 770 becomes associated with the hydrophobic copolymer particles to thereby prevent their coagulation and precipitation. It is noted that the gelatin is so selected that any charge it might have will not nullify the anionic character of the Triton 770. Other initiators such as $(NH_4)_2S_2O_8$, $Na_2S_2O_8$ and the $H_2O_2FeSO_4$ system, and other catalyst promoters such as $Na_2S_2O_5$, $Na_2S_2O_3$, and $NaHSO_3$ may be employed. Other anionic dispersing agents which are well known to the art to produce miscelles may be used in place of the Triton 770.

In establishing the operable and most desirable ranges of acrylic acid content for the acrylic—n-butyl acrylate copolymers, hydrosols and the following acrylic acid content were formed and evaluated by the process described above in Example A for wet haze by coating each out with photographic gelatin in the ratio of one part of dry polymer to two parts of dry gelatin.

TEST I

Test Sample	Approximate mole Percent Acrylic Acid	Result of Wet Haze Test
1	23.9	Clear.
2	16.6	Do.
3	8.6	Somewhat hazy.
4	3.5	Heavy haze.
5	1.8	Very heavy haze.

When the acrylic acid content is increased to more than about 24 mole percent, the shelf life of the hydrosol is sharply reduced and its viscosity increases rapidly beyond that which is practical for film coating operations. These tests establish the operable acrylic acid content for photographic emulsions to be from about 5.0 to about 24.0 mole percent with about 12 to about 18 mole percent being the most desirable. It is noted however that in certain radiation sensitive systems, low shelf life and high viscosities of the copolymer hydrosol may not be limiting to the successful formation of a plasticized gelatin vehicle. Therefore, it is not applicants' intention to limit the invention to an acrylic acid content of below about 24 mole percent except for certain specific uses.

TEST II.—ESTABLISHING EFFECTS PRODUCED BY USING ISOMERS OF n-BUTYL ACRYLATE

Hydrosols of the isomers of n-butyl acrylate were prepared and tested for wet haze in gelatin in the manner described in Example A above. Each of the copolymers were made containing about 16.6 mole percent acrylic acid with the balance being the indicated acrylate:

Test Sample	Isomer	Test Results
1	Iso-butyl acrylate	Very much hazier than with n-butyl acrylate.
2	Sec.-butyl acrylate	Somewhat hazier than with n-butyl acrylate.
3	Tert.-butyl acrylate	Slightly hazier than with n-butyl acrylate.

From these tests, it is apparent that the normal butyl ester is the most desirable, however, tertiary butyl acrylate may be used for less critical applications.

TEST III.—ESTABLISHING EFFECTS PRODUCED BY DIFFERENT ESTERIFICATION ALCOHOLS

Acrylates of the following alcohols were copolymerized with acrylic acid and tested for wet haze by the process of Example A using approximately 16.6 mole percent acrylic acid in each sample.

Test Sample	Esterification Alcohol	Test Result
1	Ethyl	Extremely hazy.
2	n-Propyl	Quite hazy.
3	n-Amyl	Only very slightly hazy.
4	n-Hexyl	Slightly hazy.
5	2-ethyl hexyl	Quite hazy.
6	n-Octyl	Deeply hazy.

From these tests, it is apparent that while n-butyl acrylate is almost in a class by itself, n-amyl and n-hexyl acrylates are after a fashion, operable.

It was experimentally determined that methacrylic acid performed satisfactorily as a substitute for acrylic acid. For example, n-butyl acrylate and methacrylic acid in the weight ratio of 9:1 were copolymerized in a hydrosol system, adjusted to pH 6, tested for wet haze in a 1:2 weight ratio of copolymer to gelatin and found to produce a haze-free coating.

Where the plasticized gelatin is to be used for photographic emulsions, the plasticizers should be from about 5% to about 50% by weight of the total plasticizer and gelatin solids. Higher percentages than these would too radically affect the operation of the gelatin with regard to the latent image formation or other photographic phenomena.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A composition of matter consisting essentially of a mixture of:

(A) gelatin, and

(B) a copolymer of

(1) at least one acid selected from the group consisting of acrylic acid and methacrylic acid, and

(2) at least one ester selected from the group consisting of n-butyl acrylate, tertiary butyl acrylate, n-amyl acrylate, and n-hexyl acrylate,

wherein the acid constitutes about 5 to about 24 mole percent of the copolymer.

2. A composition of matter consisting essentially of a mixture of:

(A) gelatin, and

(B) a copolymer of

(1) at least one acid selected from the group consisting of acrylic acid and methacrylic acid, and

(2) at least one ester selected from the group consisting of n-butyl acrylate, tertiary butyl acrylate, n-amyl acrylate, and n-hexyl acrylate,

wherein the acid constitutes about 12 to about 18 mole percent of the copolymer.

3. A composition of matter consisting essentially of a hydrosol of:

(A) gelatin, and

(B) a copolymer of

(1) at least one acid selected from the group consisting of acrylic acid and methacrylic acid, and

(2) at least one ester selected from the group consisting of n-butyl acrylate, tertiary butyl acrylate, n-amyl acrylate, and n-hexyl acrylate,

wherein the acid constitutes about 5 to about 24 mole percent of the copolymer.

4. A plasticized non-hazing composition of matter consisting essentially of a mixture of:

(A) gelatin, and

(B) a copolymer of n-butyl acrylate and acrylic acid wherein the acid constitutes about 5 to about 24 mole percent of the copolymer.

5. A plasticized non-hazing composition of matter consisting essentially of a mixture of:

(A) gelatin, and

(B) a copolymer of n-butyl acrylate and acrylic acid, wherein said acid constitutes from about 5 to about 24 mole percent of the copolymer, and wherein the copolymer solids constitute about 5% to about 50% by weight of the total solids of the copolymer and gelatin.

6. A plasticized vehicle for photographic emulsions, consisting essentially of gelatin mixed with about 5% to about 50% by weight of a copolymer of n-butyl acrylate and acrylic acid, between about 5 and about 24 mole percent of said copolymer being the acid.

7. A plasticized vehicle for photographic emulsions, consisting essentially of gelatin mixed with about 5% to about 50% by weight of a plasticizing copolymer of n-butyl acrylate and methacrylic acid, between about 5 and about 24 mole percent of said copolymer being the acid.

8. A copolymer readily adaptable for incorporation into the gelatin vehicle of radiation sensitive emulsions for plasticizing the same, consisting essentially of

(1) at least one acid selected from the group consisting of acrylic acid and methacrylic acid, and

(2) at least one ester selected from the group consisting of n-butyl acrylate, tertiary butyl acrylate, n-amyl acrylate, and n-hexyl acrylate,

wherein the acid constitutes about 5 to about 24 mole percent of the copolymeric materials.

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