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BIS(BETA-ACYLOXYETHYL)KETONES AS GELATIN HARDENERS

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ABSTRACT OF THE DISCLOSURE

Bis(beta-acyloxyethyl)ketones, such as bis(beta-acetoxyethyl)ketone, 1,5-diacetoxy-3-pentanone and 1,10-bis (chloroacetoxy)-3,8-decanedione, for example, have been found to exhibit strong activity as gelatin hardeners substantially free from detrimental photographic effects and toxicity. Compositions comprising gelatin and a hardener compound, mentioned hereinbefore, and gelatin-silver halide photographic emulsions containing a hardener compound mentioned hereinbefore are disclosed.

This invention relates to gelatin coating compositions containing bis(beta-acyloxyethyl) ketones or the like therein as hardeners.

Various compounds have been suggested as hardeners for gelatin. In many cases the hardeners which have been used for gelatin have exhibited undesirable photographic effects or have been prone to wander from the layers in which they have been placed. Some compounds suggested as hardening agents for gelatin have been objectionable because of adverse physiological properties.

One object of our invention is to provide gelatin compositions containing compounds having a good hardening effect thereon especially useful in the preparation of photographic products. Another object of our invention is to provide for the hardening of gelatin with compounds relatively free of undesirable photographic effects. A further object of our invention is to provide gelatin hardeners without undesirable physiological properties. A further object of our invention is to provide gelatin compositions containing ketone type hardeners therein. Other objects of our invention will appear herein.

We have found that compositions comprising gelatin and certain ketone type compounds are useful for obtaining coatings or layers which are resistant to the effect of hot water and to swelling. The compounds of interest as gelatin hardeners are largely of the following general structure:

$$XCH_2CH_2CO[ACO]_mCH_2CH_2X$$

in which X is an acyloxy radical of 2–5 carbon atoms which may or may not be halogen containing, m=0 or 1. A is a divalent linkage selected from the group consisting of $(CR_2)_{1-10}$ per se and $(CR_2)_{1-10}$ in which at least one CR_2 unit is replaced by a replacement selected from the group consisting of —CR=CR—, —O—, —S—, arylene and cycloalkylene radicals, R being selected from the group consisting of H and alkyl groups of 1–4 carbon atoms.

These compounds have been found to exhibit strong activity as gelatin hardeners substantially free from detrimental photographic effects and toxicity. Ordinarily the use of these hardeners involves incorporating a hardening amount in an aqueous solution of gelatin such as a composition to be used in making photographic products or in a gelatin-silver halide emulsion. The hardener is preferably incorporated in the gelatin composition in a proportion of 0.5–10 percent based on the weight of the gelatin in the composition.

These compounds are conveniently prepared from the corresponding bis(beta-chloroethyl) ketones by the combined action thereon of a carboxylic acid and its alkali metal salt using acetone as a solvent if necessary. In the case of liquid carboxylic acids an excess thereof functions well as the solvent when carrying out the reaction at normal temperatures.

The requisite bis(beta-chloroethyl)ketones are conveniently prepared by a Friedel-Crafts reaction from a dibasic acid halide and ethylene, using aluminum halide as the catalyst. In the case of certain acid halides such as succinoyl chloride, the reaction referred to does not occur and a more devious route must be used. The intermediates themselves show a slight hardening action in gelatin emulsions. The bis(beta-acyloxyethyl) ketones containing two carbonyl groups in the alkylene or arylene-alkylene chain (for instance, where m=1 in the general formula) are new compounds as are compositions thereof with gelatin.

The following examples illustrate the preparation of various intermediates, gelatin hardeners and their use as gelatin hardeners in accordance with our invention.

EXAMPLE 1

1,10-dichloro-3,8-decanedione

107 grams of anhydrous aluminum chloride and 450 ml. of dichloromethane were placed in a dry flask. The mass was cooled to 15° C., and then added dropwise was a solution of 73.2 grams of adipoyl chloride in 50 ml. of dichloromethane over a period of 10 minutes, the temperature being kept below 20° C. Ethylene was bubbled in, but no significant absorption occurred until the temperature had risen above 25° C. Fairly rapid absorption occurred at about 30° C.; the temperature was kept below 32° by intermittent cooling. At the termination of the reaction ethylene was no longer absorbed and the solids were in solution. The mixture was hydrolyzed on cracked ice drenched with concentrated hydrochloric acid. The layers were separated and the organic layer was washed once with water and dried. The mass must be kept cold throughout the process. The solvent was removd in vacuo, and the dark residue obtained was placed on a column of acid-washed alumina and eluted with benzene. The yellow eluant obtained was concentrated to about one-fifth volume in vacuo, and the residual oil was diluted with 2–3 volumes of ether and cooled. The precipitate was collected and recrystallized, giving colorless crystals which represented a 50–60 percent yield of the 1,10-dichloro-3,8-decanedione intermediate.

EXAMPLE 2

1,10-diacetoxy-3,8-decanedione

This compound was prepared from the 1,10-dichloro-3,8-decanedione of the preceding example by the procedure of Arbuzov and Volkov described in J. Gen. Chem. U.S.S.R. (Eng. transl.) 29, 3242 (1959). The crude yield was 93 percent. Repeated recrystallization from cyclohexane gave colorless crystals of 1,10-diacetoxy-3,8-decanedione. This material was employed in gelatin-silver halide photographic emulsions in concentrations of 1, 3 and 6 percent, based on the weight of the gelatin, and swelling in water of layers formed therefrom was found to be materially less than that of a layer of the emulsion without hardener. The material prepared in Example 1 was also incorporated in photographic emulsions in proportions of 1, 3 and 6 percent, and improved resistance to swelling by water of coatings made therewith was obtained. No derogatory effect on the photographic emulsion was noted in either case.

EXAMPLE 3

1,10-bis(chloroacetoxy)-3,8-decanedione

The procedure of Example 2 was repeated but modified by using acetone as the solvent and chloracetic acid and

sodium chloracetate as the carboxylic acid and the alkali metal salt thereof, respectively. The designated compound was obtained in 99 percent crude yield. Recrystallization from benzene-ligroin gave colorless crystals of 1,10-bis (chloroacetoxy)-3,8-decanedione. This material was incorporated in gelatin-silver halide emulsions in proportions of 1 and 3 percent, based on the weight of the gelatin. It was found that this compound materially reduced the swelling in water of emulsion layers containing it as compared with emulsion layers having no hardener therein and that the hardener was compatible with the photographic characteristics of the gelatin.

EXAMPLE 4

1,14-dichloro-3,12-tetradecanedione

This intermediate was prepared in a manner similar to that used in Example 1 except that sebacoyl chloride was used in place of adipoyl chloride. Pale yellow crystals were obtained in a yield of about 70 percent.

EXAMPLE 5

1,14-diacetoxy-3,12-tetradecanedione

This compound was prepared in essentially quantitative yield from the product in the preceding example, using a procedure as described in Example 2. This material was incorporated in gelatin-silver halide photographic emulsions in proportions of 1, 3 and 6 percent, based on the weight of the gelatin. The emulsion coated out in the form of layers had a much improved resistance to swelling by water as compared with layers of the emulsion containing no hardener. It was also found that this hardener was compatible with the photographic characteristics of the emulsion.

EXAMPLE 6

1,5-dichloro-3-pentanone

This intermediate was prepared by the procedure described by Baddeley and co-workers in the Journal of the Chemical Society, page 124 (1953). The resulting compound was a liquid having a boiling point of 64–68° C./0.6–0.8 mm.

EXAMPLE 7

1,5-diacetoxy-3-pentanone

This compound was prepared by the procedure of Example 2, using as the intermediate the product of the preceding example. This product was incorporated into portions of a gelatin-silver halide photographic emulsion in proportions of 1 and 5 percent, based on the weight of the gelatin, and the layers thereof were compared with layers of the emulsion without hardener. It was found that the resistance to swelling by water of such layers was materially reduced by the presence of the diacetoxy pentanone. It was also found that the hardener was compatible with the photographic properties of the emulsion with which it had been incorporated.

The swelling characteristics of the various layers was determined after the layers had been held for three days at 100° F. and 50 percent relative humidity. The swell of the layers was measured by determining the percentage of vertical swelling of the layer after it had been immersed for 5 minutes in water at 68° F. as compared with the depth of the layer prior to contact with the water.

EXAMPLE 8

Silver halide photographic emulsions in which the solid portion of the vehicle was composed of 25% gelatin and 75% of the sodium salt of ethyl acrylate-acrylic acid copolymer (80:20 acrylate to acid) were coated out on clear cellulose acetate film base at the rate of 750 mg./sq. ft. In two cases no hardener was used (controls) and in the other cases the hardeners designated were used in the proportions shown. The swell properties of the coatings are also indicated:

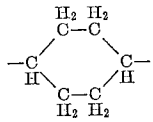
Hardener	Concentration		Percent Swell in Water
	Percent of Gelatin	Percent of Total Vehicle	
Control			440
S-200	20	5	230
S-201	20	5	350
Control			500
S-202	20	5	160

S-200=1,10-dichloro-3,8-dioxodecane.
S-201=1,10-diacetoxy-3,8-decanedione.
S-202=bis(beta-acetoxyethyl)ketone.

In the formula

$$XCH_2CH_2CO(ACO)_mCH_2CH_2X$$

representative compounds which are useful as hardeners in accordance with the invention are as follows:

A	Name
—CH=CH—	1,8-diacetoxy-4-octene-3,6-dione
—$CH_2CH_2OCH_2CH_2$—	1,11-diacetoxy-6-oxa-3,9-undecanedione
—$CH_2CH_2SCH_2CH_2$—	1,11-diacetoxy-6-thia-3,9-undecanedione
	1,4-bis(3-acetoxypropionyl)benzene
	1,4-bis(3-acetoxypropionyl)cyclohexane

The invention has been described in considerable detail with particular reference to certain 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 comprising gelatin and a compound having the formula

$$XCH_2CH_2CO(ACO)_mCH_2CH_2X$$

X is selected from the group of acyloxy radicals consisting of acetoxy and chloroacetoxy,

$$m=0-1$$

A is a divalent linkage selected from the group consisting $—(CH_2)_{1-10}—$, —CH=CH—,

$$—CH_2CH_2OCH_2CH_2—$$

$—CH_2CH_2SCH_2CH_2—$, phenylene and cyclohexylene radicals.

2. A gelatin-silver halide photographic emulsion containing a compound having the formula

$$XCH_2CH_2CO(ACO)_mCH_2CH_2X$$

X is selected from the group of acyloxy radicals consisting of acetoxy and chloroacetoxy,

$$m=0-1$$

A is a divalent linkage selected from the group consisting $—(CH_2)_{1-10}—$, —CH=CH—,

$$—CH_2CH_2OCH_2CH_2—$$

$—CH_2CH_2SCH_2CH_2—$, phenylene and cyclohexylene radicals.

3. A composition of matter comprising gelatin and 1,10-bis(chloroacetoxy)-3,8-decanedione.

4. A gelatin-silver halide photographic emulsion containing 1,10-diacetoxy-3,8-decanedione.

5. A composition of matter comprising gelatin and 1,10-bis(chloroacetoxy)-3,8-decanedione.

6. A gelatin-silver halide photographic emulsion containing 1,10-bis(chloroacetoxy)-3,8-decanedione.

7. A composition of matter comprising gelatin and 1,14-diacetoxy-3,12-tetradecanedione.

8. A gelatin-silver halide photographic emulsion containing 1,14-diacetoxy-3,12-tetradecanedione.

9. A composition of matter comprising gelatin and 1,5-diacetoxy-3-pentanone.

10. A gelatin-silver halide photographic emulsion containing 1,5-diacetoxy-3-pentanone.

11. A composition of matter comprising gelatin and bis(beta-acetoxyethyl)ketone.

12. A gelatin-silver halide photographic emulsion containing bis(beta-acetoxyethyl)ketone.

No references cited.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

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It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, lines 46 and 60, cancel "of acyloxy radiclas", each occurrence; line 71, "1,10-bis(chloroacetoxy)-3,8-decanedione" should read -- 1,10-diacetoxy-3,8-decanedione --.

Signed and sealed this 4th day of November 1969.

(SEAL)
Attest:

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