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ALPHA-ACYLTHIO-N(2-BENZOTHIAZOLYL) SUCCINIMIDES

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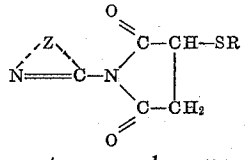
9 Claims. (Cl. 260—305)

This invention relates to improvements in the production of photographic images, especially images on paper supports prepared from silver halide emulsions, and to new chemical compounds.

Silver halide images are frequently subject to image degradation during processing, that is, during development, fixing, washing, toning, or other treatment and during the moist heat to which they are subjected on drying, as when prints are subjected to ferrow typing or hot-type glazing. This degradation of the image frequently manifests itself as "plumming" or "bronzing" of the image.

I have now found, however, that compounds which can be represented by the following general formula:

I 

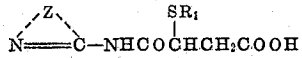
wherein R represents an acyl group, such as acetyl, propionyl, n-butyryl, isobutyryl, benzoyl, etc., or a thiocarbalkoxyl group, such as thiocarbomethoxyl, thiocarbethoxyl, thiocarbo-n-butoxyl, thiocarbo-n-octoxyl, etc., and Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the benzothiazole series, are not only effective anti-plumming agents but show no tendency to gel the emulsion and are readily soluble in organic water-miscible solvents, such as ethanol, acetone, etc.

It is, therefore, an object of my invention to provide a means for preventing image degradation in an exposed silver halide emulsion. Still another object is to provide new chemical compounds. Still another object is to provide methods for making these new compounds. Another object is to provide photographic silver halide emulsions containing these new compounds. Other objects will become apparent from a consideration of the following examples and description.

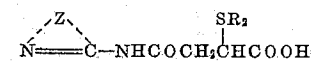
Accordingly, I realize the above objects by providing the compounds represented by Formula I above, which can be used to prevent undesirable image degradation in exposed silver halide emulsions. When any of the above compounds represented by Formula I are incorporated in silver halide emulsions, these compounds are advantageously used in a gelatino-silver-chloride emulsion or a silver chloride emulsion containing small amounts of bromide or iodide.

Silver halide emulsions in which the carrier is solely polyvinyl alcohol or hydrolyzed cellulose acetate can be used when the compounds are incorporated in the emulsion. They should be used in amounts from 0.5 g. to 10.0 grams per unit of silver halide formed from 1000 grams of silver nitrate. The same concentration of compounds should be present in the emulsion when the compounds are added by bathing the emulsion in a solution containing them. When the emulsion layer is bathed in a solution of the compound, the solution can contain up to about 5 per cent by weight of the compound.

According to my invention, I provide the new compounds represented by Formula I above by heating together a compound selected from those represented by the following two general formulas:

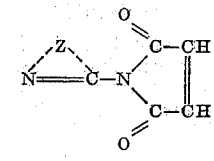
II 

and

III 

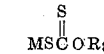
wherein Z has the values given above, and R_1 and R_2 each represents a member selected from the group consisting of a hydrogen atom, an acetyl group and a thiocarbalkoxyl group (e. g. thiocarbomethoxyl, thiocarbethoxyl, thiocarbo-n-butoxyl, thiocarbo-n-octoxyl, etc.), together with a carboxylic anhydride, such as acetic anhydride, propionic anhydride, n-butyric anhydride, isobutyric anhydride, benzoic anhydride, etc. In addition to causing ring formation, the carboxylic anhydride also causes acylation in cases wherein R_1 and R_2 each represents a hydrogen atom. The intermediates represented by Formulas II and III above can be prepared according to the methods described in my copending applications Serial Nos. 285,301 and 285,302, both filed on April 30, 1952. The aromatic nucleus of the benzothiazole group represented by Z above can be substituted by various groups, such as chlorine, bromine, methoxy, ethoxy, amino, methyl, ethyl, etc.

The compounds represented by Formula I above wherein R represents an acetyl group can also be prepared by condensing a compound selected from those represented by the following general formula:

IV 

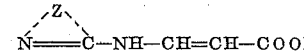
wherein Z has the values given above, together with thioacetic acid. The condensations can advantageously be carried out in the presence of an inert solvent, such as ethanol, acetone, etc.

The compounds represented by Formula I above wherein R represents a thiocarbalkoxyl group can also be prepared by heating together a compound selected from those represented by Formula IV above with a compound selected from those represented by the following general formula:

V 

wherein R_3 represents an alkyl group, such as methyl, ethyl, n-propyl, n-propyl, n-butyl, isobutyl, n-octyl, etc., and M represents an alkali metal atom, such as sodium, potassium, etc. and a sufficient amount of acid to liberate the free acid of the said alkali metal compound. Acids useful for this purpose comprise acetic acid, hydrochloric acid, sulfuric acid, etc., although it is to be understood that other acids can be used, since the purpose of the acid is simply to displace the alkali metal atom of the compounds of Formula V with a hydrogen atom.

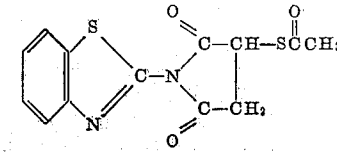
The intermediates represented by Formula IV above can advantageously be prepared by heating together a compound selected from those represented by the following general formula:

VI 

wherein Z has the values given above, together with a carboxylic anhydride. The intermediates represented by Formula VI above can be prepared according to the methods described in my copending applications Serial Nos. 285,301 and 285,302, mentioned above.

The following examples will serve to illustrate more fully the manner whereby I prepare the new compounds of my invention.

Example 1.—α-Acetylthio-N-(2-benzothiazolyl) succinimide



2.0 g. of 2-(β-carboxy-α-thiolpropionamido)benzothiazole and 10 cc. of acetic anhydride were boiled together until a clear solution was obtained. Slowly 5 cc. of acetic acid were added, followed by the slow addition of 25 cc. of water. Thereupon a light brown oil was precipitated and this was chilled overnight. The resulting hard solid was collected and washed with water. From ethyl acetate, and then ethanol, it formed flat, colorless needles, M. P. 139–140° C. The yield was 0.8 g.

Example 1a.—α-Acetylthio-N-(2-benzothiazolyl) succinimide

0.7 g. of 2-(β-carboxy-β-thiopropionamido)benzothiazole was dissolved in 3 cc. of boiling actic anhydride, followed by addition of acetic acid as directed in Example 1. A yield of 0.7 g. of pink flakes, M. P. 139–140° C., was obtained from 2 recrystallizations from ethanol.

Example 1b.—α-Acetylthio-N-(2-benzothiazolyl)-succinimide

2.8 g. of 2-(α-acetylthio-β-carboxypropionamido)-benzothiazole and 10 cc. of acetic anhydride were heated together over a free flame for two minutes. The solution was decomposed with acetic acid as described in Example 1 and the product (2.5 g.) recrystallized twice from ethanol as flat buff needles or flakes, M. P. 139° C.

Example 1c.—α-Acetylthio-N-(2-benzothiazolyl)-succinimide

This example was carired out in the same manner as described in Example 1*b* above, except that 10 cc. of propionic anhydride were employed instead of the 10 cc. of acetic anhydride used in that example. The product had M. P. 139–140° C.

Example 1d.—α-Acetylthio-N-(2-benzothiazolyl)-succinimide

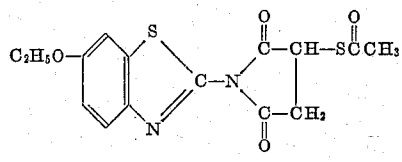
3.0 g. of 2-(β-acetylthio-β-carboxypropionamido)-benzothiazole and 10 cc. of acetic anhydride were boiled together until a clear solution was obtained and the product was treated with acetic acid and water as described in Example 1 above. A yellow oil was obtained which soon crystallized to give 1.4 g. of solid. From ethanol, it formed buff flakes, M. P. 140° C.

Example 1e.—α-Acetylthio-N-(2-benzothiazolyl)-succinimide

1.15 g. of N-(2-benzothiazolyl)maleinimide, 0.4 cc. of thioacetic acid, and 10 cc. of ethanol were refluxed for five minutes to give a clear solution. The solution was slowly cooled with inoculation to prevent boiling out. A yield of 1.5 g. of buff flakes, M. P. 138–140° C., from ethanol was obtained.

2.4 g. of 2-(β-carboxyacrylamido)benzothiazole and 10 cc. of acetic anhydride were refluxed for one minute. The deep yellow solution solidified on standing and 1.8 g. of product were obtained. It formed yellow needles, M. P. 210° C. from ethanol. The N-(2-benzothiazolyl)-maleinimide thus produced was used without further purification in the above reaction.

Example 2.—α-Acetylthio-N-6-ethoxy-2 - benzothiazolyl) succinimide



5.0 g. of 2-(α-acetylthio-β-carboxypropionamido)-6-ethoxybenzothiazole and 20 cc. of acetic anhydride were boiled together until a clear solution was obtained. On chilling, a mass of crystals separated and these were recrystallized from acetic anhydride as almost colorless prisms, M. P. 200–202° C. The yield was 3.4 g. Ethanol was also found to be a satisfactory crystallization solvent.

Example 2a.—α-Acetylthio-N-(6-ethoxy-2-benzothiazolyl) succinimide

1.0 g. of 2-(β-acetylthio-β-carboxypropionamido)-6-ethoxybenzothiazole was dissolved in 5 cc. of boiling acetic anhydride and the solution chilled. The product which crystallized formed almost colorless prisms, M. P. 199–201° C.

Example 2b.—α-Acethylthio-N-(6-ethoxy-2-benzothiazolyl)succinimide

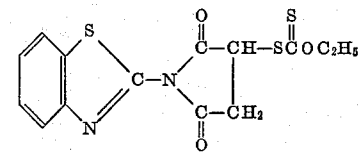
This example was carried out in exactly the same manner described in Example 2 above, except that propionic anhydride was used instead of the acetic anhydride. The product had M. P. 200–201° C.

Example 2c.—α-Acetylthio-N-(6-ethoxy-2-benzothiazolyl)succinimide

0.7 g. of N-(6-ethoxy-2-benzothiazolyl)maleinimide, 0.2 cc. of thioacetic acid, and 10 cc. of acetic acid were boiled together until dissolution occurred. On chilling, 0.6 g. of buff powder was obtained, forming pink needles, M. P. 199–201° C.

The 2-(6-ethoxy-2-benzothiazolyl)maleinimide used in the above example was prepared by boiling together 3.2 g. of 2-(β-carboxyacrylamido)-6-ethoxybenzothiazole and 10 cc. of acetic anhydride until dissolution occurred. The brown solution was chilled to give 2.25 g. of brown crystals, M. P. 174–178° C. From acetic anhydride, a solid having M. P. 174–178° C. was obtained, and this was used directly in the condensation described above.

Example 3.—α-Thiocarbethoxythiol-N-(2-benzothiazolyl)succinimide

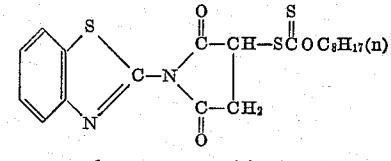


4.5 g. of 2-(β-carboxy-α-thiocarbethoxythiolpropionamido) benzothiazole and 20 cc. of acetic anhydride were heated over a free flame until the slurry had dissolved. The residual anhydride was decomposed with water, leaving a light brown oil which slowly crystallized. On two recrystallizations from ethanol, the solid formed colorless needles, M. P. 130–131° C. It weighed 3.3 g.

Example 3a.—α-Tthiocarbethoxythiol-N-(2-benzothiazolyl) succinimide

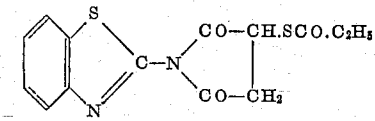
0.4 g. of N-(2-benzothiazolyl) maleinimide, 1.0 g. of potassium ethylxanthate, and 5 cc. of acetic acid were heated on the steam bath for two minutes, whereupon dissolution occurred. The addition of water gave a brown oil, the aqueous layer was decanted and the residue washed with water and dissolved in a little ethanol. On cooling, the product crystallized, M. P. 130–131° C.

Example 4.—α-Thiocarbo-n-octoxythiol-N-(2-benzothiazolyl)succinimide



This compound was prepared by heating together 2-(β-carboxy-α-thiocarbo-n - octoxythiopropionamido)benzothioazole and acetic anhydride. It was recrystallized from ethanol as fine, colorless needles, M. P. 101° C.

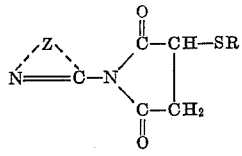
Example 5.—α-Propionylthio-N-(2-benzthiazolyl) succinimide



1.15 g. of N-(2-benzthiazolyl) maleinimide, 0.5 cc. of thio propionic acid (B. P. 106–108° C. obtained by the action of H_2S on propionic anhydride and catalysed by 1% acetylchloride) and 10 cc. of ethanol were refluxed for 15 minutes. The required substance oiled out then crystallised on chilling. Recrystallised from ethanol a yield of 1.45 g. was obtained as flat, glossy, buff needles, M. P. 120° C.

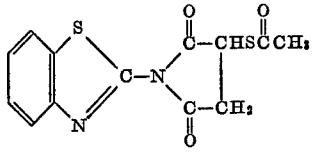
What I claim as my invention and desire secured by Letters Patent of the United States is:

1. A compound selected from those represented by the following general formula:

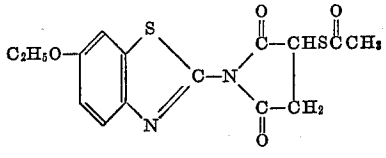


wherein Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the benzothiazole series selected from the group consisting of benzothiazole and benzothiazole having substituted thereon a radical selected from the group consisting of chlorine, bromine, methoxy, ethoxy, amino, methyl and ethyl and R represents an acyl group selected from the group consisting of an acetyl group, propionyl group, n-butyryl group, isobutyryl group, benzoyl group, and a thiocarbalkoxyl group containing from 1 to 8 carbon atoms.

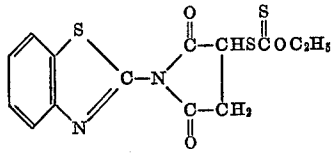
2. The compound having the following formula:



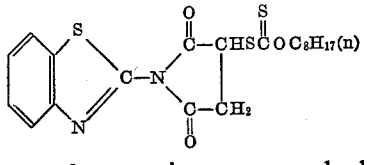
3. The compound having the following formula:



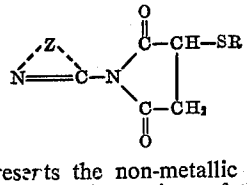
4. The compound having the following formula:



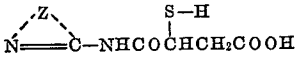
5. The compound having the following formula:



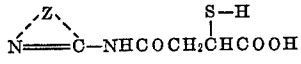
6. A process for preparing a compound selected from those represented by the following general formula:



wherein Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the benzothiazole series selected from the group consisting of benzothiazole and benzothiazole having substituted thereon a radical selected from the group consisting of chlorine, bromine, methoxy, ethoxy, amino, methyl and ethyl and R represents an acyl group comprising heating a compound selected from the group consisting of those represented by the following general formulas:

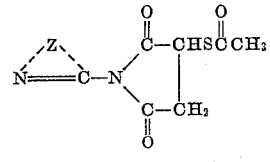


and

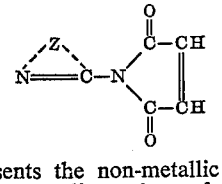


wherein Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the benzothiazole series selected from the group consisting of benzothiazole and benzothiazole having substituted thereon a radical selected from the group consisting of chlorine, bromine, methoxy, ethoxy, amino, methyl and ethyl, together with an anhydride of a monocarboxylic acid containing from 2 to 6 carbon atoms.

7. A process for preparing a compound selected from those represented by the following general formula:

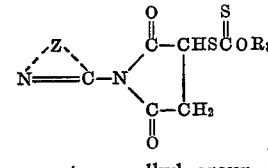


wherein Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the benzothiazole series selected from the group consisting of benzothiazole and benzothiazole having substituted thereon a radical selected from the group consisting of chlorine, bromine, methoxy, ethoxy, amino, methyl and ethyl comprising heating a compound selected from those represented by the following general formula:

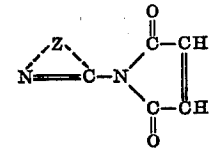


wherein Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the benzothiazole series selected from the group consisting of benzothiazole and benzothiazole having substituted thereon a radical selected from the group consisting of chlorine, bromine, methoxy, ethoxy, amino, methyl and ethyl together with thioacetic acid.

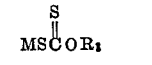
8. A process for preparing a compound selected from those represented by the following general formula:



wherein R_3 represents an alkyl group containing from 1 to 8 carbon atoms and Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the benzothiazole series selected from the group consisting of benzothiazole and benzothiazole having substituted thereon a radical selected from the group consisting of chlorine, bromine, methoxy, ethoxy, amino, methyl and ethyl comprising heating a compound selected from those represented by the following general formula:



wherein Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the benzothiazole series selected from the group consisting of benzothiazole and benzothiazole having substituted thereon a radical selected from the group consisting of chlorine, bromine, methoxy, ethoxy, amino, methyl and ethyl together with an alkali metal compound selected from those represented by the following general formula:



wherein R_3 represents an alkyl group and M represents an alkali metal atom and a sufficient amount of acid to liberate the free acid of the said alkali metal compound.

9. A process according to claim 8 wherein acetic acid is employed as the acid to liberate the free acid of the said alkali metal compound.

No references cited.