

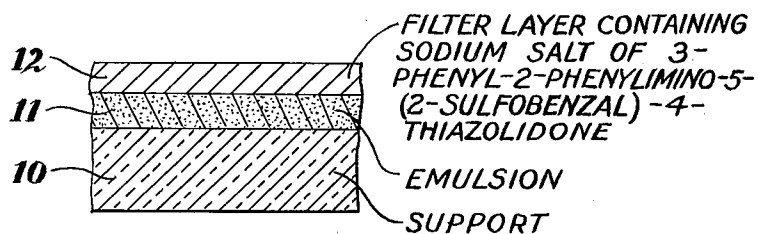
March 27, 1956

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2,739,888

PHOTOGRAPHIC ELEMENTS CONTAINING THIAZOLIDINE DERIVATIVES

Filed March 29, 1954



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PHOTOGRAPHIC ELEMENTS CONTAINING THIAZOLIDINE DERIVATIVES

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Application March 29, 1954, Serial No. 419,239

13 Claims. (Cl. 95—2)

This invention relates to new products and new photographic elements protected against the harmful effects of ultraviolet radiation.

This application is a continuation-in-part of my application Serial No. 317,864, filed October 31, 1952.

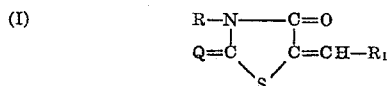
It is known that certain materials such as cellulosic films and photographic layers, are adversely affected by ultraviolet radiation when such materials are exposed to daylight. In the case of photographic layers, the ultraviolet radiation sometimes causes undesired exposure of the layer, or layers, since photographic silver halide emulsions are sensitive to blue, violet and ultraviolet regions of the spectrum, in addition to any other sensitivity which may be given them, and in the exposure of such material, it is frequently desirable to prevent the action of ultraviolet light on the sensitive emulsion. This is especially true in the case of photographic materials designed for use in color photography where the film has been sensitized to the longer wavelength regions where it is desirable to record only the rays of the visible spectrum.

Color photographs on multilayer photographic material, particularly where the dye images are formed in sensitive emulsion layers by color development, are susceptible to fading and discoloration by the action of ultraviolet radiation to which the photographs are subjected during viewing. It is also known that the residual couplers contained in the emulsion layers after formation of the picture images in certain processes are attacked by ultraviolet radiation and form a stain which is undesirable in the finished photograph. The action of ultraviolet radiation on finished color photographs is particularly noticeable in positive prints on paper or other opaque supports, since this type of print is frequently viewed in daylight where there is a high content of ultraviolet radiation. This dye fading and yellowing appears to be caused primarily by those wavelengths of light which lie close to the visual region of the spectrum, i. e. 360–400 millimicrons.

I have now found that certain new ultraviolet absorbing compounds can be used to overcome the aforementioned difficulties, without attendant harmful action by the ultraviolet absorbing compound itself.

It is, therefore, an object of my invention to provide new compounds and photographic elements protected against the harmful effects of ultraviolet radiation. A further object is to provide photographic color materials which have been protected against the harmful effects of ultraviolet radiation. Other objects will become apparent from a consideration of the following description.

The ultraviolet absorbing compounds which I propose to employ in my invention are advantageously represented by the following general formula:



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wherein R represents a hydrogen atom, an alkyl group (e. g. methyl, ethyl, β -hydroxyethyl, β -sulfoethyl, β -diethoxyethyl, propyl, isopropyl, butyl, isobutyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, lauryl, cetyl, etc.), a cycloalkyl group (e. g. cyclopentyl, cyclohexyl, etc.), an aryl group (e. g. phenyl, o-, m-, and p-tolyl, o-, m-, and p-ethylphenyl, p-isopropylphenyl, p-amylphenyl, o-, m-, and p-methoxyphenyl, o-, m-, and p-ethoxyphenyl, β -hydroxyethylphenyl, o-, m-, and p-chlorophenyl, o-, m-, and p-hydroxyphenyl, o-, m-, and p-sulfophenyl (and alkali metal salts thereof, e. g. sodium, potassium, etc.), 4-methoxy-3-sulfophenyl (and alkali metal salts thereof, e. g. sodium, potassium, etc.), 2,4-dicarboxymethylphenyl (and alkali metal salts thereof, e. g. sodium, potassium, etc.), o-, m-, and p-carboxyphenyl (and alkali metal salts thereof, e. g. sodium, potassium, etc.), 3-(3-sulfobenzamido)phenyl (and alkali metal salts thereof, e. g. sodium, potassium, etc.), o-carbobutoxyphenyl, diamylphenoxyacetoxypheyl, etc., or an aralkyl group (e. g. benzyl, β -phenylethyl, α -phenylethyl, etc., R₁ represents an aryl group (e. g. those aryl groups defined above wherein R is an aryl group), and Q represents a divalent, non-metallic atom (e. g. oxygen, sulfur, etc.) or imino radical (e. g. imino, phenylimino, o-, m-, and p-chlorophenylimino, benzylimino, β -phenylethylimino, α -phenylethylimino, o-, m-, and p-tolylimino, o-, m-, and p-ethylphenylimino, p-amylphenylimino, o-, m-, and p-ethoxyphenylimino, etc.).

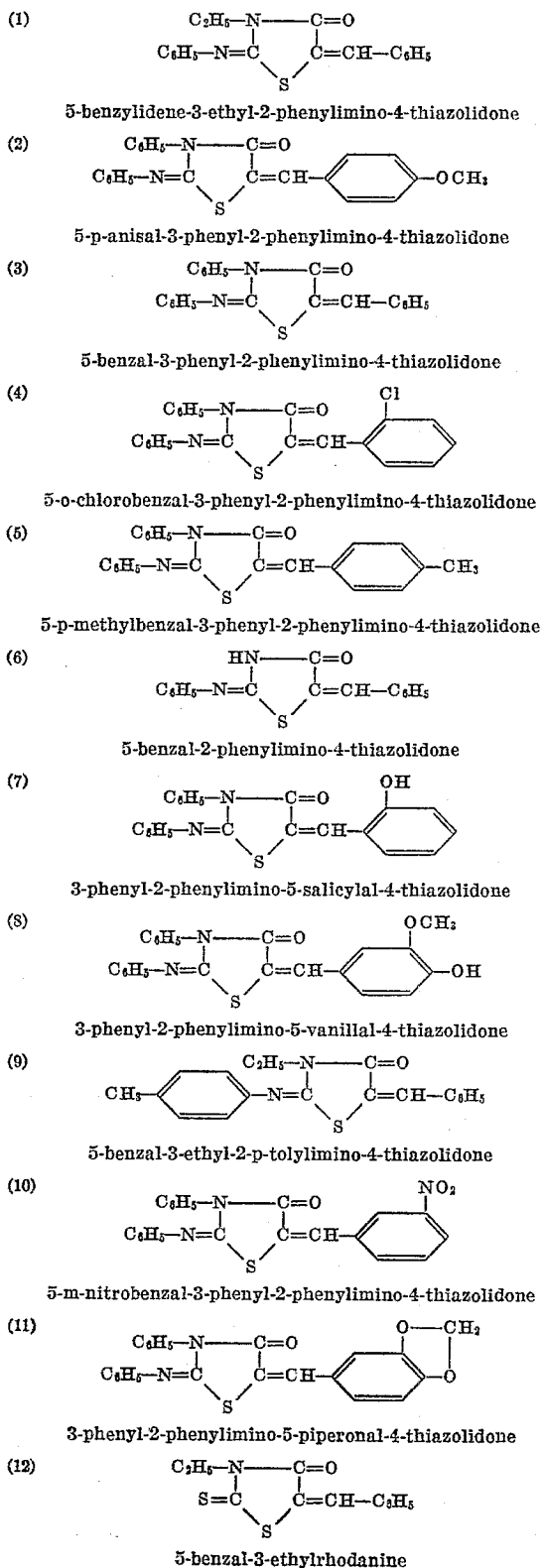
These ultraviolet absorbing compounds can be incorporated in the photographic element in a variety of ways, depending on the ultimate use of the photographic element and the degree of protection desired. Advantageously, the ultraviolet absorbing compound can be dissolved or dispersed in a solvent medium together with a colloidal binder, such as gelatin, cellulose esters (e. g. cellulose acetate, etc.), synthetic resins (e. g. polyvinyl acetals, hydrolyzed polyvinyl acetate, etc.), etc., and the resulting mixture coated over the light-sensitive layer of the photographic element. Where the photographic element is a material intended for use in color photography, the ultraviolet filter layer need not be an outer layer, but this layer can be placed over one of the layers subject to the harmful effects of ultraviolet radiation. For example, in a multilayer material comprising three differentially sensitized layers, the red sensitive layer being adjacent to the support, the green sensitive layer being superposed on the red sensitive layer, and the blue sensitive layer being outermost with respect to the other light-sensitive layers, the ultraviolet filter layer can be placed between the blue and green sensitive layers. Alternatively, the ultraviolet filter layer can be placed between the green and the red sensitive layers. If desired, the material useful in absorbing the ultraviolet radiation can be incorporated directly in the light-sensitive emulsion instead of, or in addition to, being present in another layer. The amount of ultraviolet absorbing compound used can be varied, depending upon the effect desired and the use to which the material is to be put.

The water-soluble compounds of Formula I above (e. g. those containing alkali metal salts of carboxyphenyl, sulfophenyl, etc. groups) can be incorporated into the photographic element by simply bathing the element in an aqueous solution containing the ultraviolet absorbing compound. Where the outer layer contains gelatin, the ultraviolet absorbing compound becomes adsorbed to this layer. By incorporating a resinous mordant, e. g. polyvinyl pyridine methyl p-toluenesulfonate, phenol-formaldehyde ion exchange resins, etc. in the outer gelatin layer (or an intermediate layer where desired), the photographic element can be subjected to washing or processing operations without removal of the ultraviolet

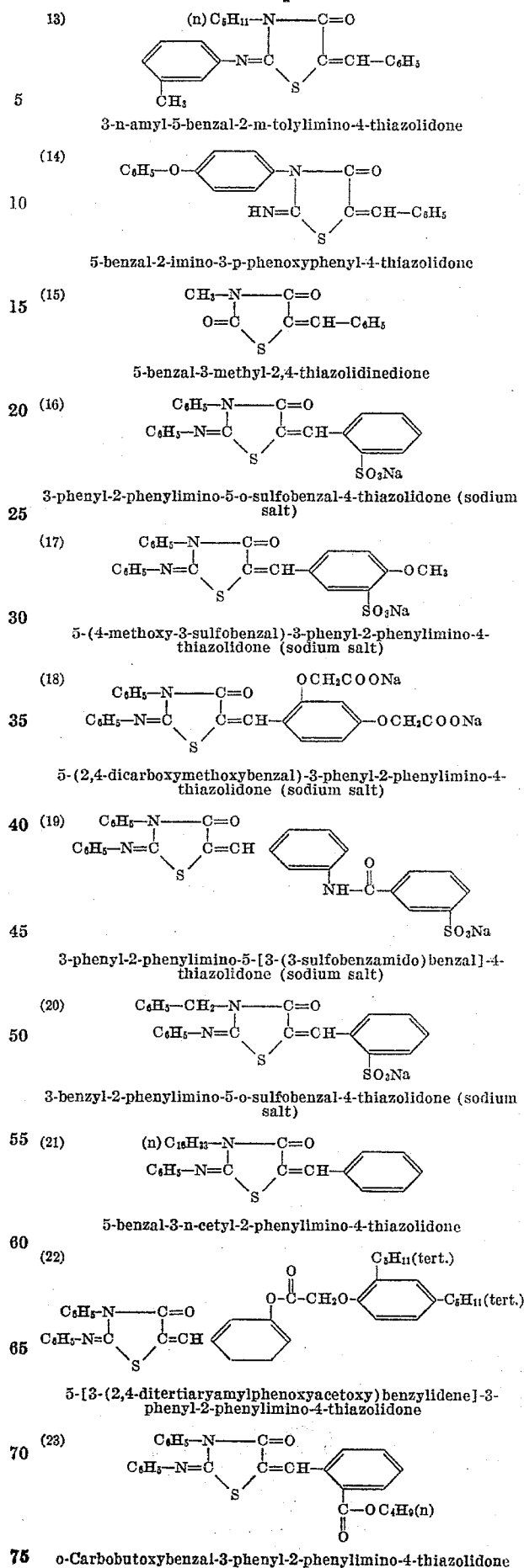
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absorbing compounds. Thus, the ultraviolet absorbing compounds can be incorporated into the photographic element before or after (i. e. during processing) exposure. The support of the photographic element can be transparent, such as a cellulose ester (e. g. cellulose acetate, etc.) support, or the support can be opaque, such as a paper support. Other supports, such as glass, metal, etc. can be employed, if desired.

Typical compounds selected from those represented by Formula I which can be used in practicing my invention comprise those represented by the following formulas:

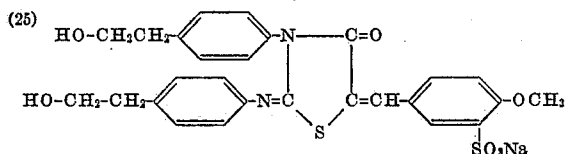
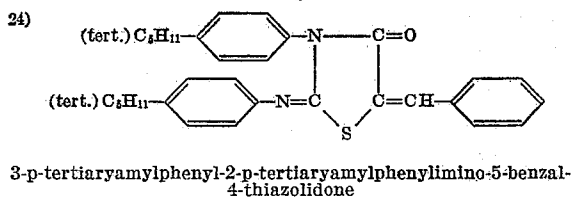


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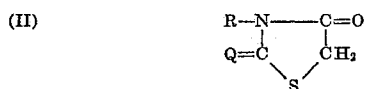


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The compounds represented by Formula I above can advantageously be prepared by condensing a compound selected from those represented by the following general formula:



wherein R and Q have the values given above, together with an aldehyde of the following general formula:

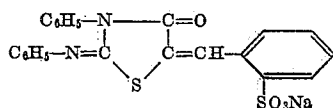


wherein R₁ has the values given above. Heat accelerates the condensations, temperatures varying from room temperature to the reflux temperature being useful. An inert diluent, e. g. acetic acid, methanol, ethanol, etc. can be used, if desired. Condensing agents, such as piperidine, acetic anhydride, alkali metal carboxylates (e. g. sodium acetate, potassium acetate, etc.), etc. can be employed, if desired.

The compounds of Formula I wherein R₁ contains a sulfo or carboxyl group (or alkali metal salts thereof, e. g. sodium, potassium, etc.) are new compounds and are especially useful in the bathing treatment mentioned above. They are useful in the process described in Edgerton and Staud application Serial No. 318,096, filed October 31, 1952, being useful either in a layer of the photographic element, or in the bathing solutions disclosed therein. The compounds of Formula I can also be added to the photographic silver halide emulsion, though usually less advantageously than when employed in a separate filter layer.

The following examples will serve to illustrate the manner whereby the compounds of Formula I can be prepared.

Example 1.—3-phenyl-2-phenylimino-5-(o-sulfobenzal)-4-thiazolidone (sodium salt)



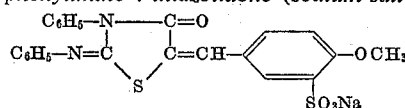
A mixture of 2.86 g. (0.01 mole) of 3-phenyl-2-phenylimino-4-thiazolidone and 2.5 g. (0.0125 mole) of o-sulfobenzaldehyde sodium salt in 50 ml. of absolute methanol containing 2 ml. of piperidine was refluxed for 2 hours. The crude product was collected by suction filtration, washed thoroughly with boiling acetone and recrystallized from boiling water.

The desired product separated on cooling in the form of pale yellowish platelets melting above 300° C. The yield was 3.3 g., which is 71% of theory.

Analysis:

	Calculated for C ₂₂ H ₁₅ O ₄ N ₂ S ₂ Na	Found
	Percent	Percent
Carbon.....	57.6	57.4
Hydrogen.....	3.3	3.1
Nitrogen.....	6.1	6.1
Sulfur.....	13.9	14.1

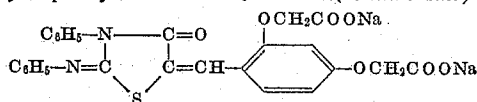
Example 2.—5-(4-methoxy-3-sulfobenzal)-3-phenyl-2-phenylimino-4-thiazolidone (sodium salt)



A mixture of 6.7 g. (0.025 mole) of 3-phenyl-2-phenylimino-4-thiazolidone and 5.5 g. (0.025 mole) of 4-methoxy-3-sulfobenzaldehyde sodium salt in 50 ml. of acetic acid and 5 ml. of acetic anhydride was refluxed under a water-cooled condenser for 8 hours. The cooled reaction mixture was poured into 400 ml. of water, and the solution heated on the steam bath to 85–90° C. The insoluble material was removed by filtration and the filtrate cooled. The solid formed was filtered and washed with 2–25 ml. portions of ice water and crystallized from boiling water. The product was a slightly tan powder, which gave the following analytical results.

	Calculated for C ₂₃ H ₁₇ N ₂ O ₅ S ₂ Na	Found
	Percent	Percent
Carbon.....	56.5	56.4
Hydrogen.....	3.5	3.3
Nitrogen.....	3.5	5.5
Sulfur.....	13.1	13.5

Example 3.—5-[2,4-bis(carboxymethoxy)benzal]-3-phenyl-2-phenylimino-4-thiazolidone (sodium salt)

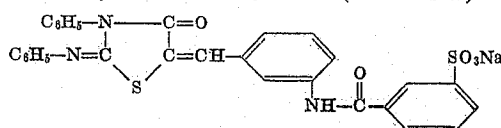


A mixture of 5.36 g. (0.02 mole) of 3-phenyl-2-phenylimino-4-thiazolidone and 5.46 g. (0.02 mole) of 2,4-bis-carbomethoxymethoxybenzaldehyde in 125 ml. of methyl alcohol containing 3 ml. of piperidine was refluxed for 2 hours. The solid formed was filtered out of the hot solution, washed with 2–25 ml. portions of cold methyl alcohol and crystallized from 200 ml. of acetonitrile. The colorless needle-like product had a melting point of 157–159° C. and gave the following analytical results:

	Calculated for C ₂₅ H ₂₁ N ₂ O ₇ S	Found
	Percent	Percent
Carbon.....	63.0	63.3
Hydrogen.....	4.5	4.6
Nitrogen.....	5.3	5.4
Sulfur.....	6.0	5.9

The dimethyl ester thus obtained was suspended in an alcoholic alkali (sodium hydroxide) solution, and the mixture shaken for several minutes. The dimethyl ester was completely hydrolyzed to the above formulated salt. This solution was then used directly for bathing film strips containing a photographic silver halide layer and a gelatin outercoat.

Example 4.—3-phenyl-2-phenylimino-5-[3-(3-sulfobenzamido)benzal]-4-thiazolidone (sodium salt)



A mixture of 5 g. (0.0135 mole) of 5-(3-aminobenzal)-3-phenyl-2-phenylimino-4-thiazolidone and 3.2 g. (0.0135 mole) of m-chlorosulfonylbenzoyl chloride in 100 ml. of dry dioxane was refluxed for 3 hours. The cooled reaction mixture was poured into 500 ml. of cold water containing 3 g. of sodium acetate and the mixture stirred until the oil first formed solidified. The solid was filtered, washed with cold water, and dried. Crystallization from acetonitrile gave a light tan powder which decomposed above 175° C. with the evolution of hydrochloric acid gas. The chlorosulfonyl compound thus produced had the following analysis:

	Calculated for C ₂₅ H ₂₀ ClN ₂ O ₄ S (541)	Found
	Percent	Percent
Carbon.....	64.0	63.8
Hydrogen.....	3.7	3.6
Chlorine.....	6.5	6.4
Nitrogen.....	7.7	7.4
Sulfur.....	5.9	5.8

The 5-[3-(3-chlorosulfonylbenzamido)benzal]-3-phenyl-2-phenylimino-4-thiazolidone thus obtained was suspended in an alcoholic alkali (sodium hydroxide) solution, whereupon the desired, above-formulated sodium salt was obtained. The resulting solution was used directly for bathing of film or paper strips having thereon a developed and fixed photographic image.

The 5-(3-aminobenzal)-3-phenyl-2-phenylimino-4-thiazolidone used in the above example was prepared as follows:

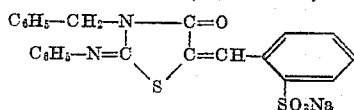
A mixture of 6 g. (0.0167 mole) of 5-(3-nitrobenzal)-3-phenyl-2-phenylimino-4-thiazolidone, 75 ml. of dioxane, 0.5 g. of sodium carbonate and 0.5 g. of Raney nickel catalyst was charged into a pressure bottle and shaken on a Parr hydrogenator under 42 pounds of hydrogen pressure at room temperature. After 3 hours the required volume of hydrogen had been absorbed and the bottle was removed from the machine and the solution filtered. The filtrate was evaporated in a vacuum, and the residue crystallized from 50 ml. of acetonitrile. The product obtained (5 g.) was light brown in color and showed a melting point of 280–282° C.

The 3-phenyl-2-phenylimino-5-(3-nitrobenzal)-4-thiazolidone used above was prepared as follows:

A mixture of 13.4 g. (0.05 mole) of 3-phenyl-2-phenylimino-4-thiazolidone, 8.3 g. (0.05 mole) of m-nitrobenzaldehyde, 200 ml. of methyl alcohol and 4.3 ml. of piperidine was refluxed for 3 hours on a steam bath under a water-cooled condenser. The precipitate formed was filtered, washed with cold methyl alcohol, and dried. The bright yellow product was insoluble in most of the common organic solvents; it crystallized difficultly from boiling ethylene glycol. It had a melting point of 225–227° C., and gave the following analytical results:

	Calculated for C ₂₇ H ₁₉ N ₂ O ₃ S	Found
	Percent	Percent
Carbon.....	65.7	65.2
Hydrogen.....	3.7	3.7
Nitrogen.....	10.4	10.3
Sulfur.....	8.0	8.0

Example 5.—3-benzyl-2-phenylimino-5-(o-sulfobenzal)-4-thiazolidone (sodium salt)



70 g. of 3-benzyl-2-phenylimino-4-thiazolidone and 70 g. of sodium-benzaldehyde-2-sulfonate (92% pure) in 700 cc. of glacial acetic acid were refluxed for 5–6 hours. After cooling to room temperature overnight, the crystals

which had separated were filtered, washed with acetic acid and dried. There were thus obtained 100 g., 85% of theory, of product. Addition of 10 g. of the o-sulfobenzaldehyde sodium salt to the filtrate and refluxing for 5 hours gave an additional 13 g. of pure material. Total yield 113 g., 96% of theory. The product was crystallized from 225 cc. of methanol to give a highly pure product.

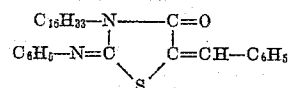
The 3-benzyl-2-phenylimino-4-thiazolidone used in the above example was obtained as follows:

A mixture of 189 g. (0.79 mole) of 1-benzyl-3-phenylthiourea, M. P. 167–8° C., 95 g. (1.0 mole) of chloroacetic acid and 95 g. (1.15 mole) of sodium acetate in 1000 cc. of ethanol was refluxed for 5–6 hours. About 15 ¾ of the alcohol was removed under reduced pressure and 400 cc. of water was added. An oil separated which soon solidified. The aqueous layer was decanted, the residue washed thoroughly with water and taken up with benzene, treated with decolorizing carbon, and dried. 20 An equal volume of ligroin was added and the solution chilled to give 149.5 g. of product as pure white crystals, M. P. 81–2° C. The mother liquors on spontaneously evaporating gave another 34 g. of product having a melting point of 79–81° C. Total yield 183 g., 83% theory.

25 The direction of cyclization was established by acid hydrolysis. Thus this product gave, on hydrolysis, an 87% yield of aniline, characterized as its acetyl derivative, M. P. 113–114° C.

In a similar manner, 1,3-di(β-phenylethyl)thiourea was 30 reacted with chloroacetic acid to provide the thiazolidone which was obtained as a solid having melting point of 25–8° C. (3-β-phenylethyl-3-β-phenylethylimino-4-thiazolidone).

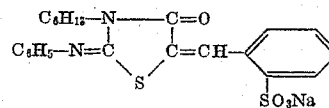
Example 6.—5-benzal-3-n-cetyl-2-phenylimino-4-thiazolidone



40 A mixture of 41.6 g. (0.1 mole) of 3-n-cetyl-2-phenylimino-4-thiazolidone (M. P. 78° C.), 0.13 mole of benzaldehyde, 12 ml. of piperidine and 200 cc. of ethanol was refluxed for 4 hours. The reaction mixture was chilled and the white crystalline product was collected by filtration and recrystallized from butanol. Yield, 43 g., M. P. 74–5° C.

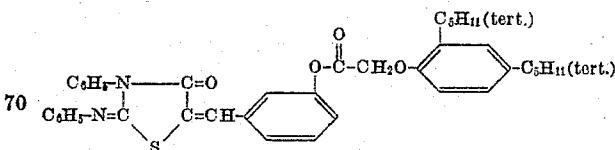
In like manner the 3-n-decyl-(M. P. 53–4° C.), 3-n-hexyl-(M. P. 77–8° C.), 2-cyclohexyl-(M. P. 123–5° C.), 50 and 3-n-butyl-(M. P. 102–103° C.) 2-phenylimino-5-benzal-4-thiazolidones were prepared.

Example 7.—3-n-hexyl-2-phenylimino-5-(o-sulfobenzal)-4-thiazolidone (sodium salt)



46 g. of 3-n-hexyl-2-phenylimino-4-thiazolidone and 60 36 g. of o-sulfobenzaldehyde sodium salt in 150 cc. of acetic acid were refluxed for 7 hours. On cooling, the reaction mixture set to a solid crystalline mass which was filtered and washed with acetic acid. Yield, 71 g.

Example 8.—5-[3-(2,4-ditertiaryamylphenoxyacetoxy)benzylidene]-3-phenyl-2-phenylimino-4-thiazolidone



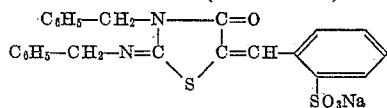
75 75 g. of 5-(3-hydroxybenzylidene)-3-phenyl-2-phenylimino-4-thiazolidone in 250 ml. of benzene was treated with 65 g. of 2,4-ditertiaryamylphenoxyacetyl chloride in

100 ml. of benzene, then 40 ml. of pyridine were added. The reaction mixture was then heated under reflux for two hours, washed first with water and then dilute sodium carbonate solution and dried. The benzene was removed by vacuum distillation and the residue triturated with ligroin. The crystalline solid which remained was re-crystallized from ethyl alcohol (95%) to give 76 g. of white crystalline solid. This was the desired compound and it had a melting point of 133–5° C.

The 5-(3-hydroxybenzylidene)-3-phenyl-2-phenylimino-4-thiazolidone used in the above example can be obtained according to the method described in application Serial No. 317,864 mentioned above, condensing together 3-hydroxybenzaldehyde and 3-phenyl-2-phenylimino-4-thiazolidone. The acid chloride used in the above example can be prepared as described in Weissberger et al. U. S. Patent 2,511,231, issued June 13, 1950 (column 9, lines 59–76 and column 10, lines 1–21).

3-phenyl-2-phenylimino-5-(3-lauroyloxybenzylidene)-4-thiazolidone was obtained in the same manner, M. P. 123–124° C., using lauroyl chloride instead of 2,4-ditertiaryamylphenoxyacetyl chloride.

Example 9.—3-benzyl-2-benzylimino-5-(*o*-sulfobenzal)-4-thiazolidone (sodium salt)



A mixture of 74 g. of 3-benzyl-2-benzylimino-4-thiazolidone, 60 g. of *o*-sulfobenzaldehyde, 20 g. of sodium acetate and 500 ml. of acetic acid was refluxed for 5 hours. Complete solution ensued. The acetic acid was evap-

orated under reduced pressure, while the reaction mixture was alternately allowed to cool and the precipitate filtered off. After all liquids had been removed, the residue and precipitates were recrystallized from water. Pure white crystals weighing 100 g. were obtained.

The 3-benzyl-2-benzylimino-4-thiazolidone used above was prepared as follows:

A mixture of 52 g. of 1,3-dibenzylthiourea, 24 g. of chloroacetic acid, 24 g. of sodium acetate, and 200 ml. of ethanol was refluxed for 5 hours. The alcohol was then removed in vacuo and the residue treated with 300 ml. of water to remove excess chloroacetic acid, sodium acetate, and sodium chloride. The insoluble portion was recrystallized from alcohol to yield 56 g. of product, M. P. 84–86° C.

Instead of using the compounds containing an acid group (e. g. carboxyl or sulfo) in the form of their alkali metal salts, they can be employed in the form of their amine addition salts (e. g. ethylamine, diethylamine, amylamine, lauryl amine, triethanolamine, etc.). The alkali metal (e. g. sodium, etc.) salt can be dissolved in water, advantageously with the aid of ethyl methyl ketone, and the amine, e. g. triethanolamine, added. The desired salt then separates on chilling the solution and it can easily be redissolved in warm water.

The 4-thiazolidones represented by Formula II above can be prepared as shown in the above examples, i. e. by condensing a thiourea together with chloroacetic acid in the presence of sodium acetate and an inert diluent.

In a manner similar to that illustrated in the above examples the following 4-thiazolidones were prepared, the results being given in Tables I and II. The extinction coefficient, ϵ , is given for some of the compounds.

TABLE I

	R'	R''	R'''	R''''	Absorption λ max. (m μ)	ϵ
(a)-----	H	H	2-SO ₃ Na	H	334	19,500
(b)-----	H	H	3-SO ₃ Na	H	355	28,000
(c)-----	4-t-C ₆ H ₁₁	4-t-C ₆ H ₁₁	2-SO ₃ Na	-OCH ₃	328	16,500
(d)-----	4-CH ₃	4-CH ₃	2-SO ₃ Na	H	330	20,000
(e)-----	4-C ₂ H ₅	4-C ₂ H ₅	2-SO ₃ Na	H	328	19,200
(f)-----	2-CH ₃	2-CH ₃	2-SO ₃ Na	H	330	11,600
(g)-----	4-C ₂ H ₅	4-OC ₂ H ₅	3-SO ₃ Na	-OCH ₃	352	25,000
(h)-----	4-C ₂ H ₄ OH	4-C ₂ H ₄ OH	3-SO ₃ Na	-OCH ₃	355	26,000

TABLE II

	R	R'	R''	R'''	Absorption λ max. (m μ)	ϵ
(i)-----	-C ₂ H ₅	-C ₂ H ₅	3-SO ₃ Na	-OCH ₃	348	25,200
(j)-----	-CH ₂ C ₆ H ₅	-CH ₂ C ₆ H ₅	2-SO ₃ Na	H	330	20,400
(k)-----	H	-C ₆ H ₅	2-SO ₃ Na	H	338	22,000
(l)-----	-C ₂ H ₅	-C ₆ H ₅	2-SO ₃ Na	H	334	15,200
(m)-----	(C ₂ H ₅ O) ₂ CHCH ₂ -	-C ₆ H ₅	2-SO ₃ Na	H	334	17,000
(n)-----	-CH ₂ C ₆ H ₅	-CH ₂ C ₆ H ₅	3-SO ₃ Na	-OCH ₃	348	26,600
(o)-----	-CH ₂ C ₆ H ₅	-CH ₂ C ₆ H ₅	3-SO ₃ Na	H	332	24,000
(p)-----	-CH ₂ CH ₂ C ₆ H ₅	-CH ₂ CH ₂ C ₆ H ₅	2-SO ₃ Na	H	330	27,000
(q)-----	-C ₆ H ₁₃ (n)	-C ₆ H ₁₃ (n)	2-SO ₃ Na	H	330	12,000
(r)-----	-CH(CH ₃)C ₆ H ₅	-CH(CH ₃)C ₆ H ₅	2-SO ₃ Na	H	330	16,000
(s)-----	-CH(CH ₃)C ₆ H ₅	-CH(CH ₃)C ₆ H ₅	3-SO ₃ Na	-OCH ₃	350	20,000
(t)-----	-C ₂ H ₅	-C ₂ H ₅	-COOH	H	329	23,200
(u)-----	-CH ₂ C ₆ H ₅	-C ₆ H ₅	2-SO ₃ Na	H	-----	-----
(v)-----	-C ₁₀ H ₁₅ (n)	-C ₆ H ₅	H	H	329	24,800
(w)-----	-C ₆ H ₁₁ (n)	-C ₆ H ₅	H	H	330	24,800
(x)-----	-C ₆ H ₁₁ (cyclo)	-C ₆ H ₅	H	H	330	27,000
(y)-----	-C ₆ H ₅ (n)	-C ₆ H ₅	H	H	330	24,600

ANALYTICAL DATA FOR COMPOUNDS OF TABLES I AND II

Compound No.	Calculated		Found	
	C	H	C	H
(a) ¹	57.6	3.3	58.0	3.7
(b)	56.5	3.5	56.4	4.0
(c)	65.0	4.6	64.7	5.1
(d)	57.0	4.2	56.5	4.1
(e)	50.0	4.7	49.8	4.8
(f)	50.0	2.9	49.8	3.1
(h) ²	59.4	4.0	59.4	3.9

¹ N calcd. 6.1, found 6.0; S calcd. 13.9, found 14.1.

² M. P. 138-9° C. from CH₃CN and water.

The following examples will serve to illustrate the application of the compounds of Formula I to photographic elements.

Example 10

0.5 g. of the sodium salt of 3-phenyl-2-phenylimino-5-(2-sulfobenzal)-4-thiazolidone (obtained as described in Example 1) was dissolved with the aid of heat in 8 ml. of water. The resulting solution was cooled somewhat, mixed with 12 cc. of an aqueous 10% gelatin solution and coated onto a support. The resultant coating showed no change after one week's exposure over an east window and gave excellent protection when overcoated on a multi-layer paper coating.

Example 11

A multilayer color photographic paper was exposed and processed, and immediately thereafter immersed for 10 minutes in a 0.5% aqueous solution of the sodium salt of 3-phenyl-2-phenylimino-5-(2-sulfobenzal)-4-thiazolidone, and dried. Window tests indicated that good protection was thus afforded against the deleterious effect of ultraviolet radiation.

Alternatively, this bath could be applied to protect or to fortify the action of an absorber already incorporated in the material.

Example 12

1.0 g. of 5-benzal-3-benzyl-2-phenylimino-4-thiazolidone was dissolved in 2 cc. of tri-o-cresyl phosphate. This solution was added to 20 cc. of 10% gelatin (aqueous) and 4 cc. of 5% aqueous ethanol, and the mixture homogenized in a colloid mill. The resultant dispersion when coated on an opaque or transparent film support effectively absorbed ultraviolet radiation.

Example 13

1.0 g. of 3-benzyl-2-phenylimino-5-(2-sulfobenzal)-4-thiazolidone sodium salt was dissolved by warming in 20 cc. of water. After mixing with 20 cc. of 10% gelatin the mixture was coated as before on opaque and transparent film supports.

Coatings prepared as described in Examples 12 and 13 above showed no loss in density on undergoing normal photographic processing and were unchanged after one week's exposure on an east window.

Example 14

1.0 g. of 5-benzal-3-n-cetyl-2-phenylimino-4-thiazolidone was dissolved with heating in 0.5 cc. of tri-o-cresyl phosphate. This solution was then added to 20 cc. of 10% gelatin and 4 cc. of ethanol. The resulting mixture was passed three times through the colloid mill, an additional 20 cc. of water being added to the original mixture in the process. Coatings prepared from the dispersion showed no loss of density on undergoing normal photographic processing and remained unchanged upon several days exposure on an east window.

Example 15

1.0 g. of 5-benzal-3-n-cetyl-2-phenylimino-4-thiazolidone was dissolved in 12 cc. of ethylacetate. The solution was mixed with 20 cc. of 10% gelatin plus 4 cc. of

5% Alkanol B aqueous solution and then milled three times. The resulting dispersion was chilled, sliced and dried. The dried material was swelled in a little cold water and added to a dispersion made by dissolving 1.0 g. of 2-(2,4-diamylphenoxyacetamino)-4,6-dichloro-5-methylphenol in 2 cc. of di-n-butyl phthalate, adding to gelatin and completing the operation as described in Example 14 above.

In a manner similar to that described in Examples 14 and 15, coatings containing 5-[3-(2,4-ditertiaryamylphenoxyacetoxy) benzylidene]-3-phenyl-2-phenylimino-4-thiazolidone were prepared. The actual coating spread was found to be somewhat higher than for the coatings obtained in Examples 14 and 15, due to the increased molecular weight of this particular compound.

In a manner similar to that illustrated in Examples 10-15, photographic elements containing a photographic silver halide emulsion layer can be treated with other ultraviolet absorbing compounds embraced by Formula I above. Where the ultraviolet absorbing compound is not water-soluble, it can be incorporated in the gelatin solution with the aid of an inert solvent, e. g. ethanol, and be uniformly dispersed throughout the gelatin solution before coating.

The accompanying drawing illustrates schematically a cross-sectional view of a photographic element containing a layer having incorporated therein the sodium salt of 3-phenyl-2-phenylimino-5-(2-sulfobenzal)-4-thiazolidone, which is representative of the ultraviolet absorbing agents which can be employed in my invention. As shown in the single figure of the drawing, a support 10 of any suitable material, such as cellulose acetate, or paper, having thereon an emulsion layer 11 is coated with a filter layer 12 having incorporated therein the sodium salt of 3-phenyl-2-phenylimino-5-(2-sulfobenzal)-4-thiazolidone, or some other ultraviolet absorbing compound selected from those represented by the above general formula (I). It will be understood that the drawing is merely representative of other structures which can be employed in my invention, and that the element can have other layers, not shown, such as additional light-sensitive layers, subbing layers, antihalation layers, etc.

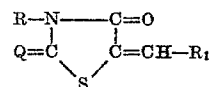
The term "an imino group" as employed herein includes the simple imino group (HN=) and its substituted derivatives (R₂-N=, wherein R₂ represents an aryl or alkyl group, such as those listed above, for example).

The solutions containing the ultraviolet absorbing compounds of my invention can also be used in bathing solutions for after treatments in photographic processes, glazes, etc.

The thioureas required for the production of the thiazolidones of Formula II wherein Q is R₂-N= can be obtained according to the method of Hofmann ("Ber.," vol. 1, page 27), i. e. by condensing ammonia or an amine having the formula R-NH₂ together with an isothiocyanate having the formula R₂-NCS, R and R₂ having the values given above.

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

1. A photographic element comprising a support, at least one photographic silver halide emulsion layer, and incorporated in one of the layers of said photographic element a compound selected from those represented by the following general formula:

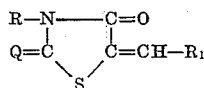


wherein R represents a member selected from the group consisting of a hydrogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, and an aryl group, R₁ represents an aryl group and Q represents an imino group.

2. A photographic element comprising a support, at least one photographic gelatin-silver halide emulsion

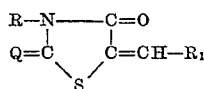
13

layer, and incorporated in one of the layers of said photographic element a compound selected from those represented by the following general formula:



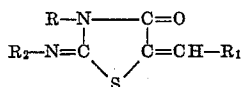
wherein R represents a member selected from the group consisting of a hydrogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, and an aryl group, R₁ represents an aryl group and Q represents an imino group.

3. A photographic element comprising a support, at least one photographic-silver halide emulsion layer, superposed on said support, and an outer gelatin layer containing a compound selected from those represented by the following general formula:



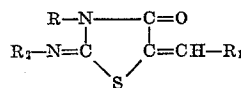
wherein R represents a member selected from the group consisting of a hydrogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, and an aryl group, R₁ represents an aryl group and Q represents an imino group.

4. A photographic element comprising a support, at least one photographic gelatino-silver halide emulsion layer, superposed on said support, and an outer gelatin layer containing a compound selected from those represented by the following general formula:



wherein R represents a member selected from the group consisting of a hydrogen atom, a primary alkyl group containing from 1 to 16 carbon atoms, a cycloalkyl group containing from 5 to 6 carbon atoms, an aralkyl group containing from 7 to 8 carbon atoms, and a mononuclear aromatic group of the benzene series, R₁ represents a mononuclear aromatic group of the benzene series, and R₂ represents a member selected from the group consisting of a mononuclear aromatic group of the benzene series and an aralkyl group containing from 7 to 8 carbon atoms.

5. A finished photographic element comprising a support having thereon a plurality of developed and fixed photographic emulsion layers containing developed-dye images, at least one of said dye images being subject to fading by the action of ultraviolet radiation, said emulsion layer containing a developed-dye image subject to fading lying between said support and a gelatin layer containing an ultraviolet absorbing compound selected from those represented by the following general formula:



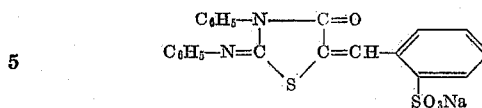
wherein R represents a member selected from the group consisting of a hydrogen atom, a primary alkyl group containing from 1 to 16 carbon atoms, a cycloalkyl group containing from 5 to 6 carbon atoms, an aralkyl group containing from 7 to 8 carbon atoms, and a mononuclear aromatic group of the benzene series, R₁ represents a mononuclear aromatic group of the benzene series, and R₂ represents a member selected from the group consisting of a mononuclear aromatic group of the benzene series and an aralkyl group containing from 7 to 8 carbon atoms.

6. A photographic element according to claim 5 wherein the support is a paper support.

7. A photographic element comprising a support, a photographic gelatino-silver halide emulsion layer, and a

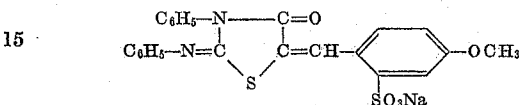
14

gelatin layer containing a compound of the following formula:



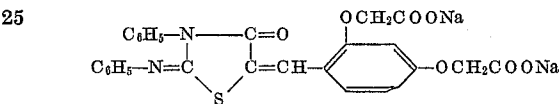
said photographic gelatino-silver halide emulsion layer lying between said support and said gelatin layer.

8. A photographic element comprising a support, a photographic gelatino-silver halide emulsion layer, and a gelatin layer containing a compound of the following formula:



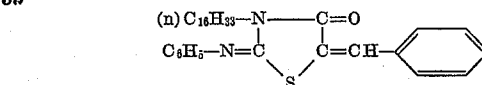
said photographic gelatino-silver halide emulsion layer lying between said support and said gelatin layer.

9. A photographic element comprising a support, a photographic gelatino-silver halide emulsion layer, and a gelatin layer containing a compound of the following formula:

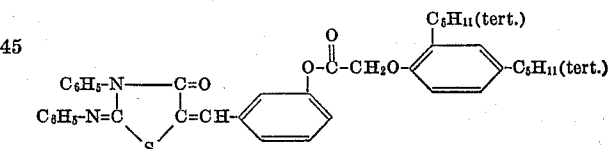


said photographic gelatino-silver halide emulsion layer lying between said support and said gelatin layer.

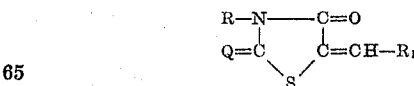
10. A photographic element comprising a support, a photographic gelatino-silver halide emulsion layer, and a gelatin layer containing a compound of the following formula:



11. A photographic element comprising a support, a photographic gelatino-silver halide emulsion layer, and a gelatin layer containing a compound of the following formula:



12. A method of preventing image degradation in a finished photographic element comprising a plurality of developed and fixed photographic emulsion layers containing developed-dye images, at least one of said dye images being subject to fading by the action of ultraviolet radiation, said emulsion layer containing a developed-dye image subject to fading lying between said support and a gelatin outer layer, which comprises applying to said photographic element from aqueous, non-colloidal solution an ultraviolet radiation absorbing compound selected from those represented by the following general formula:

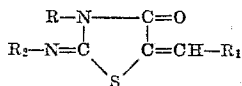


wherein R represents a member selected from the group consisting of a hydrogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, and an aryl group, R₁ represents an aryl group and Q represents an imino group.

13. A method of preventing image degradation in a finished photographic element comprising a plurality of developed and fixed photographic emulsion layers containing developed-dye images, at least one of said dye images being subject to fading by the action of ultraviolet

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radiation, said emulsion layer containing a developed-dye image subject to fading lying between said support and a gelatin outer layer, which comprises applying to said photographic element from aqueous, non-colloidal solution an ultraviolet radiation absorbing compound selected from those represented by the following general formula:



wherein R represents a member selected from the group consisting of a hydrogen atom, a primary alkyl group containing from 1 to 16 carbon atoms, a cycloalkyl group containing from 5 to 6 carbon atoms, an aralkyl group containing from 7 to 8 carbon atoms, and a mononuclear

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aromatic group of the benzene series, R₁ represents a mononuclear aromatic group of the benzene series, and R₂ represents a member selected from the group consisting of a mononuclear aromatic group of the benzene series and an aralkyl group containing from 7 to 8 carbon atoms.

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