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PHOTOGRAPHIC DEVELOPER COMPOSITION CONTAINING 2-HYDROXYMETHYL-3-PYRAZOLIDONES

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20 Claims. (Cl. 96—66)

This application is a continuation-in-part of De Marle and Donovan U.S. Serial No. 106,523 filed May 1, 1961.

This invention relates to the preparation and use of novel photographic developing agents and in particular to novel 2-substituted-3-pyrazolidones.

Various substituted 3-pyrazolidones have been described in the prior art where the 4 and 5 positions on the ring are substituted by single groups and the 4 position substituted by two groups. However, 2-substituted-3-pyrazolidones have not been previously described.

Although the 3-pyrazolidones of the prior art are very good photographic developing agents, they are characterized by having low solubility both in rate and quantity.

The water solubility of developing agents such as hydroquinone can be increased by introducing certain groups into the molecule, but the increase in solubility is accompanied by a serious loss in developing activity. Similarly, in previous attempts to make 3-pyrazolidones more water soluble with amino, sulfo, sulfonamide, quinoline, acetyl, and similar groupings, the increase in solubility has been coupled with a considerable reduction in developing activity. The substitution of a methyl group on the 2 position of a 1-phenyl-3-pyrazolidone gives a compound that is inert as a developing agent.

It is therefore an object of our invention to provide a novel class of 3-pyrazolidones which have water solubilities that are up to 10 times greater than the corresponding prior art 3-pyrazolidones but in which the solubilizing group causes little or no loss in photographic developing activity.

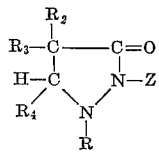
A further object is to provide a novel class of 2-substituted-3-pyrazolidone developing agents which have a greatly improved rate of solution compared to the prior art pyrazolidones.

A further object is to provide improved photographic developer formulations containing novel pyrazolidone developing agents.

A further object is to provide a process for making our novel developing agents.

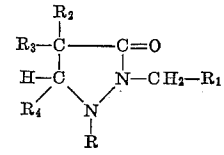
Still further objects will become apparent from the following specification and claims.

We have found that these objects can be accomplished by using the 2-substituted-3-pyrazolidone developing agents of our invention which may be represented by the general formula:

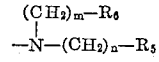
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in which Z is an aminoalkyl group or a hydroxyalkyl group; R is an aryl group, such as phenyl, p-tolyl, p-chlorophenyl, m-tolyl, p-methoxyphenyl, acetamidophenyl, m-aminophenyl, o-chlorophenyl, m-acetamidophenyl, p-β-hydroxyethylphenyl, p-hydroxyphenyl, 7-hydroxy-2-naphthyl, p-diphenyl, etc.; and R_2, R_3, and R_4 may be a hydrogen atom, an aliphatic group such as methyl, ethyl, propyl, isopropyl, butyl, secondary butyl, tertiary butyl, hydroxymethyl, hydroxybutyl, methoxyethyl, phenoxypropyl, aminoethyl, methylaminoethyl, sulfomethyl, carboxyethyl, chloromethyl, bromoethyl, etc., an aromatic group such as phenyl, naphthyl, benzyl, p-hydroxyphenyl, o-ethoxyphenyl, p-phenoxyphenyl, m-aminophenyl, p-methylaminophenyl, p-sulfophenyl, o-carboxyphenyl, p-chlorophenyl, o-bromophenyl, α-hydroxy-β-naphthyl, β-amino-α-naphthyl, p-hydroxybenzyl, o-chlorobenzyl, etc., and where R_2, R_3, and R_4 may all be the same or different.

The preferred developing agents of our invention may be represented by the following formula:

II 

in which R_1 is a hydroxyl group or a



group, in which n is an integer of 1 to 6, m is an integer of 1 to 6 such that the sum of $n+m$ is from 2 to 6, R_5 and R_6 each represent either a hydrogen atom or a hydroxyl group, so that this amino group, for example, may be a dimethylamino group, a diethylamino group, a dipropylamino group, a di-isopropylamino group, a N-methylethylamino group, a N-methylpentylamino group, a N-ethylbutylamino group, a bis-(hydroxypropyl) amino group, etc., or together represent the nonmetallic atoms necessary to complete a heterocyclic amino group, such as a pyrrolidino, a piperidino, a morpholino, a N-alkylpiperazino, a 1,2,3,4-tetrahydroquinolyl group, or their analogs substituted with lower alkyl groups having from 1 to 4 carbon atoms such as methyl, ethyl, propyl, isopropyl, butyl, secondary butyl, tertiary butyl, etc., and in which R, R_2, R_3, and R_4 are as defined above.

The novel 2-aminoalkyl-3-pyrazolidones of our invention are prepared by reacting equimolar quantities of the appropriate 3-pyrazolidone, formaldehyde, and a secondary amine preferably in the presence of suitable solvent, such as water or any solvent miscible with water and inert to the reaction, that is, not reactive with formaldehyde or amines. Preferred solvents are the lower alkanols, such as methanol through butanol and ethers like dioxane. Water is the least favored reaction medium because it is more difficult to remove when the product is to be isolated. Solvents are used to effect a single phase reaction media. Representative secondary amines that are used to advantage include secondary aliphatic amines with a total of 6 or less carbon atoms such as dimethylamine, diethylamine, dipropylamine, di-isopropylamine, N-methylethylamine, N-methylpentylamine, N-ethylbutylamine, bis(hydroxy-propyl)amine, and the like, secondary heterocyclic amines such as pyrrolidine, piperidine, N-alkylpiperazine, morpholine and their analogs substituted with lower alkyl groups having from 1 to 4 carbon atoms such as methyl, ethyl, propyl, isopropyl, butyl, secondary butyl, tertiary butyl, etc.

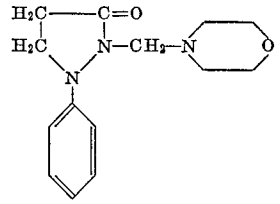
The novel 2-hydroxyalkyl-3-pyrazolidones of our invention are prepared by reacting equimolar quantities of the appropriate 3-pyrazolidone with formaldehyde in the presence of a suitable solvent such as water or a lower alkanol. It is preferable to make the reaction mixture alkaline by using a suitable base, such as a tertiary amine, for example, trimethylamine, triethylamine, N-methylmorpholine, etc., or an inorganic base such as sodium hydroxide.

The reaction is brought about by heating the mixture, usually under reflux, until the reaction is complete. Then

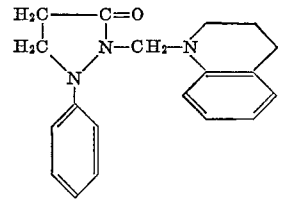
the solvent is evaporated leaving the product which is then recrystallized from suitable solvents including, for example, acetone, ligroin, ethyl acetate, benzene, and other well known solvents to prepare a pure product.

Typical representative 2-substituted-3-pyrazolidones of our invention may be illustrated by the following examples which are not to be considered as limiting our invention.

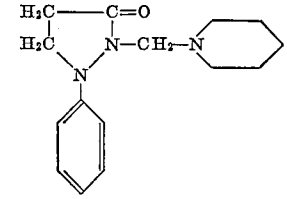
(1) 2-morpholinomethyl-1-phenyl-3-pyrazolidone



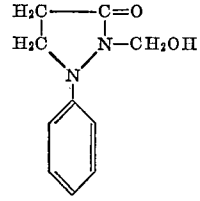
(2) 2-(1,2,3,4-tetrahydroquinolylmethyl) - 1 - phenyl-3-pyrazolidone



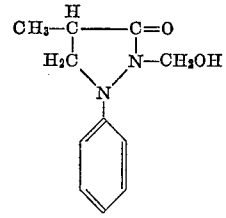
(3) 2-piperidinomethyl-1-phenyl-3-pyrazolidone



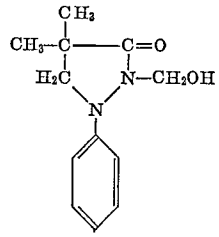
(4) 2-hydroxymethyl-1-phenyl-3-pyrazolidone



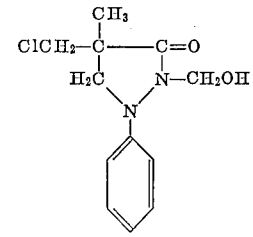
(5) 2-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone



(6) 4,4 - dimethyl-2-hydroxymethyl-1-phenyl-3-pyrazolidone

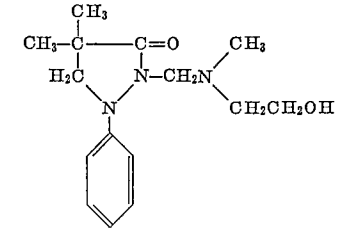


(7) 4 - chloromethyl-2-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone



(8) 1 - morpholinomethyl-4,4-dimethyl-1-phenyl-3-pyrazolidone

(9) 2 - (methyl - β - hydroxyethyl)aminomethyl-4,4-dimethyl-1-phenyl-3-pyrazolidone



(10) 2 - (di - β-hydroxyethyl)aminomethyl-4,4-dimethyl-1-phenyl-3-pyrazolidone

Our invention is further illustrated by Examples 1 through 10 which describe the specific processes used to prepare representative compounds.

EXAMPLE 1

Preparation of 2-morpholinomethyl-1-phenyl-3-pyrazolidone

To 150 ml. of methanol was added 24 ml. of 40 percent formalin and 26.1 ml. of morpholine followed by 48.6 grams of 1-phenyl-3-pyrazolidone. This mixture was refluxed for 2 hours. The methanol was evaporated. The residual oil was triturated with 150 ml. of ligroin (B.P. 90–110°). After about 0.5 hour, the oil had solidified to a mass of white crystals, M.P. 63–64° C.; these were filtered off and dried. Yield 53 grams.

Analysis for $C_{14}H_{19}O_2N_3$:

	C	H	N
Calc'd	64.8	6.9	16.1
Found	64.6	7.1	15.9

EXAMPLE 2

Preparation of 2 - (1,2,3,4 - tetrahydroquinolylmethyl)-1-phenyl-3-pyrazolidone

Tetrahydroquinoline (13.3 ml.) and 8.0 ml. of 40 percent formalin were mixed in 10 ml. of methanol and 16.2 grams of 1-phenyl-3-pyrazolidone added thereto. An additional 60 ml. of ethanol was added. The mixture was heated on the steam bath for 2 hours. The solvent was evaporated. The residue was taken up in acetone, and water was added to turbidity. When crystallization was complete, the product was filtered off and crystallized from ligroin to give white crystals of product M.P. 88° C. Yield 19 grams.

Analysis for $C_{19}H_{20}ON_3$:

	C	H
Calc'd	73.2	6.4
Found	73.4	6.8

EXAMPLE 3

Preparation of 2 - piperidinomethyl - 1-phenyl-3-pyrazolidone

Formalin (8.0 ml.) and 8.6 ml. of piperidine were mixed, then 16.2 grams of 1-phenyl-3-pyrazolidone in 60 ml. of alcohol was added. The mixture was refluxed for 1.5 hours, then allowed to evaporate spontaneously. The crystalline residue was crystallized from ligroin to give 10 grams of product, M.P. 95° C.

Analysis for $C_{15}H_{20}ON_3$:

	C	H	N
Calc'd	69.8	7.8	16.3
Found	69.8	8.1	16.0

EXAMPLE 4

Preparation of 2-hydroxymethyl-1-phenyl-3-pyrazolidone

A mixture of 18 grams of 37 percent formalin, 5 ml. of N-methyl-morpholine, 33 grams of 1-phenyl-3-pyrazolidone, and 200 ml. of ethanol was refluxed 18 hours, and evaporated to dryness. A colorless product with a taffy-like form resulted; it could not be obtained as a solid.

Analysis for $C_{10}H_{12}O_2N_2$:

	C	H	N
Calc'd	62.5	6.2	14.6
Found	62.1	6.2	15.3

In 22 ml. of water the product dissolved at 72° C.

EXAMPLE 5

Preparation of 2 - hydroxymethyl - 4 - methyl-1-phenyl-3-pyrazolidone

A mixture of 18 grams of 37 percent formalin, 5 ml. of triethylamine, 35 grams of 4-methyl-1-phenyl-3-pyrazolidone, and 200 ml. of ethanol was refluxed 18 hours, and evaporated to dryness.

Analysis for $C_{11}H_{14}O_2N_2$:

	C	H	N
Calc'd	64.0	6.8	13.6
Found	63.5	6.9	13.9

Twenty-one grams of the taffy-like product was dissolved in 21 ml. of water and 22 ml. of ethanol (it was not entirely soluble in 21 ml. of water) and used as a 33 percent solution.

EXAMPLE 6

Preparation of 4,4-dimethyl-2-hydroxymethyl-1-phenyl-3-pyrazolidone

A solution of 50 grams of 4,4-dimethyl-1-phenyl-3-pyrazolidone, 25 grams of 37 percent aqueous formaldehyde, 10 ml. of triethylamine, and 100 ml. of ethanol was refluxed 4 hours, evaporated to dryness, and crystallized from 100 ml. of ethyl acetate. The mother liquor was evaporated to dryness, and the residue crystallized from benzene. The two crops blended, yielded 86 percent, 50 grams, of good product, M.P. 118–122° C. A sample crystallized again from ethyl acetate melted at 122–123° C., and mixed with the starting material (M.P. 161–165° C.), melted at 108–130° C.

The infrared spectrum shows a strong hydroxyl band at 3.0.

Analysis for $C_{12}H_{17}O_2N_2$:

	C	H	N
Calc'd	65.6	7.3	12.7
Found	65.3	7.4	13.0

The above reaction was also run using no triethylamine and with sodium hydroxide in place of the amine. Water was used as the solvent in the reaction.

EXAMPLE 7

Preparation of 4-chloromethyl-2-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone

This compound was prepared by the method used in Example 6 but in which 4-chloromethyl-4-methyl-1-phenyl-3-pyrazolidone was used in place of the corresponding 4,4-dimethyl derivative.

The following examples will illustrate the use of our 2-substituted-3-pyrazolidones as developing agents.

EXAMPLE 8

Preparation of 1-morpholinomethyl-4,4-dimethyl-1-phenyl-3-pyrazolidone

To 9.5 g. (0.05 mole) of 4,4-dimethyl-1-phenyl-3-pyrazolidone in a mixture of 40 cc. of ethanol and 40 cc. water, was added 5.0 g. (0.6 mole) morpholine, and 0.8 cc. of 37% formalin. The mixture was warmed and stirred at steam-bath temperature. A clear solution resulted, and after about 30 minutes heating, the clear, solution was cooled when crystallization of an off-white solid occurred. This was filtered off, washed with water and dried. 12.1 g. of product, M.P. 112–115° C. were obtained. Recrystallization from 50% aqueous ethanol gave white crystals, M.P. 116–117.5° C., uncorrected. The compound was identified by I.R. spectrophotometry as the desired product.

EXAMPLE 9

Preparation of 2-(methyl-β-hydroxyethyl)aminomethyl-4,4-dimethyl-1-phenyl-3-pyrazolidone

19.0 (0.1 mole) of 4,4-dimethyl-1-phenyl-3-pyrazolidone was added to a mixture of 50 cc. ethanol and 50 cc. water. 8.0 g. (0.106 mole) of N-methylethanolamine and 10.0 ml. of 37% formalin was added. The mixture was stirred and warmed at steam-bath temperature for about 30 minutes. The clear solution resulting was cooled to 0° C. when crystallization of pinkish crystals occurred. These were removed by filtration, washed with water and dried. 9.5 grams, M.P. 157–162° C., were obtained. Recrystallization from 90% alcohol gave slightly pink crystals, M.P. 165–167° C., uncorrected. Identification was by I.R. spectrophotometry.

EXAMPLE 10

Preparation of 2-(di-β-hydroxyethyl)amino methyl-4,4-dimethyl-1-phenyl-3-pyrazolidone

19.0 g. (0.1 mole) of 4,4-dimethyl-1-phenyl-3-pyrazolidone was added to 100 cc. of 50 percent aqueous ethanol. 11 grams of diethanolamine, and 10 cc. of 37 percent formalin were added, and the resulting mixture warmed at steam-bath temperature for one hour. The reddish-colored solution was cooled to 0° C., when a deposition of slightly off-white crystals occurred. These were filtered on a Buchner, washed with 50 percent ethanol, and dried. 7.0 grams, recrystallized from aqueous ethanol, white prisms, M.P. 119–122° C., uncorrected, were obtained.

EXAMPLE 11

In this example the 2-substituted-3-pyrazolidone was the sole developing agent.

DEVELOPER

4,4-dimethyl-2-hydroxymethyl-1-phenyl-3-pyrazolidone OR	grams	3.52
2-morpholinomethyl-1-phenyl-3-pyrazolidone	grams	4.16
Sodium sulfite (anhydrous)	grams	10.0
Sodium carbonate monohydrate	grams	10.0
Potassium bromide	grams	0.04

Water to make 400 ml.

One part of the above concentrate was diluted with three parts of water. The resulting developer, when used with negative speed film having a silver bromoiodide emulsion, such as Kodak Royal Pan sheet film, produced low contrast (gamma=0.5) negatives of good emulsion speed.

Examples 12 and 13 illustrate the use of our developing agents in combination with other developing agents to produce superadditive effects.

EXAMPLE 12

These 2-substituted-3-pyrazolidones were combined with hydroquinone to produce active developers.

2- or 2,4-, or 2,4,4-substituted 1-phenyl-3-pyrazolidone	0.002	molar.
Hydroquinone	0.02	molar, 0.22 g.
Sodium sulfite (anhydrous)	0.20	molar, 2.5 g.
Sodium carbonate monohydrate	0.20	molar, 2.5 g.

Water to 100 ml.
pH adjusted (with acetic acid) to 10.0±0.05.

As indicated in the following table, the hydroquinone developer was very low in activity, requiring 4 minutes for image formation and 13 minutes for complete development of a sample of sensitometrically exposed fine grained film with a positive speed silver bromoiodide emulsion, such as Kodak Fine Grain Positive Film (density of the third step to equal 2.0). But when hydroquinone was combined with the 2-substituted-3-pyrazolidones of our invention, the image appeared immediately and development was complete in 0.9 to 3.0 minutes in identical samples of the sensitometrically exposed film.

Developing agents used in combination with hydroquinone:	Development time in minutes to develop step 3 to a neutral density of 2.0
Hydroquinone only	13
2 - Morpholinomethyl - 1 - phenyl - 3 - pyrazolidone	0.9–1.1
2-Piperidinomethyl-1-phenyl-3-pyrazolidone	1.1
2-Hydroxymethyl-1-phenyl-3-pyrazolidone	1.1
4 - Methyl-2-morpholinomethyl-1-phenyl-3-pyrazolidone	1.2
2 - Hydroxymethyl - 4-methyl-1-phenyl-3-pyrazolidone	1.2
2 - Bis(hydroxyethyl)aminoethyl - 4 - methyl - 1 - phenyl-3-pyrazolidone	3.0
4,4 - Dimethyl - 2 - morpholinomethyl-1-phenyl-3-pyrazolidone	1.4
4,4 - Dimethyl - 2 - hydroxymethyl - 1 - phenyl-3-pyrazolidone	1.3

EXAMPLE 13

The 3-pyrazolidones of our invention may be used to produce superadditive effects with weak developing agents other than hydroquinone. The conditions in this example were the same as in Example 12, except that ascorbic acid and gallic acid were substituted for hydroquinone, and the pyrazolidone was 2-piperidinomethyl-1-phenyl-3-pyrazolidone.

Weak developing agent (0.02M):	Minutes to develop step 3 to a neutral density of 2.0
Ascorbic acid	1.7
Gallic acid	2.2

No image was produced in these development times when the gallic acid and ascorbic acid were used without the 3-pyrazolidone.

The following example will illustrate the high solubility of our compounds in developer solutions as compared to the corresponding 3-pyrazolidone that is not substituted on the 2 position.

EXAMPLE 14

Increased solubility of 3-pyrazolidone is effected by appropriate substitution in the number 2 position to produce the developing agents of our invention.

The following solubilities are the grams of the 3-pyrazolidone soluble in a liter of a solution composed of 0.02 molar hydroquinone, 0.2 molar sodium sulfite, and 0.2 molar sodium carbonate, of pH 10.1 and at 68° F. The improved solubilities will be seen by comparing II and III with I, V with IV, and VII with VI.

Pyrazolidone:	Solubility (grams per liter)
(I) 1-phenyl-3-pyrazolidone	11.0
(II) 2-piperidinomethyl-1-phenyl-3-pyrazolidone	17.0
(III) 2 - morpholinomethyl - 1 - phenyl-3-pyrazolidone	80.0
(IV) 4-methyl-1-phenyl-3-pyrazolidone	5.5
(V) 2-morpholinomethyl - 4 - methyl-1-phenyl-3-pyrazolidone	50.0
(VI) 4,4-dimethyl-1-phenyl-3-pyrazolidone	2.0
(VII) 2-hydroxymethyl-4,4-dimethyl-1-phenyl-3-pyrazolidone	18.0

EXAMPLE 15

Either the rate of solubility of powdered developer formulations may be increased or a lower mixing temperature used by replacing the conventional 3-pyrazolidones with an appropriate 2-substituted-3-pyrazolidone of our invention. The following table compares two 3-pyrazolidones when substituted in the formula of Example 12.

The 3-pyrazolidone	Temperature, ° C.	Dissolving time, min.
4-methyl-1-phenyl-3-pyrazolidone	56	10
4-methyl-1-phenyl-3-pyrazolidone	33	26
2-piperidinomethyl-1-phenyl-3-pyrazolidone	32	10

EXAMPLE 16

The compounds of our invention, due to their greater solubility, can be used to produce more concentrated liquid developers than possible with other 3-pyrazolidones as is illustrated in the formulas that follow. Concentrated liquid X-ray developer 1 contains 4,4-dimethyl-1-phenyl-3-pyrazolidone at its solubility limit of 3.3 grams/liter while developer 2 contains 7.7 grams/liter of our developing agent 2-hydroxymethyl-4,4-dimethyl-1-phenyl-3-pyrazolidone.

Concentrated developer formula

	1	2
Hydroquinone, g	66.7	66.7
4,4-dimethyl-1-phenyl-3-pyrazolidone, g	3.3	0
2-Hydroxymethyl-4,4-dimethyl-1-phenyl-3-pyrazolidone, g	0	7.7
Sodium bisulfite, g	180.0	180.0
45 percent potassium hydroxide solution, ml	360.0	360.0
Borax, 5 mole, g	33.3	33.3
Potassium bromide, g	33.6	33.6
Potassium iodide, g	0.67	0.67
Water to, ml	1,000.0	1,000.0

For use: Take 100 ml. of the concentrate and (1) add 3.0 grams of sodium bisulfite, (2) dilute with water to 666 ml., and (3) adjust pH to 10.5.

Sensitometrically exposed X-ray film having a coarse grain silver bromoiodide emulsion such as Kodak Blue Brand X-Ray Film was developed in the working developer solutions prepared from the concentrated developer solution 1 and from solution 2, to give each processed film sample a speed of 100. These film samples were washed, fixed, washed and dried in the normal manner and the gamma and fog were determined from the developed images.

Another sample of the same sensitometrically exposed film was developed to a speed of 100 in a developer having the following composition:

Working X-ray developer Formula 3

	Grams
p-Methylaminophenol sulfate	2.2
Hydroquinone	8.8
Sodium sulfite (anhydrous)	72.0
Sodium carbonate (anhydrous)	48.0
Potassium bromide	4.0
Water to 1000 ml.	

The gamma and fog values were determined from this developed image. The following table, Table I, summarizes the development times required to develop the identical film samples to a speed of 100 with the developing agent used in the developer, its concentration, and the gamma and fog produced in the film by development.

TABLE I

Developing agent used with hydroquinone	Concentration of developing agent in—		Dev. time in minutes	Gamma	Fog in density, units
	Concentrated developer, grams/liter	Working developer, grams/liter			
p-Methylaminophenol sulfate		2.2	4.8	2.06	0.19
4,4-dimethyl-1-phenyl-3-pyrazolidone	[1] 3.3	0.5	6.3	2.09	0.25
4,4-dimethyl-2-hydroxymethyl-1-phenyl-3-pyrazolidone	7.7	1.17	4.1	1.78	0.21

[1] Solubility limit.

From the preceding table it can be seen that the working developer solution prepared from a concentrated developer formulation containing 4,4-dimethyl-1-phenyl-3-pyrazolidone at its solubility limit as a developing agent with hydroquinone had only about 76 percent of the developing activity shown by a working solution of a prior art rapid X-ray developer containing p-methylaminophenol sulfate with hydroquinone while the working developer solution prepared from the concentrated developer containing our developing agent 4,4-dimethyl-2-hydroxymethyl-1-phenyl-3-pyrazolidone with hydroquinone gave a developing activity about 16 percent greater than the activity of prior art rapid X-ray developer. Our concentrated developer formulation has the big advantage over the prior art rapid X-ray developer of giving tremendous saving in shipping weight as well as in storage space requirements since one part of the concentrate will produce 6.6 parts of the working developer.

It is very unexpected that the 2-substituted-3-pyrazolidones of our invention are active developing agents. 2-methyl-1-phenyl-3-pyrazolidone, for example, has no developing activity at all while 2-hydroxymethyl-1-phenyl-3-pyrazolidone of our invention has good developing activity.

Not only do the 2-substituents used on our developing agents give greatly increased solubility without loss in developer activity as has been demonstrated herein, but these substituents produce developers which are characterized by having greatly reduced fogging action in the photographic developing process. This is illustrated in the following examples.

EXAMPLE 17

Developer solutions were prepared from the following stock solution:

	Grams
Sodium sulfite (desiccated)	25.0
Sodium metaborate octahydrate	33.9
Potassium bromide	0.5
Hydroquinone	10.0
Water, distilled to 1 liter.	
Adjust pH to 10.0.	

Developing agent	Concentrate	Stock solution added, ml.
(A) 4,4-dimethyl-1-phenyl 3-pyrazolidone.	0.4 g. (.002 mole) in 10 ml. methanol.	500
(B) 4,4-dimethyl-2-hydroxymethyl-1-phenyl-3-pyrazolidone.	0.46 g. (.002 mole) in 10 ml. methanol.	500
(C) 4,4-dimethyl-2-morpholinomethyl-1-phenyl-3-pyrazolidone.	0.61 g. (.002 mole) in 10 ml. methanol.	500

The developer solutions were cooled to 68° F. and used to develop high silver bromide content industrial X-ray film strips equally exposed. The strips were placed in developer solution which was agitated for 15 secs. After 5 minutes at 68° F., the strips were fixed, washed, and dried.

The following results were obtained:

Developing agent	Fog	Step No. 3	Step No. 11
A	0.33	.50	1.75
B	0.25	.45	1.75
C	0.21	.45	1.63

These data show that equimolar concentrations of 4,4 - dimethyl-2-hydroxymethyl-1-phenyl-3-pyrazolidone and 4,4-dimethyl-2-morpholinomethyl-1-phenyl-3-pyrazolidone develop latent image at about the same rate as 4,4-dimethyl - 1 - phenyl-3-pyrazolidone, giving comparable densities in the middle density range but with appreciably less fog.

EXAMPLE 18

Developers were prepared having the following composition.

Constituent:	Composition of developer in grams
1-phenyl-3-pyrazolidone	1.5
Hydroquinone	25.0
Sodium sulfite (anhydrous)	60.0
Sodium metaborate.$8H_2O$	35.0
Ethylenediamine tetracetic acid tetrasodium salt	5.0
Potassium bromide	5.0
Glutaraldehyde bis(sodium bisulfite)	15.0
5-methylbenzotriazole	0.12
Water to 1 liter.	

(pH of developer solution adjusted with NaOH to ±0.1 of the desired level.)

An unexposed sample of high silver bromide content industrial X-ray film was developed for 5 minutes in the above developer solution at a pH of 9.6 at 75° F. Other film samples were processed in other samples of this developer which had been adjusted to a pH of 9.8, and a pH of 10.0. This was repeated with other samples of the same film but using a developer at the pH of 9.6 and 9.8 and in which the 1-phenyl-3-pyrazolidone was substituted at the 2 position with a hydroxymethyl group. The series was repeated using a developer with 1-phenyl-3-pyrazolidone substituted on the 2 position with a morpholinomethyl group in a developer with a pH of 9.6, 9.8 and 10.0. The following table summarizes the fog density measurements made on these samples of film.

2-substituent on the 1-phenyl-3-pyrazolidone developing agent	Fog	pH
None	0.2	9.6
Hydroxymethyl	0.27	9.6
Morpholinomethyl	0.14	9.6
None	0.9	9.8
Hydroxymethyl	0.6	9.8
Morpholinomethyl	0.26	9.8
None	2.0	10.0
Morpholinomethyl	0.34	10.0

The valuable low fogging characteristic of our developer solutions is apparent from this table. For example, an increase in pH from 9.6 to 10.0 in the prior art developer produced a 10 fold increase in fog while our developer containing 2 - morpholinomethyl-1-phenyl-3-pyrazolidone produced only about a 2.4 fold increase in fog for the same pH change.

The novel 2 - substituted-3-pyrazolidone developing agents of our invention can be used to advantage in developer compositions used for developing any photographic emulsion layers containing silver halide such as silver chloride, silver bromide, silver iodide, silver chlorobromide, silver bromoiodide, silver chlorobromoiodide, etc. Our developer compositions may contain a 2-substituted-3-pyrazolidone as the sole developing agent or may contain this developing agent in combination with other developing agents to give superadditive effects or to give other desired effects. Other developing agents which are commonly used with the developing agents of our invention include the following: hydroquinone; hydroquinone substituted on the 2, 3, 5, or 6 carbons or any combination of these with lower alkyl groups such as methyl, ethyl, propyl, butyl, etc., with alkoxy groups, halogen atoms, such as chlorine, bromine, fluorine etc. and with other groups commonly used as substituents; resorcinol; catechol; ascorbic acid; gallic acid; the aminophenols such as p-methylaminophenol sulfate; the phenylenediamines; etc. In addition to the developing agent or agents, our developer usually contains an alkali such as sodium carbonate, potassium carbonate, trisodium phospate, sodium pyroborate, sodium metaborate, sodium hydroxide, potasium hydroxide, etc. Our compositions may contain a preservative such as an alkali sulfite, for example, sodium sulfite, potassium sulfite, etc., an alkali bisulfite, such as sodium bisulfite, potassium bisulfite, etc., an alkali metabisulfite, such as sodium metabisulfite, potassium metabisulfite, etc. Other material may be added to our developer compositions such as the sequestering agents of Henn, U.S. 2,625,476, issued January 13, 1952, and Henn et al., U.S. 2,656,273, issued October 20, 1953; the stabilizers of Haist et al., U.S. 2,875,048, issued February 24, 1959; antifoggants commonly used such as benzotriazole; development restrainers such as the alkali bromides, iodides, etc.; and other addenda commonly used.

Our novel 2-substituted-3-pyrazolidones are particularly valuable for preparing concentrated developer solutions. Their high solubility in developer solutions makes it possible to use them over a wide range of concentrations as well as at concentrations as much as 9 times greater than possible with the corresponding prior art 3-pyrazolidones.

The developing agents of our invention are incorporated in dry powder developer compositions of the types described by Kridel et al., U.S. Patents 2,666,702 and 2,666,703, issued January 19, 1954; Wiitala et al., U.S. Patents 2,682,464 and 2,682,465, issued June 29, 1954; Henn et al., U.S. Patent 2,685,513, issued August 3, 1954; and Baxendale et al., U.S. Patent 2,816,026, issued December 10, 1957. The dry compositions contain in addition to the developing agent, an alkali, and a preservative such as described previously and may contain any of the other addenda described. A sufficient amount of each of these dry chemicals is used in making the compositions so that the solutions prepared from them have the desired concentrations.

Our developing agents are also incorporated in combined dry developer and fixer compositions. For this purpose any fixing agent available in a dry form such as an alkali thiosulfate, for example, sodium thiosulfate, potassium thiosulfate, etc., is incorporated in any of the dry developer compositions described above.

Our developing agents are valuable for incorporation in silver halide emulsion layers or in layers contiguous to silver halide emulsion layers. These developing agents may be the sole developing agent or they may be used in conjunction with other developing agents for development of the emulsion layer. Photographic elements incorporating our developing agents are designed for different development processes. For example, some of them are designed for developing by the mere application of aqueous alkaline solution. Other elements may have alkaline material incorporated in them so that development may be accomplished simply by applying water or by heating the element so as to make available for development, moisture that is already in the element. Still other elements may require for development the application of a conventional aqueous developer solution which contains the same or a different developing agent, alkali, a developer preservative and other conventional developer addenda.

Our developing agents are particularly advantageous for incorporating in photographic elements where short development times are required since our novel 2-substituted-3-pyrazolidones are characterized by rapid development acceleration. The following example illustrates the incorporation of a typical developer in a photographic emulsion, however, it is to be understood that our invention is not to be limited to this one example.

EXAMPLE 19

Samples of washed silver bromide gelatin emulsion were provided. To the respective samples of melted emulsion were added aqueous solutions of the 3-pyrazolidone compounds indicated in the following table. The samples were coated successively on a paper stock and dried. The samples were then given continuous wedge exposures and developed for 20, 45, and 60 seconds, development being carried out at 68° F. in a developer having the following composition.

Water	ml	500
p-Methylaminophenol sulfate	g	3.0
Sodium sulfite, desiccated	g	45.0
Hydroquinone	g	12.0
Sodium carbonate, monohydrated	g	80.0
Potassium bromide	g	2.0

Water to make 2.5 g.

Sensitometric evaluation of the developed samples produced the data tabulated in the following table. In considering the data, the comparison of development acceleration effect of using the 3-pyrazolidone compounds in the emulsions should be made between samples developed for 20 seconds since an acceleration effect is more pro-

nounced in early stages of development. It is apparent from the data that the development acceleration effect from 4,4 - dimethyl-2-hydroxymethyl-1-phenyl-3-pyrazolidone is more pronounced than that from 4,4-dimethyl-1-phenyl-3-pyrazolidone.

TABLE II

Addendum	Concentration, mg. per mole silver halide	Bar Gamma Development Time in seconds			D_{max} Development Time in Seconds		
		20	45	60	20	45	60
4,4-dimethyl-1-phenyl-3-pyrazolidone	1,750	.97	1.95	2.03	1.00	1.41	1.45
4,4-dimethyl-2-hydroxymethyl-1-phenyl-3-pyrazolidone	1,750	1.13	2.01	2.01	1.08	1.39	1.42

The development acceleration effect produced by 4,4-dimethyl - 2 - hydroxymethyl-1-phenyl-3-pyrazolidone is most pronounced at 20 seconds development where it will be noted that 16.5% higher gamma is obtained than is obtained with an emulsion incorporating 4,4-dimethyl-1-phenyl-3-pyrazolidone.

Similarly other 2-substituted-3-pyrazolidone developing agents of our invention are incorporated to advantage in light sensitive silver halide emulsion layers. These layers can contain silver chloride, silver bromide, silver iodide, silver chlorobromide, silver bromoiodide, etc., sensitized or unsensitized and may contain any of the addenda commonly used in making developer incorporating emulsions such as alkali sulfites, antifogging agents, etc.

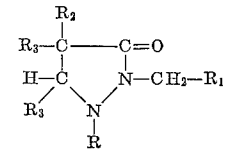
Our novel 2-substituted-3-pyrazolidone developing agents are valuable for use in the porous layer of processing elements used to carry the photographic developing or developing and fixing chemicals for web processing. Such processing elements and web processes using these elements are described in the copending Tregillus et al. U.S. Serial No. 835,473 filed August 24, 1959. Our developing agents are incorporated in the porous hydrophilic colloid layer of the processing element either alone or with other chemicals that are needed for development or development and fixing. When only the developing agent is incorporated in the colloid layer, the other chemicals may be added to this layer by soaking it just before use with a solution of either all or part of the requisite chemicals, while the rest of the chemicals are incorporated in the photographic element so the requisite chemicals are available for processing when the photographic element and processing element are contacted in the presence of water. Our developing agents, for example, are substituted for the 1-phenyl-3-pyrazolidone, 4,4-dimethyl-1-phenyl-3-pyrazolidone and other developing agents used in the processing elements of U.S. Serial No. 835,473.

Our novel class of 2-substituted-3-pyrazolidone developing agents includes the 2-hydroxyalkyl-1-phenyl-3-pyrazolidones which are prepared by reacting the appropriate 1-phenyl-3-pyrazolidone with formaldehyde, preferably in a single phase medium made alkaline with a suitable inorganic alkali such as an alkali metal hydroxide or an organic base such as a *tertiary amine*, and includes the 2-aminoalkyl-1-phenyl-3-pyrazolidones which are prepared by reacting the appropriate 1-phenyl-3-pyrazolidone with formaldehyde and the appropriate *secondary amine*. These 2-substituted-3-pyrazolidones are characterized by having water solubilities that are up to 8 or 9 times the solubilities of the corresponding prior art 3-pyrazolidones. Our developing agents are further characterized by having developing activities that are comparable to the corresponding prior art compounds that are unsubstituted in the 2 position. These valuable properties characterizing our developing agents are quite unexpected since previous attempts to increase the solubility of prior art 3-pyrazolidones have produced either inactive compounds or compounds having low developing activity. 2-methyl-1-phenyl-3-pyrazolidone, for example, is inert, producing no photographic development when used in a developer solution. It is particularly unexpected to find that 2-hydroxymethyl-1-phenyl-3-pyrazolidone has good developing activity that is comparable to that of 1-phenyl-3-pyrazolidone. Some of our developing agents are still further characterized by producing developed film with substantially lower fog than is produced by the corresponding 1-phenyl-3-pyrazolidone developer, particularly at high pH levels. Our novel developing agents are valuable for use in photographic developer solutions particularly when they must be used at high concentrations such as in concentrated developer solutions, in dry developer, and in dry combined developer-fixer compositions. Our 2-substituted-3-pyrazolidone developing agents are valuable for incorporation in light-sensitive silver halide emulsion layers. These emulsion layers are characterized by having substantially higher development rates than the corresponding prior art emulsion layers.

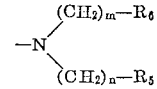
The invention has been described in detail with particular reference to preferred embodiments thereof but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. An alkaline photographic developer solution containing a compound having the formula:

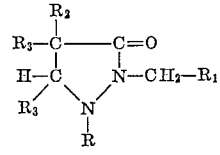


in which R is an aryl group having from 6 to 10 carbon atoms; R_1 is a member selected from the class consisting of the hydroxyl group and a

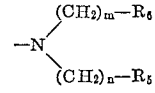


group in which n is an integer of from 1 to 6, and m is an integer of from 1 to 6 such that the sum of $n+m$ is an integer of from 2 to 6; R_5 and R_6 are each selected from the group consisting of hydrogen, hydroxyl and together with the (CH_2) groups and the nitrogen atom form a member selected from the group consisting of pyrrolidino, lower alkyl substituted pyrrolidino, piperidino, lower alkyl substituted piperidino, N-lower alkylpiperazino, morpholino, lower alkyl substituted morpholino, 1,2,3,4-tetrahydroquinolino and lower alkyl substituted 1,2,3,4-tetrahydroquinolino, in which the said lower alkyl groups have from 1 to 4 carbon atoms; and R_2, R_3 and R_4 are each selected from the group consisting of hydrogen, alkyl of 1 to 4 carbon atoms and phenyl.

2. A photographic developer in dry form comprising an alkaline material and a compound having the formula:

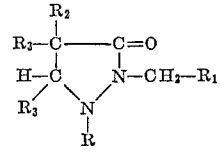


in which R is an aryl group having from 6 to 10 carbon atoms; R_1 is a member selected from the class consisting of the hydroxyl group and a

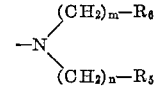


group in which n is an integer of from 1 to 6, and m is an integer of from 1 to 6, such that the sum of $n+m$ is an integer of from 2 to 6; R_5 and R_6 are each selected from the group consisting of hydrogen, hydroxyl and together with the (CH_2) groups and the nitrogen atom form a member selected from the group consisting of pyrrolidino, lower alkyl substituted pyrrolidino, piperidino, lower alkyl substituted piperidino, N-lower alkylpiperazino, morpholino, lower alkyl substituted morpholino, 1,2,3,4-tetrahydroquinolino, and lower alkyl substituted 1,2,3,4-tetrahydroquinolino, in which the said lower alkyl groups have from 1 to 4 carbon atoms; and R_2, R_3 and R_4 are each selected from the group consisting of hydrogen, alkyl of 1 to 4 carbon atoms and phenyl.

3. A combined photographic developer and fixer in dry form containing (1) a compound having the formula:

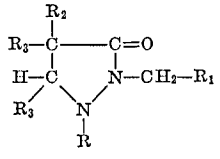


in which R is an aryl group having from 6 to 10 carbon atoms; R_1 is a member selected from the class consisting of the hydroxyl group and a

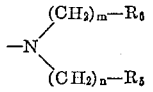


group in which n is an integer of from 1 to 6, and m is an integer of from 1 to 6 such that the sum of $n+m$ is an integer of from 2 to 6; R_5 and R_6 are each selected from the group consisting of hydrogen, hydroxyl and together with the (CH_2) groups and the nitrogen atom form a member selected from the group consisting of pyrrolidino, lower alkyl substituted pyrrolidino, piperidino, lower alkyl substituted piperidino, N-lower alkylpiperazino, morpholino, lower alkyl substituted morpholino, 1,2,3,4-tetrahydroquinolino and lower alkyl substituted 1,2,3,4-tetrahydroquinolino, in which the said lower alkyl groups have from 1 to 4 carbon atoms; and R_2, R_3 and R_4 are each selected from the group consisting of hydrogen, alkyl of 1 to 4 carbon atoms and phenyl, (2) an alkaline material, and (3) a fixing agent.

4. A light-sensitive silver halide emulsion layer containing a compound having the formula:

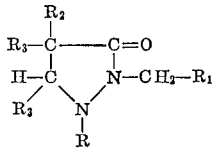


in which R is an aryl group having from 6 to 10 carbon atoms; R_1 is a member selected from the class consisting of the hydroxyl group and a

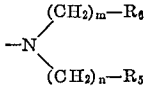


group in which n is an integer of from 1 to 6, and m is an integer of from 1 to 6 such that the sum of $n+m$ is an integer of from 2 to 6; R_5 and R_6 are each selected from the group consisting of hydrogen, hydroxyl and together with the (CH_2) groups and the nitrogen atom form a member selected from the group consisting of pyrrolidino, lower alkyl substituted pyrrolidino, piperidino, lower alkyl substituted piperidino, N-lower alkylpiperazino, morpholino, lower alkyl substituted morpholino, 1,2,3,4-tetrahydroquinolino and lower alkyl substituted 1,2,3,4-tetrahydroquinolino, in which the said lower alkyl groups have from 1 to 4 carbon atoms; and R_2, R_3 and R_4 are each selected from the group consisting of hydrogen, alkyl of 1 to 4 carbon atoms and phenyl.

5. A photographic element comprising a support and at least two water-permeable, hydrophilic colloid layers, at least one of said layers containing photosensitive silver halide and at least one of said layers containing a compound having the formula:

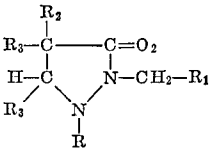


in which R is an aryl group having from 6 to 10 carbon atoms; R_1 is a member selected from the class consisting of the hydroxyl group and a

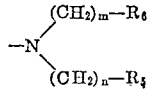


group in which n is an integer of from 1 to 6, and m is an integer of from 1 to 6 such that the sum of $n+m$ is an integer of from 2 to 6; R_5 and R_6 are each selected from the group consisting of hydrogen, hydroxyl and together with the (CH_2) groups and the nitrogen atom form a member selected from the group consisting of pyrrolidino, lower alkyl substituted pyrrolidino, piperidino, lower alkyl substituted piperidino, N-lower alkylpiperazino, morpholino, lower alkyl substituted morpholino, 1,2,3,4-tetrahydroquinolino and lower alkyl substituted 1,2,3,4-tetrahydroquinolino, in which the said lower alkyl groups have from 1 to 4 carbon atoms; and R_2, R_3 and R_4 are each selected from the group consisting of hydrogen, alkyl of 1 to 4 carbon atoms and phenyl.

6. A photographic processing web comprising at least one hydrophilic colloid layer containing a compound having the formula:



in which R is an aryl group having from 6 to 10 carbon atoms; R_1 is a member selected from the class consisting of the hydroxyl group and a



group in which n is an integer of from 1 to 6, and m is an integer of from 1 to 6 such that the sum of $n+m$ is an integer of from 2 to 6; R_5 and R_6 are each selected from the group consisting of hydrogen, hydroxyl and together with the (CH_2) groups and the nitrogen atom form a member selected from the group consisting of pyrrolidino, lower alkyl substituted pyrrolidino, piperidino, lower alkyl substituted piperidino, N-lower alkylpiperazino, morpholino, lower alkyl substituted morpholino, 1,2,3,4-tetrahydroquinolino and lower alkyl substituted 1,2,3,4-tetrahydroquinolino, in which the said lower alkyl groups have from 1 to 4 carbon atoms; and R_2, R_3 and R_4 are each selected from the group consisting of hydrogen, alkyl of 1 to 4 carbon atoms and phenyl.

7. An alkaline photographic developer solution containing 2-morpholinomethyl-1-phenyl-3-pyrazolidone.

8. An alkaline photographic developer solution containing 2-piperidinomethyl-1-phenyl-3-pyrazolidone.

9. An alkaline photographic developer solution containing 2-hydroxymethyl-1-phenyl-3-pyrazolidone.

10. An alkaline photographic developer solution containing 4-methyl-2-morpholinomethyl-1-phenyl-3-pyrazolidone.

11. An alkaline photographic developer solution containing 4,4-dimethyl-2-hydroxymethyl-1-phenyl-3-pyrazolidone.

12. A light-sensitive silver halide emulsion layer containing 2-morpholinomethyl-1-phenyl-3-pyrazolidone.

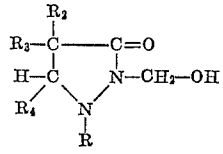
13. A light-sensitive silver halide emulsion layer containing 2-piperidinomethyl-1-phenyl-3-pyrazolidone.

14. A light-sensitive silver halide emulsion layer containing 2-hydroxymethyl-1-phenyl-3-pyrazolidone.

15. A light-sensitive silver halide emulsion layer containing 4-methyl-2-morpholinomethyl-1-phenyl-3-pyrazolidone.

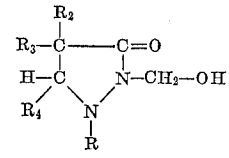
16. A light-sensitive silver halide emulsion layer containing 4,4-dimethyl-2-hydroxymethyl-1-phenyl-3-pyrazolidone.

17. An alkaline photographic developer solution containing a compound having the formula:



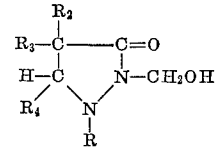
in which R is a member selected from the class consisting of phenyl, tolyl, methoxyphenyl, aminophenyl, chlorophenyl, hydroxyethylphenyl, hydroxyphenyl, acetamidophenyl, diphenyl, and 7-hydroxy-2-naphthyl; and R_2, R_3 and R_4 are each selected from the class consisting of hydrogen, a phenyl, a naphthyl, and an alkyl of 1 to 4 carbon atoms substituted by a group selected from the class consisting of hydrogen, hydroxy, methoxy, phenoxy, amino, methylamino, sulfo, carboxy, chloro, and bromo.

18. A light-sensitive silver halide emulsion layer containing a compound having the formula:



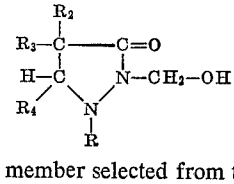
in which R is a member selected from the class consisting of phenyl, tolyl, methoxyphenyl, aminophenyl, chlorophenyl, hydroxyethylphenyl, hydroxyphenyl, acetamidophenyl, diphenyl, and 7-hydroxy-2-naphthyl; and R_2, R_3 and R_4 are each selected from the class consisting of hydrogen, a phenyl, a naphthyl, and an alkyl of 1 to 4 carbon atoms substituted by a group selected from the class consisting of hydrogen, hydroxy, methoxy, phenoxy, amino, methylamino, sulfo, carboxy, chloro, and bromo.

19. A photographic element comprising a support and at least two water-permeable, hydrophilic colloid layers, at least one of said layers containing photosensitive silver halide and at least one of said layers containing a compound having the formula:



in which R is a member selected from the class consisting of phenyl, tolyl, methoxyphenyl, aminophenyl, chlorophenyl, hydroxyethylphenyl, hydroxyphenyl, acetamidophenyl, diphenyl, and 7-hydroxy-2-naphthyl; and R_2, R_3 and R_4 are each selected from the class consisting of hydrogen, a phenyl, a naphthyl, and an alkyl of 1 to 4 carbon atoms substituted by a group selected from the class consisting of hydrogen, hydroxy, methoxy, phenoxy, amino, methylamino, sulfo, carboxy, chloro, and bromo.

20. A photographic processing web comprising at least one hydrophilic colloid layer containing a compound having the formula:



in which R is a member selected from the class consisting of phenyl, tolyl, methoxyphenyl, aminophenyl, chlorophenyl, hydroxyethylphenyl, hydroxyphenyl, acetamidophenyl, diphenyl, and 7-hydroxy-2-naphthyl; and R_2, R_3 and R_4 are each selected from the class consisting of hydrogen, a phenyl, a naphthyl, and an alkyl of 1 to 4 carbon atoms substituted by a group selected from the class consisting of hydrogen, hydroxy, methoxy, phenoxy, amino, methylamino, sulfo, carboxy, chloro, and bromo.

No references cited.

NORMAN G. TORCHIN, *Primary Examiner.*