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3,364,029

PHOTOGRAPHIC ANTIHALATION COMPONENTS

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20 Claims. (Cl. 96-84)

This invention concerns antihalation layer components which provide light absorbent material which can be destroyed or removed by normal photographic processing.

It is desirable in photographic products to have some form of antihalation layer which absorbs light to avoid undesirable reflections from the film base or interfaces between the emulsion layer and the film base, causing additional exposure of the silver halide emulsion. In a conventional method, an antihalation layer containing pigments or dyes which can be easily removed in an alkaline solution, is coated on the reverse side of the film base. Normal processing in an alkaline developer solution causes the antihalation layer to be dissolved. However, when the alkaline soluble material, used as a carrier for the antihalation dye or pigment, is dissolved, this results in contamination of the developer solution.

The neutral density, which is desired, has usually required two or three dyes to obtain a neutral absorption of the light across the spectrum. This is particularly important in color processes requiring a neutral density layer such as that disclosed in Millikan U.S. application Ser. No. 159,057, filed Dec. 13, 1961, now abandoned.

In some photographic elements substances have been added directly to the silver halide emulsion, such as carbon black or other pigments which serve to absorb light, but these materials are not easily removed and add to the overall density of the processed photographic element. This type of antihalation material is used in photographic products where the support is opaque, such as paper, aluminum or similar material.

It has been desirable to find a material with a neutral color which would act as an antihalation material which can be added either to the emulsion itself or to an undercoating, but which could be removed or destroyed during normal photographic processing without contaminating the processing solution. However, such a material would have to be compatible with a light sensitive coating such as a silver halide emulsion and should not appreciably affect the speed of the emulsion when incorporated directly therein or utilized contiguous thereto.

We have found that oxodi-(8-quinolyloxo)-vanadic (V) acid (commonly called vanadium oxinate) can be used as an antihalation agent.

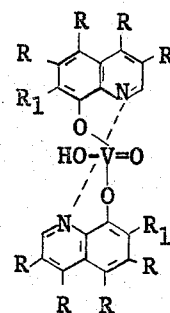
One object of this invention is to provide an antihalation material which provides a light absorbing substance which can be removed in an alkaline solution. Another object is to provide a photographic element having an incorporated antihalation layer in which the light absorbing material can be removed during normal photographic processing. A further object is to provide an antihalation material which is compatible with a light sensitive silver halide emulsion and which does not have an appreciable effect on the speed of the silver halide emulsion when used as an undercoat for antihalation purposes. A still further object is to provide a method of obtaining antihalation protection for a light sensitive element on the same side of the support as the silver halide emulsion. Additional objects will be apparent from the following disclosure.

In carrying out our invention, we employ an 8-hydroxyquinoline vanadium complex. In our preferred embodiment, the vanadium oxinate, dispersed in a water permeable colloid such as gelatin, or other hydrophilic mate-

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rials, such as collodion, albumin, cellulose derivatives, certain synthetic resins (polyvinyl alcohol) and the like, is used as an undercoat. Over this material is coated the light sensitive silver halide emulsion. When the exposed light sensitive emulsion is developed in an alkaline solution, the vanadium oxinate loses its color. For some purposes, the vanadium oxinate may also be incorporated directly in the emulsion. It may be used as an overcoat for providing an overall density or when exposure is to be made through the support.

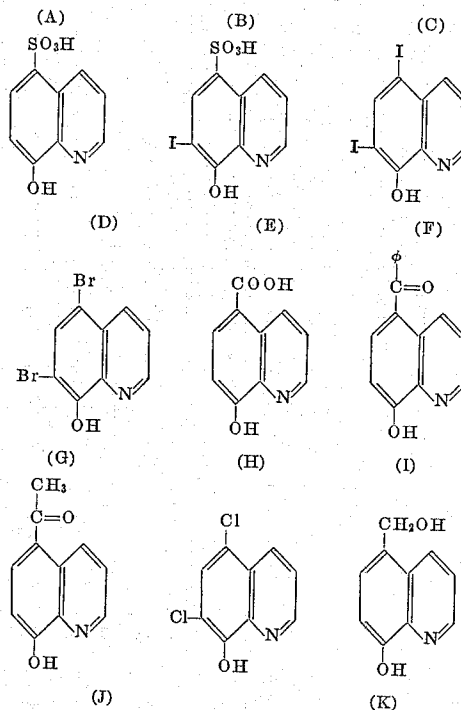
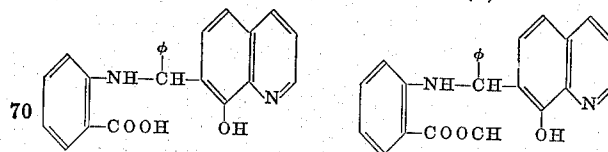
The following generic formula illustrates the vanadium complexes which can be used:



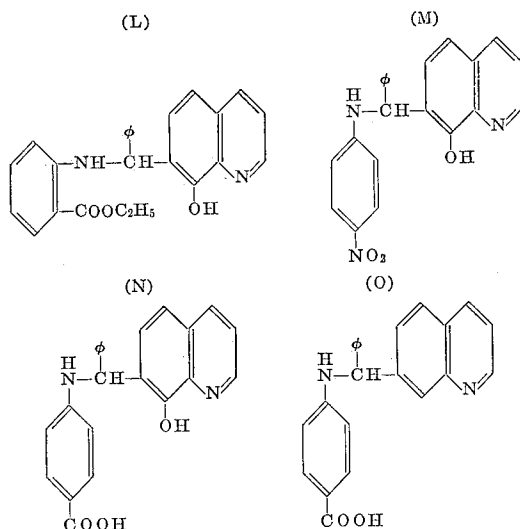
R may be the same or different and represents H, SO₃H, halogen, carboxy, acyl, substituted acyl, alkyl (1-20 carbon atoms), aryl, etc.

R₁ represents the same group as R but also α -anilino-benzyl and substituted α -anilino-benzyl.

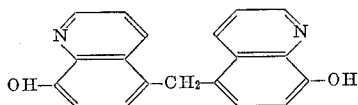
The following 8-hydroxyquinoline derivatives are typical of those, for example, which form complexes with vanadium (V), which can be used as removable antihalation layers:



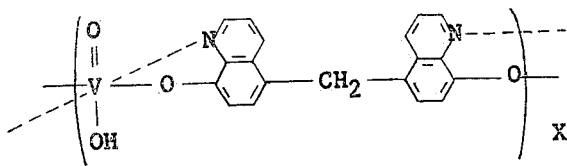
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Polymeric complexes may also be utilized for antihalation protection. For example:



5,5'-methylene bis(8-hydroxyquinoline) yields the following complex in which X represents an integer greater than 1:



Any bifunctional group that doesn't destroy the color of the pigment may be substituted for the $-\text{CH}_2-$ in linking the two hydroxyquinoline rings.

A useful amount of from 5 mg. to 2.5 grams per square foot of the vanadium oxinate may be employed in the gelatin-undercoat. However, more or less of the material may be utilized depending on the density required and the ability to remove the material during the processing cycle.

The particular supports are not critical and include those known in the art, including paper, glass, metal, polymeric materials such as cellulose acetate, polyesters, polystyrene, polyolefins, polyamides, etc. The light sensitive silver halide may be conventional silver salts such as silver chloride, silver bromide, silver iodide, silver chlorobromide, silver chloroiodide, silver bromoiodide and silver bromochloroiodide.

It will also be understood that this antihalation material can be used in an undercoat or in any layer of a multi-layer system. It may be used with advantage in a diffusion transfer system where the light sensitive emulsion is coated on a paper support or in a system wherein a silver halide emulsion is coated over a nucleated layer and the light sensitive emulsion removed following exposure, development and formation of a positive image in the nucleated layer. It may also be used in colloid transfer systems and in the formation of lithographic plates where the emulsion is coated on a support which does not permit the use of an antihalation layer which must be removed in its entirety.

It will be appreciated that the particle size of the pigment is not critical but depends upon the desired dispersion, the method of dispersing the pigment, such as, for instance, whether it is in a contiguous layer, in the light sensitive composition, etc., or the like. A useful average particle size is from 1-2 microns and the pigment may be obtained by any of the conventional methods of preparing pigments such as by precipitation, ball-milling, etc.

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It will also be appreciated that the light sensitive emulsions which can be used with the antihalation material of this invention may be sensitized chemically, spectrally, etc., employing compounds known in the art for these purposes.

The antihalation layers of this invention can be used where such layers are useful, under any light sensitive materials. For instance, they can be used under light sensitive materials such as those shown in U.S. Patent 2,548,537, Example 2, and U.S. Patent 2,791,504, column 5, lines 39-62.

The antihalation compounds of this invention can be used, for example, under light sensitive azide polymer layers such as those described in U.S. Patent 2,948,610; light sensitive cinnamic acid ester polymers described in U.S. Patent 2,690,966; bichromate sensitized materials such as those described in U.S. Patent 2,448,861; the light sensitive layers described in U.S. Patent 3,038,800 and in the product described in U.S. Patent 2,607,683.

The following examples are intended to illustrate our invention but not to limit it in any way.

Example 1

To a stirred solution of 75 ml. of 10% gelatin solution at 40° C. was added a solution of 3 grams of 8-hydroxyquinoline in 50 ml. of ethanol followed by a warm solution of 1.3 grams of sodium metavanadate in 25 ml. of water. The pH of the solution then was lowered to between 5 and 6 by addition of 60% aqueous citric acid. As this was done, the black vanadium complex formed as a dispersion in the gelatin solution. The dispersion was coated at various thicknesses on a thin base. A sample of dispersion diluted 1:1 with 5% gelatin solution was coated on cellulose acetate film base at approximately 10 ml./ft.² to give a layer with a diffuse transmission density of 0.72. A sample of this coating was immersed in Kodak Developer D-72 at room temperature for two minutes, washed with a little water, immersed in acid sodium thiosulfate fix and then given a final wash. This treatment reduced the transmission density to 0.06.

Example 2

A warm dispersion prepared as in Example 1 was chilled, noodled, and washed one hour after it had been kept one hour at room temperature. This dispersion was diluted with one part of 5% gelatin solution and coated as in the first example. A sample coated at approximately 10 ml./ft.² had a diffuse transmission density of 0.79. Immersion of this coating in Kodak Developer D-72 and fix as described above reduced the transmission density to 0.12.

Example 3

(A) A solution of 14.2 grams of 8-hydroxyquinoline in 200 ml. of alcohol and a solution of 6.0 grams of sodium meta-vanadate in 135 ml. of water were added to 300 grams of 10% gelatin at 40° C. The pH was lowered to 5.0 by slow dropwise addition of 2N sulfuric acid. The resulting dispersion of black complex was stirred 5 minutes at 40° C. before chilling. After the gelatin was set the dispersion was noodled and washed for five hours. The washed noodles were melted, 50 grams of 10% gelatin was added and the dispersion was diluted to 1500 ml. with water. This composition was coated on a clear film base at 6.4 g./ft.² to give a density of 0.34. The film was overcoated with a fine-grain silver chlorobromide gelatin emulsion at 190 mg. Ag/ft.² and 222.5 mg. gelatin/ft.².

(B) 6.75 grams of 8-hydroxyquinoline-5-sulfonic acid was suspended in 100 ml. of water. Sodium hydroxide solution was added to bring the pH to 7.2 and a solution of ferric ammonium citrate (3.1 grams in 4.5 ml. of water) was added. After stirring for one hour at 20° C., the pH was steady at 6.0. The deep colored so-

lution was filtered and evaporated to dryness under a vacuum to yield 9.0 grams of ferric complex of 8-hydroxyquinoline-5-sulfonic acid. To 34 ml. of an aqueous solution containing 2 grams of the ferric complex of 8-hydroxyquinoline-5-sulfonic acid was added 200 grams of 10% gelatin. The resulting solution was diluted to 500 ml. and coated on a film base at 11.3 grams per square foot to give a layer of a density of 0.20. A fine grain silver chlorobromide emulsion was coated over the layer as in part A.

The same chlorobromide emulsion was coated on a transparent film base with a conventional antihalation backing on the reverse side as a control. The antihalation layer contained a dispersion of carbon black in a binder which remains stabilized in an alkaline developer solution and was removed in solution. After exposure of samples of each coating on an Eastman Ib Sensitometer, the strips were developed in the following developer for 2 minutes at 80° F.

	Grams
Elon (N-methyl-p-aminophenol sulfate) -----	2.2
Na ₂ SO ₃ (anhydrous) -----	72.0
Hydroquinone -----	8.8
Na ₂ CO ₃ (anhydrous) -----	130.0
KBr -----	4.0
H ₂ O to make 1 liter.	

The following results were obtained:

	Relative Speed	Contrast
Control.....	100	2.2
A.....	82	1.9
B.....	12.3	1.86

The pigment of the invention can also be coated in a layer which contains a synthetic vehicle along with gelatin. The pigment is decolorized and washed out of a synthetic vehicle-gelatin layer just as it is in an all gelatin layer.

The ferric compound is soluble and, therefore, is not readily dispersed in a light sensitive coating. Moreover, the iron compound does not have a neutral color but was greenish, which is generally unsatisfactory for photographic purposes. When used with a light sensitive silver halide emulsion, the iron compound desensitizes the emulsion as is evident from the above table.

Example 4

A coating on a clear base of vanadium oxinate in a layer containing two parts of the polymer latex of copoly-(butyl acrylate-acrylic acid) (90:10 weight ratio) to one part of gelatin was prepared so that a density of 0.68 resulted. A sample of this coating was processed for two minutes at 80° C. in a Metol-hydroquinone developer followed by two minutes in acid sodium thiosulfate fix and then was washed for 30 minutes. The density of the sample was reduced to 0.05 by this treatment.

Example 3 describes vanadium oxinate as a pigment used in a gelatin layer beneath a silver halide emulsion layer. This pigment can also be used in a non-gelatin antihalation backing layer in which the pigment and the binder are removed during normal photographic processing. Such a backing has the advantage over those containing carbon or similar pigments which do not dissolve, in that no dark color or sludge is introduced into the processing solutions.

Example 5

To 50 ml. of water were added 1.0 gram of vanadium oxinate and 2.0 ml. of 28% ammonium hydroxide. The mixture was stirred two hours to obtain a solution. To this solution was added 1.5 grams of copoly(methacrylic acid-methyl methacrylate) (1:1 mole ratio); stirring was continued until the polymer dissolved. The solution was coated on a polyterephthalate film base at approximately 5 ml./ft.² and then dried to give a film with a density of 0.65. On standing, the density rose to 0.86.

A sample of this coating was agitated for one minute in a Metol-hydroquinone developer and then given a brief wash. The density of the processed film was 0.04; that is, the same as that of the base. The used developer solution contained no dark colored or insoluble material.

The same behavior was observed with a coating of vanadium oxinate in a water-organic solvent mixture containing cellulose acetate hydrogen phthalate as the polymeric binder.

Example 6

A dispersion of vanadium oxinate in 4.5% gelatin prepared as in Example 3 was melted to 40° C. and varying amounts were added to a fine-grain silver chlorobromide emulsion at 40° C. to give a range of pigment to silver ratios from 2 grams of pigment per mole of silver to 25 grams of pigment per mole of silver. The various mixtures were coated on a polyterephthalate film base to give a constant silver coverage of 236 mg./ft.².

The coatings were processed four minutes in D-19 developer followed by a sodium thiosulfate fix and a wash. This treatment gave, with each coating, a clear film with no residual pigment density or stain.

It will be appreciated that the 8-hydroxyquinoline vanadium complexes of this invention can be used over coatings which are sensitive to high energy rays such as silver halide emulsions intended for use with X-rays, beta rays, gamma rays, cosmic rays, and the like. The sensitive coatings can be provided with an overcoating containing the 8-hydroxyquinoline vanadium complex of sufficient density to avoid exposure of the sensitive coating from light rays, yet the sensitive coating can be exposed through the protective coating to high energy rays. Upon development with a customary alkaline developing bath, or upon imbibing alkaline solution, the complex becomes colorless and the image is readily visible. Various modifications of coatings and layers may be used depending upon the intended purpose. For instance, there may be a sensitive coating on each side of the support with a complex containing layer over each of the sensitive coatings. For some purposes, there may be an incorporated intensifying screen which can be used in conjunction with the sensitive coating.

As used herein, coatings sensitive to high energy rays are intended to include those which may be light sensitive but which are primarily intended for use with radiations other than visible light, including X-rays, gamma rays, cosmic rays and the like.

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

We claim:

1. A photographic element comprising a support having thereon at least one light sensitive coating and having on the same support at least one layer containing an 8-hydroxyquinoline vanadium complex which becomes substantially colorless under alkaline conditions.

2. A photographic element comprising a support having thereon at least one light sensitive silver halide emulsion and having on the same support at least one layer contain-

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ing an 8-hydroxyquinoline vanadium complex which becomes substantially colorless under alkaline conditions.

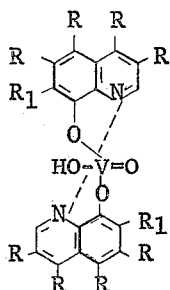
3. A photographic element comprising a support having thereon a light sensitive silver halide emulsion containing an 8-hydroxyquinoline vanadium complex which becomes substantially colorless under alkaline conditions.

4. A photographic element comprising a support having on at least one side a silver halide emulsion and on the same support at least one layer containing an 8-hydroxyquinoline vanadium complex which becomes substantially colorless under alkaline conditions.

5. A photographic element comprising a support having on at least one side a silver halide emulsion sensitive to high energy rays and having on the same support at least one layer containing an 8-hydroxyquinoline vanadium complex which becomes substantially colorless under alkaline conditions.

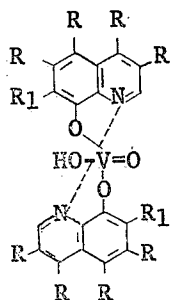
6. A photographic element comprising a support having on at least one side a silver halide emulsion sensitive to high energy rays and containing an 8-hydroxyquinoline vanadium complex which becomes substantially colorless under alkaline conditions.

7. A photographic element comprising a support having thereon a light sensitive coating and contiguous thereto at least one layer containing an 8-hydroxyquinoline vanadium complex having the following formula:



in which R represents a group selected from the class consisting of hydrogen, SO_3H , halogen, carboxyl, acyl (1-20 carbon atoms), substituted acyl (1-20 carbon atoms), alkyl (1-20 carbon atoms) and aryl, and R_1 represents a member selected from the class consisting of R, α -anilino-benzyl and substituted α -anilino-benzyl.

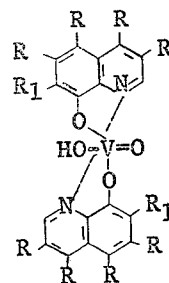
8. A photographic element comprising a support having thereon a light sensitive silver halide emulsion and having at least one layer contiguous thereto containing an 8-hydroxyquinoline vanadium complex having the following formula:



in which R represents a group selected from the class consisting of hydrogen, SO_3H , halogen, carboxyl, acyl (1-20 carbon atoms), substituted acyl (1-20 carbon atoms), alkyl (1-20 carbon atoms) and aryl, and R_1 represents a member selected from the class consisting of R, α -anilino-benzyl and substituted α -anilino-benzyl.

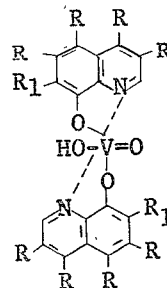
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9. A photographic element comprising a support having on at least one side a silver halide emulsion sensitive to high energy rays and having contiguous thereto at least one layer containing an 8-hydroxyquinoline vanadium complex having the following formula:



in which R represents a group selected from the class consisting of hydrogen, SO_3H , halogen, carboxyl, acyl (1-20 carbon atoms) substituted acyl (1-20 carbon atoms) alkyl (1-20 carbon atoms) and aryl, and R_1 represents a member selected from the class consisting of R, α -anilino-benzyl and substituted α -anilino-benzyl.

10. A photographic element comprising a support having thereon a light sensitive silver halide emulsion containing an 8-hydroxyquinoline vanadium complex having the following formula:



in which R represents a group selected from the class consisting of hydrogen, SO_3H , halogen, carboxyl, acyl (1-20 carbon atoms), substituted acyl (1-20 carbon atoms), alkyl (1-20 carbon atoms) and aryl, and R_1 represents a member selected from the class consisting of R, α -anilino-benzyl and substituted α -anilino-benzyl.

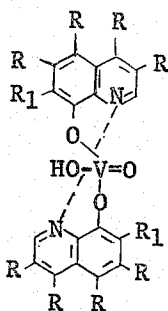
11. A photographic element comprising a support having thereon at least one light sensitive coating and having contiguous thereto at least one layer containing an antihalation protecting amount of an 8-hydroxyquinoline vanadium complex which becomes substantially colorless under alkaline conditions.

12. A photographic element comprising a support having thereon a light sensitive silver halide emulsion and having contiguous thereto at least one layer containing an antihalation protecting amount of an 8-hydroxyquinoline vanadium complex which becomes substantially colorless under alkaline conditions.

13. A photographic element comprising a support having on at least one side a silver halide coating sensitive to high energy rays and having contiguous thereto at least one layer containing an 8-hydroxyquinoline vanadium complex sufficient to render the layer substantially opaque to visible light, said complex rendered substantially colorless under alkaline conditions.

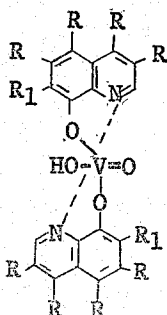
14. A photographic element comprising a support having thereon a light sensitive coating and having contiguous thereto at least one layer containing an antihalation pro-

tecting amount of an 8-hydroxyquinoline vanadium complex having the following formula:



in which R represents a group selected from the class consisting of hydrogen, SO_3H , halogen, carboxyl, acyl (1-20 carbon atoms), substituted acyl (1-20 carbon atoms), alkyl (1-20 carbon atoms) and aryl, and R_1 represents a member selected from the class consisting of R, α -anilinobenzyl and substituted α -anilinobenzyl.

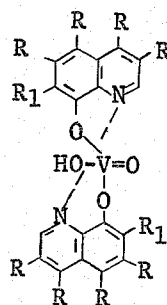
15. A photographic element comprising a support having thereon a light sensitive silver halide emulsion and having contiguous thereto at least one layer containing an antihalation protecting amount of an 8-hydroxyquinoline vanadium complex having the following formula:



in which R represents a group selected from the class consisting of hydrogen, SO_3H , halogen, carboxyl, acyl (1-20 carbon atoms), substituted acyl (1-20 carbon atoms), alkyl (1-20 carbon atoms) and aryl, and R_1 represents a member selected from the class consisting of R, α -anilinobenzyl and substituted α -anilinobenzyl.

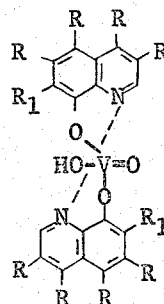
16. A photographic element comprising a support having on at least one side of the support a coating sensitive to high energy rays and contiguous to the sensitive coating, at least one layer containing an 8-hydroxyquinoline vanadium complex in an amount sufficient to render the layer substantially opaque to visible light, said complex having the following formula:

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in which R represents a group selected from the class consisting of hydrogen, SO_3H , halogen, carboxyl, acyl (1-20 carbon atoms), substituted acyl (1-20 carbon atoms), alkyl (1-20 carbon atoms) and aryl, and R_1 represents a member selected from the class consisting of R, α -anilinobenzyl and substituted α -anilinobenzyl.

17. A photographic element comprising a support having thereon a light sensitive silver halide emulsion containing an antihalation protecting amount of an 8-hydroxyquinoline vanadium complex having the following formula:



in which R represents a group selected from the class consisting of hydrogen, SO_3H , halogen, carboxyl, acyl (1-20 carbon atoms), substituted acyl (1-20 carbon atoms), alkyl (1-20 carbon atoms) and aryl, and R_1 represents a member selected from the class consisting of R, α -anilinobenzyl and substituted α -anilinobenzyl.

18. A photographic element comprising a support having thereon a light sensitive coating and having contiguous thereto at least one layer containing vanadium oxinate.

19. A photographic element comprising a support having thereon a light sensitive silver halide emulsion and having contiguous thereto at least one layer containing vanadium oxinate.

20. A photographic element comprising a support having thereon a silver halide emulsion containing vanadium oxinate.

References Cited

- Blair, A. J., et al., "Chemistry of Some 8-Hydroxyquinoline Complexes of Vanadium," Chem. Abstracts, 1958 vol. 52, pp. 8823b.

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