United States Patent

Mackey

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[54] PHOTOGRAPHIC MATERIALS CONTAINING ANTI-HALATION DYESTUFFS

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[52] **U.S. Cl.** **96/84**, 96/87

[51] **Int. Cl.** **G03c 1/84**, G03c 1/78

[58] **Field of Search** 96/89, 87, 67

[56] **References Cited**

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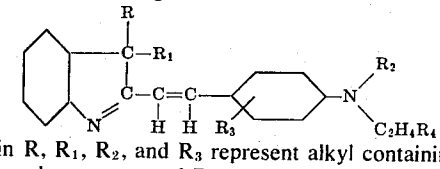
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EXEMPLARY CLAIM

1. A light-sensitive photographic film element comprising at least one light-sensitive gelatin silver halide emulsion coated on a film base and wherein at least one of the layers comprising said film element contains a water-soluble anti-halation dyestuff having a broad absorption in the green region of the spectrum comprising a quaternary ammonium salt of a dyestuff of the following structural formula:



wherein R, R_1, R_2, and R_3 represent alkyl containing from 1 to 4 carbon atoms and R_4 represents a member selected from the group consisting of cyano and halogen.

10 Claims, No Drawings

PHOTOGRAPHIC MATERIALS CONTAINING ANTI-HALATION DYESTUFFS

The present invention relates in general to the provision of photographic materials having excellent anti-halation properties and in particular to the provision of improved anti-halation dyestuffs for such purposes.

As is well known, it is recognized practice in the preparation of light-sensitive photographic materials and particularly those of the gelatino-silver halide type, to include in at least one of the layers of said material one or more light-screening agents. The inclusion of such light-screening agents is particularly vital in connection with the fabrication of photographic film elements wherein quality of image resolution is of primary importance. Thus, the property of one or more layers of the photographic film element to diffuse incident actinic radiation, i.e., to undergo internal light-scattering, tends to vitiate any possibility of obtaining image reproduction possessed of the requisite image definition or resolution. The adverse effects attributable to the tendency of a given photographic material to undergo light-scattering are invariably manifested in the form of unsharp, blurry and distorted images. As will be further recognized, the overall contrast, density, etc., of the image reproduction likewise suffer considerably since that portion of the exposure radiation which undergoes light-scattering is rendered substantially unavailable for useful purposes. There results, of course, a net reduction in available exposure product and, consequently, serious impairment of quality of image reproduction.

The provision of anti-halation dyes suitable for use in the fabrication of photographic film elements has proved particularly problematical in connection with the manufacture of panchromatic film materials. Thus, the dyes heretofore promulgated for such use have proved to be objectionable in one or more important aspects. Perhaps the primary objection relates to the fact that in many instances the anti-halation dyestuff selected for such use is not capable of ready removal from the photographic film element in the normal course of post-exposure photographic processing, i.e., development, fixing and washing. Ideally, of course, the anti-halation dyestuff should possess the properties of being easily decolorized, remaining colorless while exhibiting ready solubility in the various processing solutions employed in connection with the photographic development operation.

In many instances it is preferred practice to include the anti-halation dyestuff as an ingredient of the light-sensitive composition per se as to be distinguished from a non-light-sensitive auxiliary layer, e.g., a backing layer. Moreover, this procedure is permitted solely in those instances wherein the anti-halation dyestuff is totally devoid of any tendency to deleteriously affect the light-sensitive composition. Thus, it is imperative that the anti-halation dyestuff exhibit substantially no tendency to desensitize the emulsion medium or otherwise disrupt the emulsion sensitometric characteristics.

It has been ascertained in practice that many of the anti-halation dyestuffs heretofore recommended in the art prove notoriously deficient in one or more of the aforedescribed desiderata, thereby necessitating resort to the use of ancillary techniques of a remedial nature whereby to compensate for such shortcomings. However, the limitations imposed by economical feasible practice invariably militate against the feasibility of such corrective procedures.

In accordance with the discovery forming the basic of the present invention, it has been ascertained that anti-halation dyestuffs selected from a relatively delimited class of materials provide exceptional advantage when employed in the fabrication of light-sensitive photographic elements.

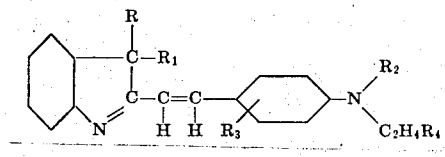
Thus, the primary object of the present invention resides in the provision of anti-halation compositions wherein the foregoing disadvantages are eliminated or at least mitigated to a substantial extent.

Another object of the present invention resides in the provision of anti-halation dyestuffs which are readily removable from photographic film elements as a concomitant to post-exposure photographic processing.

A further object of the present invention resides in the provision of anti-halation dyestuffs beneficially adapted for use in both light-sensitive and non-light-sensitive layers of photographic film elements, said dyestuffs being totally devoid of any tendency to deleteriously affect the sensitometric characteristics of the light-sensitive layer.

Other objects and advantages of the present invention will become more apparent hereinafter as the description proceeds.

The attainment of the foregoing and related objects is made possible in accordance with the present invention which, in its broader aspects, includes the provision of anti-halation compositions containing at least one dyestuff, comprising a quaternary ammonium salt of a dyestuff of the following structural formula:



wherein R, R_1, R_2, and R_3 represent alkyl and preferably lower alkyl having one to four carbon atoms, e.g., methyl, ethyl, propyl, isopropyl, butyl, etc., and R_4 represents cyano or halogen, e.g., chloro, bromo, etc.

Dyestuffs falling within the ambit of the foregoing structural formula are uniquely typified in possessing each of the properties considered desirable in a dyestuff product suitable for anti-halation uses. Moreover, problems associated with the retention of dyestuff in the photographic element subsequent to photographic processing are virtually eliminated since the dyestuffs contemplated herein are rapidly decolorized as a result of photographic processing and more importantly exhibit a pronounced tendency to diffuse or otherwise migrate from the film element by relatively simple means. Thus, for example it is found that such dyestuffs may be removed from photographic film elements by simply contacting such film element with ordinary tap water, no developer or other alkaline media being necessary.

Perhaps the salient advantage presented by the anti-halation dyestuffs of the present invention resides in the fact that they exhibit absolutely no tendency to mordant gelatin, the latter being commonly employed as a film-forming dispersing medium in the preparation of layers for photographic film elements. In view of this property, any possibility of recolorization is minimized if not completely eliminated.

As previously pointed out, the anti-halation, filter or screening dyestuffs described herein are eminently suitable for use as ingredients of the light-sensitive composition per se and/or an auxiliary layer, e.g., an anti-halation layer which may be cast in known manner on the back of a suitable film support. When provided in the form of a separate layer, the anti-halation composition may comprise simply a mixture of the anti-halation dyestuff and suitable film-forming, organic, binder, preferably soluble in alkaline media. The term organic, film-forming binders as used in the context of the present invention is intended to include synthetically derived polymeric substances, naturally occurring organic colloids, etc., whose aqueous solutions, dispersions, emulsions, etc., yield continuous films on drying. It is, of course, preferred that the film-forming material selected for use be soluble in alkaline media and therefore capable of ready removal when subjected to the alkaline environments characterizing the post-exposure photographic processing baths.

As examples of film-forming materials suitable for use in the practice of the present invention there may be mentioned in particular gelatin, copolymers of an alkyl vinyl ether with maleic anhydride polymers of acrylic acid, methacrylic acid, etc. In any event, film-forming materials having the requisite solubility in alkaline media are well known in the art, being extensively described in the published literature both patent and otherwise.

When included as an ingredient of the light-sensitive layer, the anti-halation dyestuff may be added at any convenient stage of emulsion preparation. According to either embodiment, i.e., whether added to a separate layer and/or light-sensitive emulsion layer, the dyestuff may be employed in concentrations varying over a relatively wide range, the sole and obvious requirement being that the dyestuff be present in amounts sufficient to provide the necessary degree of sun-screening. In any event, it is found that dyestuff concentrations falling within the range of from about 1.0 parts to about 35.0 parts per 1,000 parts of colloidal carrier material are sufficient to negotiate the broad spectrum of anti-halation problems likely to be encountered in use. It will further be understood that departures from the aforesaid ranges may be dictated in a particular circumstance, depending upon the requirements of the processor.

The anti-halation dyestuffs described herein are adapted primarily for use with panchromatic photographic emulsions of the silver halide, gelatin type, i.e., silver bromide, silver chloride, silver chlorobromide, silver bromoiodide and silver chlorobromoiodide. Emulsions of this type may be coated upon any of the conventional film base materials, the latter including, for example, film-forming plastic materials, e.g., polyesters, polycarbonates, etc., as well as cellulose materials, e.g., cellulose acetate, cellulose triacetate, cellulose acetate butyrate, and the like.

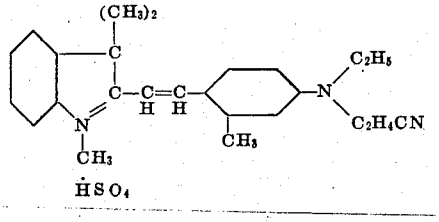
In those instances wherein the anti-halation dyestuff is intended to be introduced into the photographic element in the form of a separate backing layer it is understood that the coating composition in question may be further provided with one or more auxiliary agents for purposes of expediting the deposition of a uniform, homogeneous coating. Thus, any of the coating aid materials conventionally employed in the art for such purposes may be utilized, such as saponin or any of the synthetic surface-active agents. In addition, a suitable hardening agent such as formaldehyde may likewise be included.

The anti-halation dyestuffs of the present invention are available commercially under the tradename designation "-Genacryl." In any event, such dyestuffs may be readily and conveniently prepared by merely quaternizing a dyestuff of the formula given hereinbefore with any of the conventional quaternizing agents such as dimethyl sulfate.

The following examples are given for purposes of illustration only and are not to be considered as necessarily limiting the scope of the present invention.

EXAMPLE 1

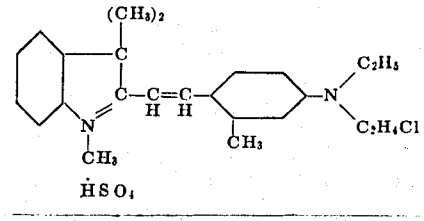
To a composition containing gelatin, water, aldehyde hardener and coating aid (saponin) are added 20 parts by weight per 1,000 parts by weight of gelatin of a dyestuff of the following formula:



The coating composition thus formulated is coated on the backside of a cellulose acetate film base, the latter carrying on its opposite side a light-sensitive gelatin silver halide emulsion. The anti-halation layer thus deposited has broad absorption in the green region of the spectrum. The film element is thereupon exposed, developed, fixed and washed in conventional manner. The dye coating bleaches rapidly on immersion in the photographic processing solutions and is readily discharged from the layer. Complete discharge of dyestuff results, there being no evidence of dye residue upon visual inspection of the processed photographic film element. The image reproduction obtained is of excellent photographic quality, i.e., resolution, contrast, density, etc., this observation being confirmed by comparison with a control sample of photographic film omitting the anti-halation dyestuff but otherwise identical in composition. On processing of the latter, there is obtained an image of blurry, unsharp quality, having sub-optimum contrast, density, etc.

EXAMPLE 2

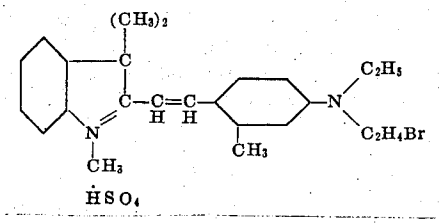
Example 1 is repeated, except that the anti-halation dyestuff employed corresponds to the following structural formula:



Results similar to those described in Example 1 obtained, i.e., the photographic element containing the above-described dyestuff exhibits vastly superior photographic quality when compared to a control sample devoid of anti-halation dyestuff.

EXAMPLE 3

Example 1 is repeated, except that the anti-halation dyestuff employed corresponds to the following structural formula:



Results similar to those described in Example 1 are obtained.

EXAMPLES 4 – 6

Examples 1–3 are repeated, except that in each instance the anti-halation dyestuff is added to the light-sensitive gelatino-silver chloro-bromide emulsion. layer. Upon completion of post exposure processing, i.e., development, fixing, washing, etc., there is obtained an image reproduction of outstanding quality.

EXAMPLE 7

Example 1 was repeated with the exception that 10 parts of the dye were used per 1,000 parts of gelatin and that the layer containing the anti-halation dye was placed between the film base and the silver bromoiodide emulsion. The results obtained were essentially the same as those reported in Example 1.

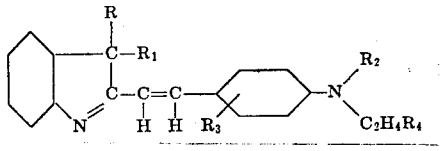
EXAMPLE 8

Examples 4–6 were repeated with the exception that the screening dyes were applied to the coated films prior to exposure by imbibing 50 square feet of film with aqueous solutions containing from 10 mg. to 80 mg. per liter of solution. The results obtained were essentially the same as those obtained in Examples 4–6.

The present invention has been disclosed with respect to certain preferred embodiments thereof, and there will be obvious to persons skilled in the art modifications, equivalents or variations thereof which are intended to be included within the spirit and scope of this invention.

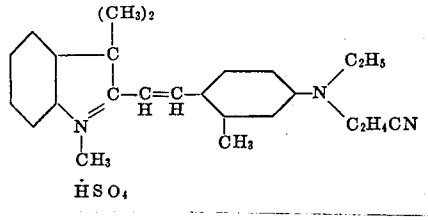
What is claimed is:

1. A light-sensitive photographic film element comprising at least one light-sensitive gelatin silver halide emulsion coated on a film base and wherein at least one of the layers comprising said film element contains a water-soluble anti-halation dyestuff having a broad absorption in the green region of the spectrum comprising a quaternary ammonium salt of a dyestuff of the following structural formula:

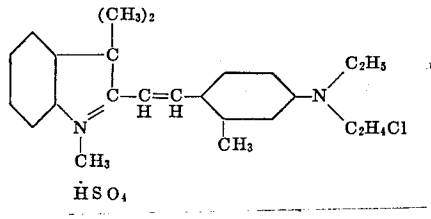


wherein R, R_1, R_2, and R_3 represent alkyl containing from one to four carbon atoms and R_4 represents a member selected from the group consisting of cyano and halogen.

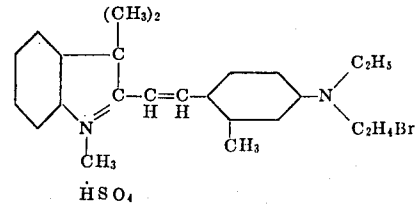
2. A film element according to claim 1 wherein said dyestuff comprises a compound of the following structural formula:



3. A film element according to claim 1 wherein said dyestuff comprises a compound of the following structural formula:



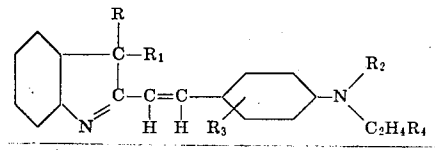
4. A film element according to claim 1 wherein said dyestuff comprises a compound of the following structural formula:



5. A film element according to claim 1 wherein said anti-halation dyestuff is present in a backing layer, the latter being disposed on the side on the film base opposite to the light sensitive gelatin silver halide emulsion side.

6. A film element according to claim 1 wherein said anti-halation dyestuff is present in a light sensitive silver halide emulsion layer.

7. A coating composition comprising a film-forming alkali soluble organic binder and a water-soluble anti-halation dyestuff having a broad absorption in the green region of the spectrum comprising a quaternary ammonium salt of a dyestuff of the following structural formula:



wherein R, R_1, R_2, and R_3 represent alkyl containing from one to four carbon atoms and R_4 represents a member selected from the group consisting of cyano and halogen.

8. A composition according to claim 7 further containing a light-sensitive silver halide salt.

9. A composition according to claim 7 wherein said organic binder comprises gelatin.

10. A film element according to claim 1 wherein said anti-halation dye is present in a screening layer which is placed between and in integral contact with the film base and the emulsion layer.

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