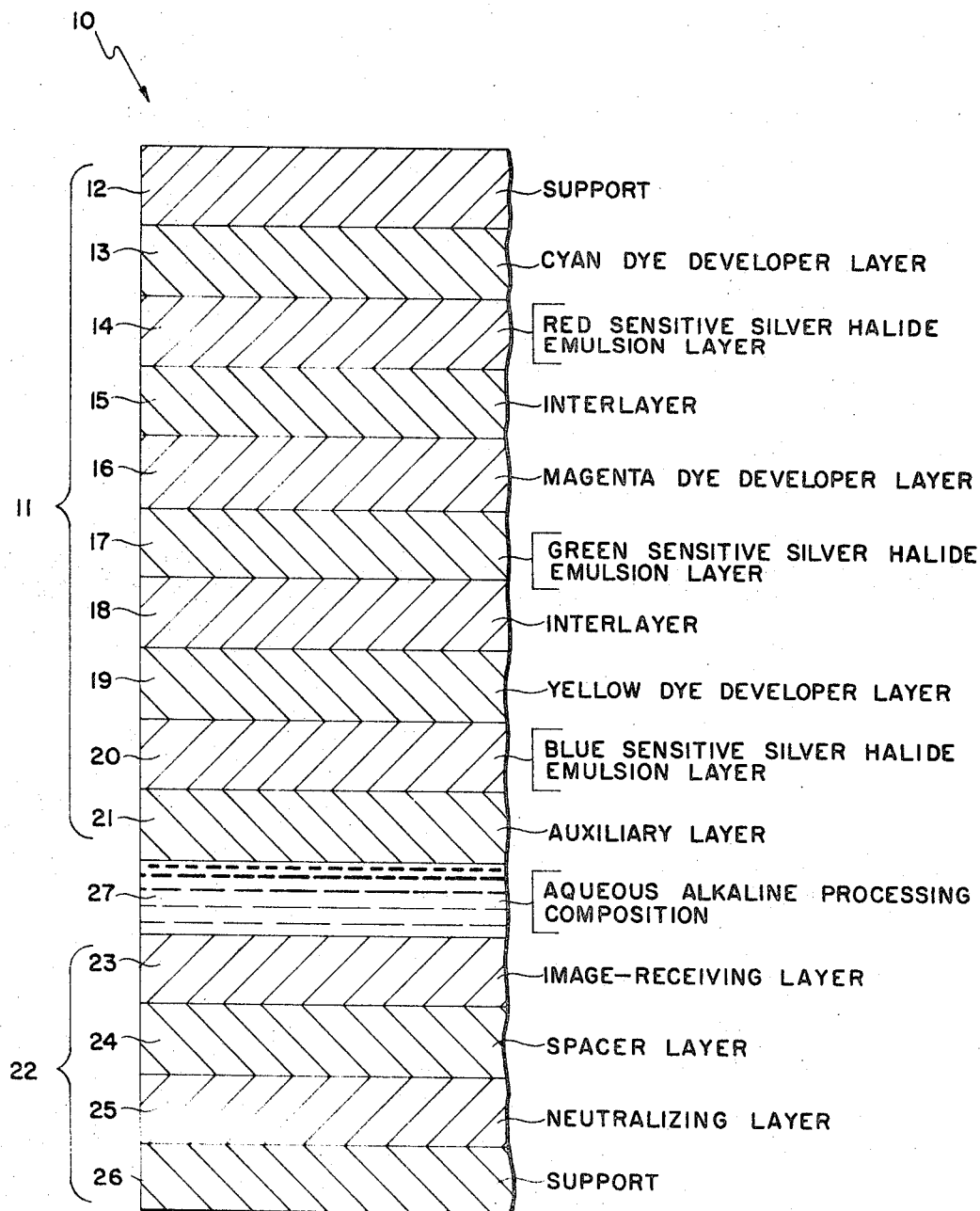


April 20, 1971

S. M. BLOOM ET AL
 PHOTOGRAPHIC PRODUCTS AND PROCESSES COMPRISING
 ALKALI-HYDROLYZABLE ANTIFOGGANT PRECURSORS
 Filed Sept. 3, 1968

3,575,699



INVENTORS
Stanley M. Bloom
 and
Howard G. Rogers
 BY *Brown and Mikulka*
 and
Sheldon W. Rothstein
 ATTORNEYS

1

3,575,699

PHOTOGRAPHIC PRODUCTS AND PROCESSES COMPRISING ALKALI-HYDROLYZABLE ANTI- FOGGANT PRECURSORS

Stanley M. Bloom, Waban, and Howard G. Rogers,
Weston, Mass., assignors to Polaroid Corporation, Cam-
bridge, Mass.

Filed Sept. 3, 1968, Ser. No. 756,838

Int. Cl. G03c 1/34, 5/54, 7/00

U.S. Cl. 96—3

33 Claims

ABSTRACT OF THE DISCLOSURE

Antifoggant precursors of the Formula A—Z, wherein A is an antifoggant nucleus resultant from the deprotonization of the antifoggant A—H, and Z is a moiety which masks the antifoggant functionality of A, provide substantially no antifoggant effect on photographic systems in which they are contained until cleavage of the masking moiety from the antifoggant nucleus is accomplished.

The present invention relates to photography and more particularly to photographic products and processes.

It has been extensively reported in literature pertaining to photography that photosensitive silver halide emulsions, and particularly photosensitive gelatino-silver halide emulsions, have a tendency to lose sensitivity and to become spontaneously developable without exposure to light. This phenomenon, characterized as "chemical fog," may be defined as the density above base level that is developed in emulsion areas that have received no intentional exposure and, in general, is not uniformly distributed over a selectively photoexposed emulsion, being greatest in the unexposed areas and decreasing with increased exposure in a non-linear manner.

In both silver and color photographic systems, the latter where silver halides are used to control image dye formation, fog results in a loss of image acuity.

Chemical fog may be divided into two classes: inherent fog, that is, fog which is emulsion initiated; and induced fog, that is, fog which is initiated during development. Induced fog appears to be due to physical development about extra-granular centers and inherent fog is probably due to the presence of grains bearing a catalytic site sensitivity speck which is unavoidably introduced and which is equivalent in its properties to latent image. Induced fog accordingly may be unaffected by the level of inherent fog. Thus it will be readily appreciated that an emulsion susceptible to the development of chemical fog requires silver halide grains possessing a catalytic center of sufficient size to be spontaneously developable and/or grains unprotected from non-discriminatory development.

Various and sundry procedures and additives have been disclosed in the art to provide an increase in the stability of photosensitive silver halide emulsions by reducing the tendency of photosensitive compositions to fog. These procedures usually increase the speed-to-fog ratio; otherwise there would be no point in using them unless the requirement for a low fog level completely overrides that for sensitivity. In general, the methods available for the control of fog are to increase the bromide ion concentration during the emulsion fabrication process; select "fog free" gelatins, i.e., gelatins which are free of fogging contaminants and which have desirable ratios of restrainer to sensitizer; reduce the level of chemical sensitization; and add inorganic or organic fog retarding adjuncts.

This invention relates primarily to the latter item above, and more particularly to the use of a specified class of organic antifoggant precursors.

2

Accordingly, it is a primary object of the present invention to provide novel photographic products, and processes utilizing same, which exhibit decreased susceptibility to fog formation.

Another object of the present invention is to provide novel processes and products, particularly adapted for obtaining monochromatic and multichromatic images by diffusion transfer, which exhibit decreased fog formation throughout an extended temperature range.

A still further object of the present invention is to provide novel photographic elements comprising not less than one silver halide emulsion having associated therewith specified transfer image-forming components which exhibit increased effective processing temperature latitude.

Another object of the instant invention is to provide novel antifoggant precursors for use in photographic environments, said antifoggant precursors possessing substantially no antifoggant properties until contacted with a processing composition.

A further object of the instant invention is to provide a mechanism whereby the active site on an antifoggant compound is masked until said compound is contacted with an alkaline processing solution.

An additional object of the present invention is to provide novel hydrolyzable compounds which possess antifoggant properties only in their hydrolyzed state.

Another object of the present invention is to minimize changes in film speed of a given photographic system as a function of temperature and to control fog of said system throughout the operating temperature range thereof.

Other objects of the instant invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the process involving the several steps and the relation and order of one or more of such steps with respect to each of the others and the product possessing the features, properties and the relation of the elements which are exemplified in the following detailed disclosure and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention reference should be had to the following detailed description taken in connection with the accompanying drawing wherein:

FIG. 1 is a diagrammatic enlarged cross-sectional view of one embodiment of a film unit for obtaining multicolor images by a diffusion transfer photographic process illustrating the association of elements during one stage of the performance of a diffusion transfer process, the thickness of the various materials being exaggerated.

In diffusion transfer processes for the formation of transfer images, an exposed photographic emulsion is developed and, substantially concurrently therewith, an imagewise distribution of transfer image-forming components is provided as a function of the point-to-point degree of development. At least part of that imagewise distribution is transferred by diffusion to a contiguous image-receiving layer to provide the desired transfer image formation to that layer.

In diffusion transfer processes for the formation of silver transfer images, an exposed silver halide emulsion is developed and, substantially concurrently therewith, an imagewise distribution of soluble silver complex is obtained by reaction of a silver solvent with silver halide of the emulsion as a function of its point-to-point degree of exposure. Preferably, the photosensitive silver halide emulsion is developed with a viscous processing composition which is spread between an element comprising the silver halide emulsion and a print-receiving element comprising a suitable silver precipitating layer. The processing composition affects development of the emulsion and substantially simultaneously therewith forms a soluble silver complex, for example, a thiosulfate or thiocyanate, as

a function of the point-to-point degree of emulsion exposure. This soluble silver complex is, at least in part, transported in the direction of the print receiving element and the silver thereof is largely precipitated in the silver precipitating layer of said element to form a transfer image therein.

U.S. Pats. Nos. 2,647,049; 2,661,293; 2,698,798; and 2,802,735 disclose subtractive color diffusion transfer processes wherein color coupling techniques are utilized which comprise, at least in part, reacting one or more developing agents and one or more color formers, as a function of the photoexposure of a photographic emulsion, to provide a color image to a superposed image-receiving layer. U.S. Pat. No. 3,019,124 discloses the manufacture of photographic color screen elements particularly adapted for employment in multicolor diffusion transfer processes; and U.S. Pats. Nos. 2,968,554 and 2,983,606 disclose diffusion transfer processes where in a color screen element is utilized to provide a multicolor transfer image to a superposed image-receiving layer. U.S. Pats. Nos. 2,774,668; 2,983,606; and 3,345,163 disclose diffusion transfer processes wherein complete dyes are utilized to provide a color transfer image to a superposed image-receiving layer.

As disclosed in the aforementioned U.S. Pat. No. 2,983,606, a photosensitive element containing a dye developer and a silver halide emulsion is exposed and wetted by a liquid processing composition, for example, by emersion, coating, spraying, flowing, etc., in the dark, and the exposed photosensitive element is superposed prior to, during or after wetting on a sheet-like support element which may be utilized as an image-receiving element. In a preferred embodiment, the liquid processing composition is applied to the photosensitive element in a substantially uniform layer as the photosensitive element is brought into superposed relationship with the image-receiving layer. The liquid processing composition permeates the emulsion to initiate development. The dye developer is immobilized or precipitated in, for example, exposed areas as a function of the development. Such immobilization is apparently, at least in part, due to a change in the solubility characteristics of the dye developer upon oxidation; particularly with regard to its solubility in alkaline solutions. It may also be due in part to a tanning effect on the emulsion by oxidized developing agent and in part to a localized exhaustion of alkali as a result of development. In the exposed and partially exposed areas of the emulsion, the dye developer, unreacted and diffusible, provides an imagewise distribution of unoxidized dye developer dissolved in a liquid processing composition as a function of the point-to-point degree of exposure of the silver halide emulsion. At least part of this imagewise distribution of unoxidized dye developer is transferred by imbibition to a superposed image-receiving layer or element. Under certain conditions the layer of liquid processing composition may be utilized as the image-receiving layer. The image-receiving element receives a depthwise diffusion of dye developer without appreciably disturbing the imagewise distribution thereof to provide the color transfer image. The image-receiving element may contain agents adapted to mordant or otherwise fix dye developer. If the color of the transferred dye developer is affected by change in the pH of the image-receiving element, this pH may be adjusted to provide a pH affording the desired color. The desired dye image carried by the image-receiving layer may be separated from the photosensitive element by stripping at the end of a suitable imbibition period.

Dye developers are compounds which contain in the same molecule both the chromophoric system of a dye and also a silver halide developing function. By a "silver halide developing function" is meant a grouping adapted to develop exposed silver halide. A preferred silver halide developing function is a hydroquinonyl group. Other suitable developing functions include ortho-dihydroxyphenyl and ortho- and para-amino substituted hydroxy-

phenyl groups. In general, the development function includes a benzenoid developing function, that is, an aromatic developing group which forms quinonoid or quinone substances when oxidized.

An extensive compilation of such compounds is set forth in the aforementioned U.S. Pat. No. 2,983,606 and, in particular, in the various U.S. patents and copending applications incorporated by reference therein.

In general, the preferred dye developers comprise monoazo and anthraquinone dyes which possess one or two hydroquinonyl groups attached to the auxochromophoric system of the dye by means of a conjugation-interrupting divalent group such as, for example, an alkylene group.

Multicolored images may be obtained using color image-forming components, such as, for example, the previously mentioned dye developers, in diffusion transfer processes, by several techniques. One such technique contemplates the use of a photosensitive silver halide stratum comprising at least two sets of selectively sensitized minute photosensitive elements arranged in the form of a photosensitive screen. Transfer processes of this type are disclosed in the previously noted U.S. Pat. No. 2,983,606. In such an embodiment each of the minute photosensitive elements has associated therewith an appropriate dye developer in or behind a silver halide emulsion portion. In general, a suitable photosensitive screen prepared in accordance with the disclosure of said patent comprises minute red sensitized emulsion elements, minute green sensitized emulsion elements and minute blue sensitized emulsion elements arranged in side-by-side relationship in a screen pattern and having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer.

Another process for obtaining multicolor transfer images utilizing dye developers employs an integral multi-layer photosensitive element such as is disclosed in the aforementioned U.S. Pats. Nos. 2,983,606 and 3,345,163, wherein at least two selectively sensitized photosensitive strata and associated dye developers are superposed on a single support and are processed simultaneously and without separation with a single common image-receiving layer. A suitable arrangement of this type comprises a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum, and a blue-sensitive silver halide emulsion stratum, said emulsions having associated therewith respectively, for example, a cyan dye developer, a magenta dye developer and a yellow dye developer. The dye developer may be utilized in the silver halide emulsion layer, for example, in the form of particles, or it may be employed as a layer behind the appropriate silver halide emulsion stratum, for example, a layer of dye developer applied by the use of a coating solution containing about 0.5 to 8%, by weight, of the respective dye developer. Each set of silver halide emulsion and associated dye developer strata may be separated from other sets by suitable interlayers, for example, gelatin and the synthetic polymeric materials disclosed in copending application of Lloyd D. Taylor, Ser. No. 641,669, filed May 26, 1967, now U.S. Pat. No. 3,421,892. In certain instances it may be desirable to incorporate a yellow filter in front of the green-sensitive emulsion and such yellow filter may be incorporated in an interlayer. However, where desirable, a yellow dye developer of appropriate spectral characteristics which is present in a state capable of functioning as a yellow filter may be employed. In such instances a separate yellow filter may be omitted.

The preceding color image-forming components, that is, dye developers, are preferably selected for their ability to provide colors that are useful in carrying out subtractive color photography, i.e., cyan, magenta and yellow. It should be noted that it is within the scope of this invention to use mixtures of dye developers, for example, to obtain a desired color, e.g., black. Thus, it is to be understood that the expression "color" as used herein is in-

tended to include the use of a plurality of colors to obtain black, as well as the use of a single black dye developer.

United States Pat. No. 3,362,819, issued on Jan. 9, 1968, to Dr. Edwin H. Land, discloses image-receiving elements, particularly adapted for employment in color diffusion transfer processes, for example, of the type disclosed in aforementioned U.S. Pat. No. 2,983,606, which comprises a support layer possessing on one surface thereof, in sequence, a polymeric acid layer, a timing layer or spacer layer in the preferred embodiment, and an image-receiving layer adapted to provide a visible image upon transfer to said layer of diffusible dye image-forming substance.

As set forth in the last-mentioned application, the polymeric acid layer comprises polymers which contain acid groups, such as carboxylic acid and sulfonic acid groups, which are capable of forming salts with alkali metals, such as sodium, potassium, etc., or with organic bases, particularly quaternary ammonium bases, such as tetramethyl ammonium hydroxide, or potentially acid-yielding groups, such as anhydrides or lactones, or other groups which are capable of reacting with bases to capture and retain them. The acid-reacting group is, of course, non-diffusible from the acid polymer layer. In the preferred embodiments disclosed, the acid polymer contains free carboxyl groups and the transfer processing composition employed contains a large concentration of sodium and/or potassium ions. The acid polymers stated to be most useful are characterized by containing free carboxyl groups, being insoluble in water in the free acid form, and by forming water-soluble sodium and/or potassium salts. One may also employ polymers containing carboxylic acid anhydride groups, at least some of which preferably have been converted to free carboxyl groups prior to imbibition. While the most readily available polymeric acids are derivatives of cellulose or of vinyl polymers, polymeric acids from other classes of polymers may be used.

The acid polymer layer is disclosed to contain at least sufficient acid groups to effect a reduction in the pH of the image layer from a pH of about 12 to 14 to a pH of at least 11 or lower at the end of the imbibition period, and preferably to a pH of about 5 to 8 within a short time after imbibition. The pH of the processing composition employed preferably is of the order of at least 12 to 14.

It is, of course, necessary that the action of the polymeric acid be so controlled as not to interfere with either development of the negative or image transfer of unoxidized dye developers. For this reason, the pH of the image layer is kept at a level of pH 12 to 14 until the positive dye image has been formed after which the pH is reduced very rapidly to at least about pH 11, and preferably about pH 9 to 10, before the positive transfer image is separated and exposed to air. Unoxidized dye developers containing hydroquinonyl developing radicals diffuse from the negative to the positive as the sodium or other alkali salt. The diffusion rate of such dye image-forming components thus is at least partly a function of the alkali concentration, and it is desired that the pH of the image layer remain on the order of 12 to 14 until transfer of the necessary quantity of dye has been accomplished. The subsequent pH reduction, in addition to its desirable effect upon image light stability, serves a highly valuable photographic function by substantially terminating further dye transfer. The processing technique thus effectively minimizes changes in color balance as a result of longer imbibition times in multicolor transfer processes using multilayer negatives.

The spacer layer of the last-mentioned copending application, for example, an inert spacer layer comprising polyvinyl alcohol or gelatin or a temperature inversely permeable polymeric material as disclosed in copending U.S. application Ser. No. 447,100, filed Apr. 9, 1965, now abandoned and replaced by continuation-in-part U.S. application Ser. No. 664,503, filed on Aug. 30, 1967, and

now U.S. Pat. No. 3,455,686, acts to "time" control the pH reduction by the polymeric acid layer. This timing is disclosed to be a function of the rate at which the alkali diffuses through the spacer layer. It was stated to have been found that the pH does not drop until the alkali has passed through the spacer layer, i.e., the pH is not reduced to any significant extent by the mere diffusion into the interlayer but the pH drops quite rapidly once the alkali diffuses through the spacer layer.

As examples of materials, for use as the image-receiving layer, mention may be made of solution dyeable polymers such as nylon, as, for example, N-methoxymethyl polyhexamethylene adipamide; partially hydrolyzed polyvinyl acetate; polyvinyl alcohol with or without plasticizers; cellulose acetate with fillers, as, for example, one-half cellulose acetate and one-half oleic acid; gelatin; and other materials of a similar nature. Preferred materials comprise polyvinyl alcohol or gelatin containing a dye mordant such as poly-4-vinylpyridine, as disclosed in U.S. Pat. No. 3,148,061.

As has been alluded to above, the presence of an antifoggant in a photographic system may be responsible for reducing both inherent and induced fog and will, therefore, produce a more attractive end product, both from aesthetic and technological points of view. Such products doubtless have a competitive advantage over other photographic products not quite as attractive or technologically efficient. The antifoggant composition is particularly helpful in minimizing or preventing reaction of a dye developer with unexposed silver halide and may be added to the processing composition and/or to one or more processing composition-permeable layers of the photosensitive and/or image-receiving elements. The pertinent art has recognized many compounds which have fog inhibiting characteristics, such as sodium and potassium bromide and iodide, certain imidazoles, triazoles, tetrazoles, thiazoles, indazoles pyrazoles, pyrimidines, purines, etc.

At low temperatures, when processing composition is distributed upon the contact surface of a selectively exposed photosensitive element of the aforementioned tripack configuration, development begins first in the blue-sensitive emulsion, since it contacts the processing composition before the other layers. Temperature-retarded development, however, is slowed up even more by the restraining properties of antifoggant present and results, for example, in increased uncontrolled yellow dye developer transfer from the blue-sensitive emulsion to the image-receiving layer before complete developmental control has been established. This causes what may be termed "yellow stain". It will be evident that at high temperatures the precise opposite happens, that is, the development rate is accelerated to a point where the restraining effect of the antifoggant is of insufficient consequence. The blue-sensitive emulsion will then be developed and the properly developed silver, combined with the fog present, will cause an over-control and thereby hold back the desired imagewise yellow dye diffusion and result in an undesired shift in color balance of the transfer image.

It has now been discovered that a given antifogging composition may be modified in such a way as to mask the primary site or sites responsible for the antifogging effect, said masking moieties preventing interaction between photosensitive silver halides and the antifogging composition. It has additionally been found that if such moieties are capable of being removed from said compound by a mechanism such as, for example, hydrolysis, the antifogging nucleus will then be available to act upon the system. It will additionally be evident that such a hydrolysis mechanism will be directly dependent upon the ambient temperature since the rate of hydrolysis is a direct function of temperature, said rate doubling approximately every 10° C. increase in temperature. Such hydrolyzable antifoggant precursors are preferably sub-

stantially nondiffusible and at least substantially less diffusible in their unhydrolyzed form than in their hydrolyzed form. It is theorized that the rate of hydrolysis of the said antifoggant precursors is dependent upon temperature, and, therefore, provides an effective means of controlling the availability of antifoggant in a given photographic system and insuring that development is carried out as unimpeded as possible by antifoggant effect in order to provide the optimum fog to image ratio which may be obtained at a given development temperature. It is also considered possible that, rather than the hydrolysis rate being the critical factor, the primary stimulus for the temperature-dependent release effect achieved herein may be solution rate; that is, the rate of solution of antifoggant precursor in processing composition may be the basic parameter in determining the amount of antifoggant available to the system at any given time. It is to be understood that the precise mechanism through which antifoggant is released into a photographic environment has not been ascertained with certainty. Accordingly, the theories propounded herein are considered to be mere suggestions of possible mechanisms of operation and in no way limit the scope of the invention disclosed and claimed herein. Substantially any moiety which, upon hydrolysis, is capable of leaving the antifoggant nucleus intact may be utilized provided said moiety imparts no deleterious effects upon the antifoggant functionality. Among such antifogging precursors are those disclosed and claimed in copending application of Jerome Reid and David Carlson filed on the same date as the instant application, U.S. Ser. No. 756,884 wherein metal-complexed antifoggant compounds are disclosed and claimed.

While antifoggant precursors which are readily hydrolyzable in acidic, basic and neutral mediums are contemplated by the instant invention it is preferred to utilize compounds which are principally base hydrolyzed or, more specifically, which are hydrolyzed to a greater degree in base than, for example, in water. The rate of release of such preferred compounds should be directly proportional to the concentration of hydroxyl ions, i.e., the higher the pH, the greater the rate of hydrolysis, temperature being constant. In instances where the antifoggant precursor is substantially hydrolyzed by water, said precursor may be encapsulated by any known technique in a medium which is saponified by, for example, alkali processing composition as, for example, cellulose acetate, benzoic anhydride containing polymers, etc. and incorporated directly in the film unit to insure a long shelf life.

Generically speaking, the compounds included in the instant invention comprise antifoggant precursors which, prior to being activated, possess substantially no antifoggant properties; while after activation they substantially reduce fogging in a given silver halide photographic system. It is apparent that such precursors are extremely valuable in a photographic system which is to be utilized throughout a wide processing temperature range if their mechanism of activation is regulated as a function of processing temperature.

The antifoggant precursors of the present invention may be visualized with respect to the formula:



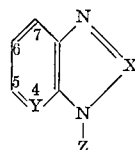
where A is an antifoggant nucleus resultant from the deprotonization of the antifoggant A—H, and Z is any moiety or moieties whose removal provides the requisite activation to the antifoggant nucleus. Z, therefore, may be considered to be any substituent which blocks the antifoggant functionality of the A nucleus; while after removal of the Z moiety or moieties the A nucleus is rendered effective as an antifoggant and the Z moiety or moieties are not deleterious to the antifoggant functionality of said antifoggant A.

A preferred subclass of antifoggant precursors within the context of the present invention may be visualized with respect to the formula:



wherein: Z is as described above and F is the nonmetallic atoms necessary to complete a heterocyclic antifoggant nucleus. Specifically included within the atoms comprising F are carbon, oxygen, selenium, sulfur, nitrogen, etc.

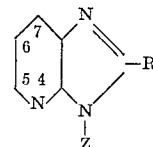
A further preferred group of antifoggant precursors within the above subclass may be visualized with reference to the formula:



wherein: Y is carbon or nitrogen; X is nitrogen or C—R, where R is hydrogen or lower alkyl, i.e., containing less than six carbon atoms; and Z is as described above.

It has been disclosed in U.S. patent application Ser. No. 689,611, of Howard G. Rogers, filed on Dec. 11, 1967, and now U.S. Pat. No. 3,473,924 that certain compounds which may be generically defined as azabenzimidazoles provide excellent antifoggant functionality to photographic systems, and particularly diffusion transfer photographic systems, and may be adapted for advantageous employment therein to provide increased latitude at the temperature range which is considered operative for the given system. Such compounds have been found to inhibit the formation of fog with substantially no sacrifice in the effective speed of the photographic process in which it is utilized.

It has been discovered that a certain class of antifoggant precursors derived from the azabenzimidazole nucleus provides superior antifoggant activity to a given photographic system only after hydrolysis of said compounds has occurred. These compounds may generically be represented by the formula:

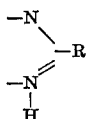


wherein:

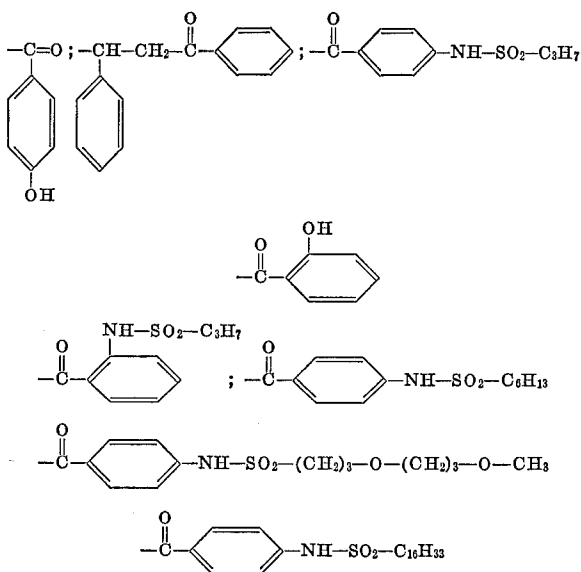
R is a selected from the group consisting of hydrogen and lower alkyl groups, i.e., containing less than six carbon atoms; and Z is any group which is subject to cleavage from the azabenzimidazole nucleus by hydrolysis, as described above.

It will be appreciated particularly with reference to U.S. patent application Ser. No. 689,611 cited above, that the compounds represented by the two formulae next above may contain various substituents in the 5 and/or 6 position which enhance the antifoggant functionality of the compounds and are considered to be included within the scope of the present invention. More particularly, among the substituents which may be substituted in the 5 and/or 6 position are halogen, lower alkyl, e.g., containing less than six carbon atoms, nitro, amino, hydroxy, lower alkoxy, i.e., containing less than six carbon atoms, aryl, sulfonamido, and carboxamido groups, it being understood that such substituents may together constitute the atoms necessary to complete a cyclic structure, as, for example,

9

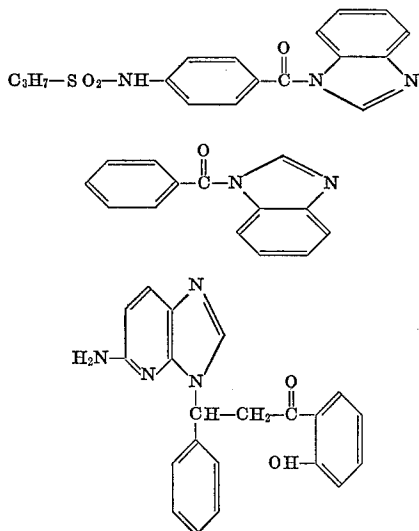


With regard to the substituent Z, it should be appreciated that the only requisite for determining its constitution is that it be capable of masking the antifoggant functionality of the given antifoggant radical until some stimulus for removal of said Z moiety, e.g., hydrolysis, is imparted to the system. Among the radicals most suitable for utilization as the Z moiety are acyl and β -acyl alkalene radicals. Exemplary of such removable radicals which are representative of Z are:

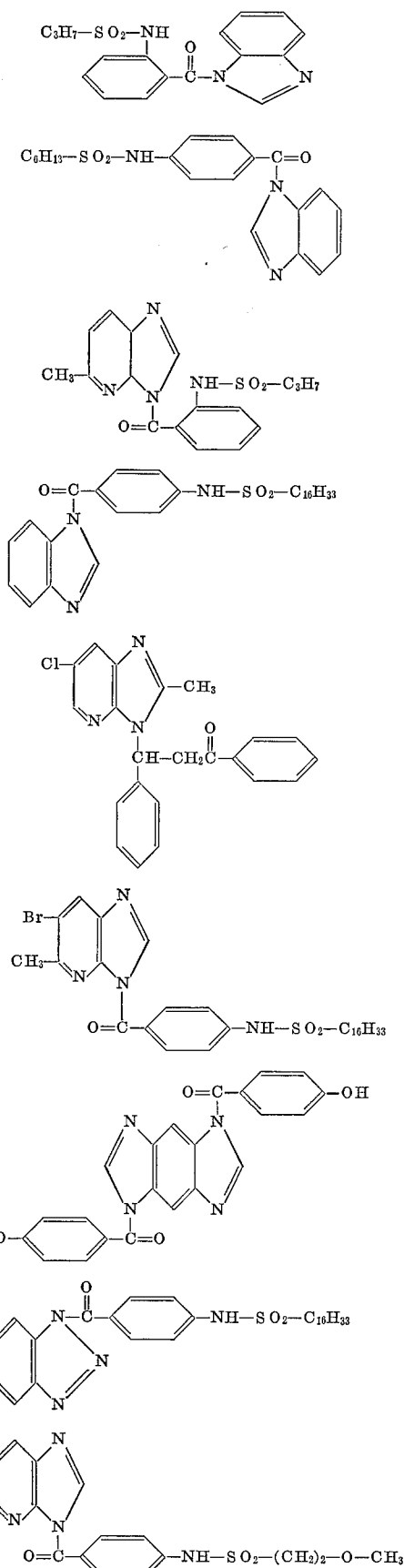


It has been theorized that the antifoggant compounds displaying the strongest antifoggant activity possess weak electron donor moieties at the 5 and/or 6 position in the generic formula next above. Accordingly, in the most preferred embodiments of the present invention substituents in the 5 and/or 6 position should inherently be weak electron donors. It will be additionally appreciated that R and any substituents which may be in the 5 and/or 6 position above are intended to encompass equivalents thereof including situations wherein the substituents in the 5 and 6 position above are taken together to form an annulated hydrocarbon ring system.

Illustrative of the compounds which may be utilized in the present invention are:



10



At the option of the operator it has been determined that the antifoggant precursors of the present invention may be used alone or in conjunction with viable antifoggants. For example, with respect to a typical color

film processing composition containing a conventional antifoggant, such as benzotriazole and the like, generally in the order of about 2%, the antifoggants of the present invention may be added to the system with a concomitant reduction in the percentage of or elimination of the benzotriazole or like antifoggant. Under certain conditions utilization of small amounts of a second antifoggant may be found desirable to provide limited antifogging and restraining properties at very low temperatures.

In a preferred embodiment of the present invention, a photosensitive element is employed which is specifically adapted to provide for the production of a multicolor dye transfer image and comprises a dimensionally stable support layer carrying at least two selectively sensitized silver halide emulsion strata each having a dye developer material of predetermined color associated therewith which is soluble and diffusible in alkali at a first pH.

The preferred photosensitive image-receiving element comprises an alkaline solution permeable polymeric layer dyeable by the dye developer; a polymeric spacer layer comprising a polymer possessing decreasing alkaline solution permeability with increasing temperature; an alkaline solution permeable polymeric acid layer containing sufficient acidifying groups to effect reduction, subsequent to substantial multicolor transfer dye image formation, of the image-receiving element from the first pH to a second pH, at which the dye image-providing material is insoluble and nondiffusible; and a dimensionally stable support layer.

The silver halide emulsions comprising the multicolor photosensitive laminate preferably possess predominant spectral sensitivity to separate regions of the spectrum and each has associated therewith a dye, which is a silver halide developing agent and is, most preferably, substantially soluble in the reduced form only at the first pH, possessing a spectral absorption range substantially complementary to the predominant sensitivity range of its associated emulsion. In the preferred embodiment, each of the emulsion strata, and its associated dye, is separated from the remaining emulsion strata, and their associated dye, by separate alkaline solution permeable polymeric interlayers.

In such preferred embodiment of the invention, the silver halide emulsion comprises photosensitive silver halide dispersed in gelatin and is about 0.6 to 6 microns in thickness; the dye itself is dispersed in an aqueous alkaline solution polymeric binder, preferably gelatin, as a separate layer about 1 to 7 microns in thickness; the alkaline solution permeable polymeric interlayers, preferably gelatin, are about 1 to 5 microns in thickness; the alkaline solution permeable and dyeable polymeric layer is transparent and about 0.25 to 0.4 mil. in thickness; the polymeric spacer layer intermediate the dyeable polymeric layer and the polymeric acid layer is transparent and about 0.1 to 0.7 mil. in thickness; the alkaline solution permeable polymeric acid layer is transparent and about 0.3 to 1.5 mils. in thickness; and each of the dimensionally stable support layers are alkaline solution impermeable and about 2 to 6 mils. in thickness. It will be specifically recognized that the relative dimensions recited above may be appropriately modified, in accordance with the desires of the operator, with respect to the specific product to be ultimately prepared.

In the preferred embodiment of the present invention's film unit for the production of a multicolor transfer image, the respective silver halide/dye developer units of the photosensitive element will be in the form of a tripack configuration which will ordinarily comprise a cyan dye developer/red-sensitive emulsion unit contiguous the dimensionally stable support layer, the yellow dye developer/blue-sensitive emulsion unit most distant from the support layer and the magenta dye developer/green-sensitive emulsion unit intermediate those units, recognizing

that the relative order of such units may be varied in accordance with the desires of the operator.

Reference is now made to FIG. 1 of the drawings wherein there is illustrated a preferred film unit of the present invention.

As illustrated in FIG. 1, film unit 10 comprises a photosensitive laminate 11 including, in order, dimensionally stable support layer 12, preferably a flexible sheet material; cyan dye developer layer 13; red-sensitive silver halide emulsion layer 14; interlayer 15; magenta dye developer layer 16; green-sensitive silver halide emulsion layer 17; interlayer 18; yellow dye developer layer 19; blue-sensitive silver halide emulsion layer 20; auxiliary layer 21, which may contain an auxiliary silver halide developing agent; and an image-receiving element 22, including image-receiving layer 23; spacer layer 24; neutralizing layer 25; and dimensionally stable support layer 26, preferably a flexible sheet material.

As shown in the drawing, the multilayer exposed photosensitive element 11 is shown in processing relationship with an image-receiving element 22 and a layer 27 of processing solution distributed intermediate elements 11 and 22.

In the performance of a diffusion transfer multicolor process employing film unit 10, the unit is exposed to radiation, actinic to photosensitive laminate 11.

Subsequent to exposure, film unit 10 may be processed by being passed through opposed suitably gapped rolls in order to apply compressive pressure to a frangible container in order and to effect rupture of the container and distribution of alkaline processing composition 27, having a pH at which the cyan, magenta and yellow dye developers are soluble and diffusible, intermediate dyeable polymeric layer 23 and auxiliary layer 21.

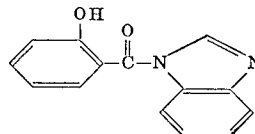
Alkaline processing solution 27 permeates emulsion layers 14, 17 and 20 to initiate development of the latent images contained in the respective emulsions. The cyan, magenta and yellow dye developers, of layers 14, 17 and 20, are immobilized, as a function of the development of their respective associated silver halide emulsions, preferably substantially as a result of their conversion from the reduced form to their relatively insoluble and nondiffusible oxidized form, thereby providing imagewise distributions of mobile, soluble and diffusible cyan, magenta and yellow dye developer, as a function of the point-to-point degree of their associated emulsion's exposure. At least part of the imagewise distributions of mobile cyan, magenta and yellow dye developer transfers, by diffusion, to aqueous alkaline solution permeable polymeric layer 23 to provide a multicolor dye transfer image to that layer. Subsequent to substantial transfer image formation, a sufficient portion of the ions comprising aqueous alkaline solution 27 transfers, by diffusion, through permeable polymeric layer 23, permeable spacer layer 24, and to permeable polymeric acid layer 25, whereby alkaline solution 27 decreases in pH, as a function of neutralization, to a pH at which the cyan, magenta and yellow dye developers, in the reduced form, are insoluble and nondiffusible, to provide thereby a stable multicolor dye transfer image.

Subsequent to substantial transfer image formation, print-receiving element 22 may be manually dissociated from the remainder of the film unit, for example, by stripping.

The following examples are considered illustrative only and should not be taken in a limiting sense.

EXAMPLE 1

The compound, 1-(2'-hydroxy benzoyl)benzimidazole,



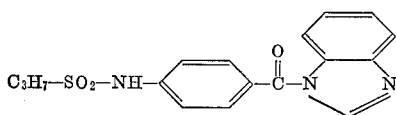
13

was synthesized according to the following procedure:

3 gms. of benzimidazole were suspended in ethyl acetate and 5.25 gms. of 2-hydroxybenzoyl chloride was dissolved in ethyl acetate and added portionwise to the benzimidazole. The reactants were stirred at room temperature overnight. The mixture was then heated and filtered to remove the insoluble benzimidazole hydrochloride. The filtrate was evaporated to dryness and recrystallized from chloroform to give a white solid with a melting point of 166 to 170° C.

EXAMPLE 2

The compound, 1-(4'-propanesulfonamido benzoyl) benzimidazole,

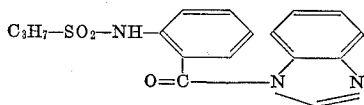


was synthesized according to the following procedure:

14.2 gms. of propane sulfonyl chloride was added to 13.7 gms. of p-amino benzoic acid in 100 ml. of pyridine. The reactants were stirred for two hours at room temperature and poured onto ice. The crude product was suspended in boiling ethyl acetate. Next, enough methanol was added to give a clear solution. This solution, was treated with Norit, was filtered and concentrated. A white solid with a melting point over 250° C. crystallized out. this was discarded and the filtrate was further concentrated to a very small volume whereupon a tan solid with a melting point of 174 to 175° C. crystallized out. The infrared spectrum of this material was consistent with 4-propane sulfonamido benzoic acid. 24.3 gms. of the 4-propane sulfonamido benzoic acid was heated with 40 gms. of phosphorous pentachloride to 150° C. As soon as the melt was homogeneous it was cooled and triturated with hexane to give a crude product comprising 4-propane sulfonamido benzoyl chloride. The product was recrystallized from a benzene/hexane solution to give a white crystalline product with a melting point of 125-126° C. 1.2 gms. of benzimidazole was then suspended in ethyl acetate and 1.3 gms. of 4-propane sulfonamido benzoyl chloride was added portionwise. The mixture was stirred at room temperature for several hours, then heated to reflux, and the benzimidazole hydrochloride was filtered off. The filtrate was concentrated to a small volume and a crude product crystallized out. It was recrystallized from ethyl acetate/acetone and was found to have a melting point of 215-217° C.

EXAMPLE 3

The compound, 1-(2'-propanesulfonamido benzoyl) benzimidazole,



was prepared according to the following procedure:

70 gms. of 2-amino benzoic acid was dissolved in 350 ml. of 8% aqueous sodium hydroxide solution. 101 gms. of propane sulfonyl chloride was added portionwise while maintaining the temperature below 60° C. and the pH above 9. The solution was allowed to stand for 15 minutes, was acidified, and the crude product was filtered off. This crude material, 2-propane sulfonamido benzoic acid, was heated with 42 gms. of phosphorous pentachloride to a temperature of 150° C. When the melt was homogeneous it was cooled to room temperature and triturated with

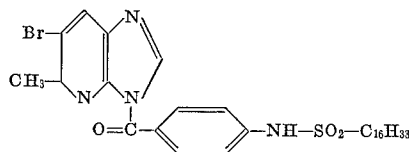
14

hexane. The product, 2-propane sulfonamido benzoyl chloride was recrystallized from ethyl acetate in a Dry Ice bath and was a tan solid with a melting point of 63-65° C.

4 gms. of benzimidazole was then suspended in ethyl acetate and 3.3 gms. of the 2-propane sulfonamido benzoyl chloride was added portionwise. The reaction was stirred overnight, was filtered, and the filtrate concentrated. Next the filtrate was dissolved in chloroform containing some oxalic acid. This was stirred for a couple of hours and filtered. The filtrate was concentrated to give a dark oil. This dark oil was dissolved in ethyl ether leaving behind an insoluble residue. The ethyl ether solution was concentrated to give a yellow oil containing white crystals. The oil was dissolved again in ethyl ether. This time it was dissolved leaving the crystals behind. The ether solution was dried with magnesium sulfate, filtered, and concentrated to give a light yellow oil. The MMR and IR were consistent with the consigned structure of the 1-(2'-propanesulfonamido benzoyl) benzimidazole.

EXAMPLE 4

The compound 6-bromo-3-(4'-hexadecane-sulfonamido benzoyl)-5-methyl-4-azabenzimidazole,

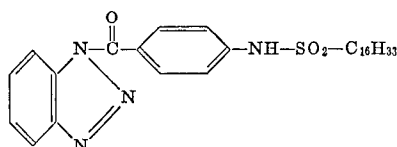


was made according to the following procedure: 23.3 gms. of 4-amino-benzoic acid was dissolved in 350 ml. of pyridine while keeping the temperature at 5° C. 50 gms. of 1-hexadecanesulfonyl chloride was added portionwise waiting after each addition until it had all reacted and gone into solution. The total time of addition was 10 hours. After the addition was completed the mixture was stirred at room temperature for 16 hours., the pyridine was evaporated off on a vacuum rotary evaporator with a steam bath temperature of 60° C. The thick pink paste that was obtained was dried in a vacuum oven then recrystallized from methyl Cellosolve (400 ml.) obtaining a white pink solid. It was recrystallized once more from methyl Cellosolve and 46.2 gms. of a white solid 4-hexadecane-sulfonamido-benzoic acid with a melting point of 191-193° C. was obtained. 46 gms. of the 4-hexadecane-sulfonamido-benzoic acid was suspended in 700 ml. of benzene and 15 gms. of oxalyl chloride, dissolved in 20 ml. of benzene, was added dropwise to the suspension. The mixture was heated at reflux temperature for 2 hours after which there still was undissolved solid. Two more gms. of oxalyl chloride was added and reflux was continued for another three hours. The reaction mixture was then cooled to room temperature. The small amount of solid present was filtered off and the benzene was evaporated on a rotary evaporator with a steam bath temperature of 50° C. To the resulting thick paste about 200 ml. of petroleum ether was added giving a white solid which was repeatedly washed with petroleum ether. 42 gms. of solid 4-hexadecane-sulfonamido-benzoyl chloride with a melting point of 78°-83° C. was recovered. 19 gms. of 6-bromo-5-methyl-4-azabenzimidazole, 20 gms. of 4-hexadecane-sulfonamido-benzoyl chloride and 800 ml. of ethyl acetate were mixed and allowed to stir at room temperature for 48 hours. The solution became quite thick after a couple of hours at which time another 200 ml. of ethyl acetate was added. The mixture was taken down to dryness then suspended in 1 l. of water. The solid was filtered off and washed repeatedly with water. After drying, the solid in a vacuum oven it was recrystallized from 1,2-dimethoxyethane (about 500 ml.) twice. 9.7 gms. of 6-bromo-3-(4-hexadecane-sulfonamido-benzoyl)-5-methyl-4-azabenzimidazole with a melting point of 186-187° C. was recovered.

15

EXAMPLE 5

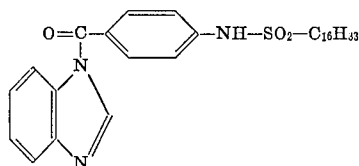
The compound 1 - (4 - hexadecanesulfonamidobenzoyl) 4-benzotriazole,



was synthesized according to the following procedure: 5.9 gms. of benzotriazole, 8.5 gms. of 4-hexadecanesulfonamidobenzoyl chloride and 400 ml. of ethyl acetate were mixed and stirred at room temperature for 48 hours. The mixture was taken down to dryness, suspended in 1 l. of water, and the solid was filtered off. The solid was recrystallized from a mixture of 20% ethyl acetate, 80% ethanol, 7.6 gms. of 1-(4-hexadecanesulfonamidobenzoyl) 4-benzotriazole with a melting point of 142–144° C. was recovered.

EXAMPLE 6

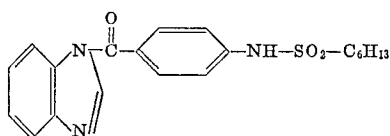
The compound 1 - (4 - hexadecanesulfonamidobenzoyl) benzimidazole,



was prepared according to the following procedure: To 30 ml. of ethyl acetate 2 gms. of 4-hexadecanesulfonamidobenzoyl chloride was added along with 1.06 gms. of benzimidazole. The mixture was stirred for 24 hours at room temperature, then evaporated to dryness at reduced pressure. The residue was mixed with 100 ml. of water and filtered. The precipitate, 1-(4-hexadecanesulfonamidobenzoyl)benzimidazole was recrystallized from benzene and had a melting point of 164–165° C.

EXAMPLE 7

The compound 1-(4-hexanesulfonamidobenzoyl)benzimidazole,



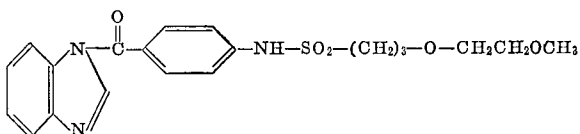
was prepared according to the following procedure: To 500 ml. of benzene was added 32.8 gms. of 4-hexanesulfonamidobenzoyl chloride. The mixture was partially distilled to remove residual water. To the remaining slurry was added 15 ml. of oxalyl chloride and the mixture was refluxed 10 hours to produce a clear solution. The solvent was distilled to dryness at reduced pressure to give a solid residue. To this was added 600 ml. of dry ethyl acetate and, with stirring, 20.2 gms. of benzimidazole. Temperature rose to 35° C. After one hour the mixture was filtered. The precipitate was dried and washed with water and dried again. It weighed 18.2 gms. The ethyl acetate filtrate was evaporated to dryness, the residue was washed with water and dried, and then washed with dichlorometh-

16

ane. This weighed about 18 gms. It was combined with the above solid and the whole recrystallized from a mixture of 20% ethyl acetate and 80% ethanol. 16.3 gms. of the 1-(4-hexanesulfonamidobenzoyl)benzimidazole with a melting point of 192°–194° C. was recovered.

EXAMPLE 8

The compound, 1-[4'-(3''-(2'''-methoxyethoxy)propane sulfonamido]benzoyl]-benzimidazole,



was prepared according to the following procedure: To 20 ml. of dry benzene was added 2 gms. of 4-[3'-(2''-methoxyethoxy)propane sulfonamido] benzoic acid (prepared by reacting methoxyethoxy propane sulfonyl chloride with p-amino benzoic acid (see Example 2)) and 1.1 ml. of ovalyl chloride. The mixture was heated 1 hour at 80° C. and then distilled under reduced pressure at 40° C. To the oily residue was added 25 ml. of ethyl acetate and 1.49 gms. of benzimidazole. After 1 hour stirring the mixture was filtered and the filtrate evaporated to dryness. The combined precipitate and residue was washed first with water then with dilute hydrochloric acid, then again with water. The undissolved solid was dried and recrystallized from 1,1-2,2-tetrachloroethane. 1.51 gms. of 1-[4'-(3''-(2'''-methoxyethoxy)propane sulfonamido]benzoyl]benzimidazole with a melting point of 163°–165° C. was recovered.

EXAMPLE 9

An image-receiving element was prepared by coating a cellulose nitrate subcoated baryta paper with the partial butyl ester of polyethylene/maleic anhydride copolymer prepared by refluxing, for 14 hours, 300 gms. of DX-840-31 Resin [trade name of Monsanto Chemical Co., St. Louis, Mo., for high viscosity poly-(ethylene/maleic anhydride)], 140 gms. of n-butyl alcohol and 1 cc. of 85% phosphoric acid to provide a polymeric acid layer approximately 0.3 mil thick. The external surface of the acid layer was coated with a 1% solution of polyvinyl alcohol in water to provide a polymeric spacer layer approximately 0.30 mil thick. The external surface of the spacer layer was then coated with a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine, at a coverage of approximately 600 mgs. per square foot, to provide a polymeric image-receiving layer approximately 0.40 mil thick. The thus-prepared image-receiving element was then baked at 180° F. for 30 minutes and then allowed to cool.

A multicolor, multilayer photosensitive element was prepared in a manner similar to that disclosed in the aforementioned U.S. Pat. No. 3,345,163 and detailed hereinbefore. In general, the photosensitive elements comprised a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum. In turn, the emulsions had dispersed behind them in water-immiscible organic solvents and contained in separate gelatin polymeric layers, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer. A polymeric interlayer was positioned between the yellow dye developed layer and the green-sensitive emulsion stratum, and also between the magenta dye developer layer and the red-sensitive emulsion stratum. The particular dye developers employed in the

photosensitive elements were 1,4-bis-(α -methyl- β -hydroquinonyl-ethylamino) - 5,8 - dihydroxyanthraquinone (a cyan dye developers); 2-(p-[2',5'-dihydroxyphenethyl]-phenylazo)-4-isopropoxy-1-naphthol (a magenta dye developer); and 1-phenyl-3-n-hexyl-carbamyl-4-(p-[hydroquinonyl-ethyl]-phenylazo)-5-pyrazolone (a yellow dye developer). The last-mentioned yellow and magenta dye developers are disclosed in U.S. Pat. No. 3,134,764 and the cyan dye developer is disclosed in U.S. Pat. No. 3,135,606.

In order to demonstrate the unique advantages of the present invention, comparative studies utilizing 5-methyl-6-bromo-4-azabenzimidazole antifoggant, which is disclosed in the above-mentioned U.S. application of Howard G. Rogers, Ser. No. 689,611, was utilized in a given diffusion transfer photographic system is unmasked and masked form according to the teachings of the present invention. In addition, as a control, the same photographic process was utilized without any antifoggant in the system. In order to appreciate the temperature latitude characteristics which may be achieved according to the instant invention, tests were carried out at 50°, 75° and 100° F.

Initially a negative manufactured as described above, is overcoated with a thin layer of gelatin at a weight of .014 gm. per square foot of negative material. The negatives which are to be utilized in testing the masked antifoggant, instead of being overcoated merely with gelatin, contain in the overcoat an additional .014 gm. of hydrolyzable antifoggant precursor which, in this case is, 6-bromo-3 - (4' - hexadecanesulfonamido benzoyl)-5-methyl-4-azabenzimidazole. The developing solution utilized in the system containing the antifoggant precursor is identical to that utilized in the system containing no antifoggant and comprises:

Water—95 cc.
Hydroxyethyl cellulose—3.8 gms.
Potassium hydroxide—10 gms.
Benzyl- α -picolinium bromide—2.5 gms.

The system which contains a viable antifoggant initially is treated with a developing composition identical to that above with the exception that 0.344 gms. of the antifoggant, 5-methyl-6-bromo-4-azabenzimidazole, is included therein.

All of the multicolor photosensitive negative elements were exposed to a step-wedge to selectively filtered radiation and processed by spreading the aqueous liquid processing composition between said multicolor negative elements and image-receiving elements manufactured as described above as they were brought into superposed relationship in the absence of actinic radiation. After an imbibition of one minute in the cases where the development was carried out at 75° and 100° F., and 2 minutes, 15 seconds when the development was carried out at 50° F. the image-receiving element was separated from the remainder of the film-assembly. The following tabulations collectively and succinctly presents the results achieved during the instant comparative testing.

COMPARATIVE STUDY AT 50° F.

	System without antifoggant	System with 5-methyl-6-bromo-4-azabenzimidazole	System containing 6-bromo-3-(4'-hexadecanesulfonamido benzoyl)-5-methyl-4-azabenzimidazole
Relative Speed ¹	1.22	0.82	1.23
D _{max}			
Red.....	.87	1.13	.88
Green.....	1.23	1.71	1.30
Blue.....	1.40	1.90	1.52
D _{min}			
Red.....	.12	.21	.07
Green.....	.11	.17	.08
Blue.....	.11	.22	.09
D _{max} : Divergence.....	.53	.77	.64

¹ 0.6 reflection density on green curve.

COMPARATIVE STUDY AT 75° F.

	System without antifoggant	System with 5-methyl-6-bromo-4-azabenzimidazole antifoggant	System containing 6-bromo-3-(4'-hexadecanesulfonamido benzoyl)-5-methyl-4-azabenzimidazole
Relative speed ¹	(?)	1.11	1.37
D _{max}			
Red.....	.56	.88	.67
Green.....	.52	1.30	.89
Blue.....	.35	1.60	1.09
D _{min}			
Red.....	0.5	.08	.05
Green.....	.06	.10	.05
Blue.....	.07	.10	.05
D _{max} : Divergence.....	.21	.72	.42

¹ 0.6 reflection density on green curve.

² Not available.

COMPARATIVE STUDY AT 100° F.

	System without antifoggant	System with 5-methyl-6-bromo-4-azabenzimidazole antifoggant	System containing 6-bromo-3-(4'-hexadecanesulfonamido benzoyl)-5-methyl-4-azabenzimidazole
Relative speed ¹	(?)	1.22	1.36
D _{max}			
Red.....	.32	.96	.87
Green.....	.26	1.20	.96
Blue.....	.19	1.38	1.02
D _{min}			
Red.....	.04	.06	.03
Green.....	.06	.09	.06
Blue.....	.06	.10	.05
D _{max} : Divergence.....	.13	.42	.15

¹ 0.6 reflection density on green curve.

² Not available.

In the 75° and 100° F. comparative evaluations the system containing no antifoggant was substantially inviable and never achieves the .6 ordinate on the reflection density scale due to uncontrolled formation of fog, which is incident from the D_{max} information for this system. It will be initially recognized that the presence of the hydrolyzable antifoggant precursor has substantially no inhibiting effect on the film at 50° F. The speed is approximately the same as the system without antifoggants while the D_{max}'s are greater and the D_{min}'s are smaller. When compared with the system containing a viable antifoggant it is noted that the use of the antifoggant precursor produces a marked increase in speed as well as a substantial decrease in stain, or D_{min}.

At 75° F. utilization of the masked antifoggant again provides higher speed to the system and substantially less stain which is likewise true at 100° F. Of further consequence is the fact that the color divergence, that is, the ordinate difference between the color curve having the highest D_{max} and the color curve having the lowest D_{max} is, in all instances, less when the antifoggant precursor is utilized than when the initially viable antifoggant is employed. The divergence in the control can be substantially discounted because of the extremely low reflection densities achieved. It will be evident from a consideration of the temperature-speed-D_{max} relationship depicted in the above comparative charts that in the instance of the antifoggant precursor, very little antifoggant is available in the cold temperatures, and more is progressively released as the temperature increases to provide a film product with a substantially constant speed over a wide temperature range.

It has been found that when the compounds of the present invention are incorporated directly into the photosensitive emulsion of a diffusion transfer photographic product, a degree of stabilization is achieved. That is to say that substantially the same picture quality results with a newly made product as with a product which has been stored under other than reduced temperature conditions for an extended period. Accordingly, it will be appreciated that within the context of the present invention, stabilization properties may be anticipated with the

incorporation of the herein disclosed antifoggant precursors in photographic emulsions as an unexpected bonus.

In general, the optimum concentration of the agent to be employed as an antifoggant precursor should be determined empirically for each given specific photographic system. A typical concentration range is between 0.005 to 5.0 mgs. per mg. of silver halide present in the silver halide emulsion of concern depending on the fogging characteristics of said emulsion. Although concentrations in excess of the given range may be employed an increase in the concentration beyond certain empirical limits generally provides no additional beneficial results. Conversely, concentrations below that of the designated range merely decrease fog control at high temperatures below the effective levels generally sought but, nonetheless, do not negate the achievement of some beneficial fog control.

The agents themselves may be initially disposed in any one or more processing composition permeable layers of the film unit's photosensitive and/or image-receiving elements, at any stage during their manufacture.

It will be appreciated that within the context of the present invention, the "bulkiness" of specific antifoggant nucleus materials may be adjusted to provide an anchoring or diffusion-inhibiting function within a given photographic system. Such a design might easily be applicable to situations where it is desirable to localize antifoggant activity in the immediate vicinity of a given emulsion in order to maintain a desired antifoggant concentration range in the area of that emulsion. Moieties which have been found quite useful for this purpose are long chain fatty acid groups as, for example, octyl, stearyl, etc.

It should also be appreciated that the time within the development cycle at which the antifoggant composition "sees" the alkaline processing composition may be adjusted by judicious placement of said antifoggant within the photographic system. In this manner it will be seen that the release of antifoggant for use in conjunction with a given emulsion may be delayed until the end of the fog induction period in the antifoggant-associated emulsion.

The liquid processing composition referred to for effecting monochromatic and multicolor transfer processes comprises at least an aqueous solution of an alkaline compound, for example, diethylamine, sodium hydroxide sodium carbonate, etc. and possesses a pH in excess of 12 preferably. If the liquid processing composition is to be applied to the emulsion by being spread thereon, preferably in a relatively thin uniform layer, it may include a viscosity-increasing compound constituting a film-forming material of the type which, when said composition is spread and dried, forms a relatively firm and relatively stable film. A preferred film-forming material is a high molecular weight polymer such as a polymeric, water-soluble ether which is inert to an alkaline solution such as, for example, a hydroxyethyl cellulose or sodium carboxymethyl cellulose. Other film-forming materials or thickening agents whose ability to increase viscosity is substantially unaffected if left in solution for a long period of time may also be used. The film-forming material is preferably contained in the processing composition in suitable quantities to impart to said composition a viscosity in excess of 1,000 centipoises at a temperature of approximately 24° C. and preferably of the order of 1,000 to 200,000 centipoises at said temperature. Illustrations of suitable liquid processing compositions may be found in the several patents and copending applications herein mentioned and also in examples herein given. Under certain circumstances, it may be desirable to apply a liquid processing composition to the photosensitive element prior to exposure, in accordance with the technique described in U.S. Patent No. 3,087,816, issued Apr. 30, 1963.

It will be noted that the liquid processing composition employed may contain an auxiliary or accelerating developing agent, such as p-methylaminophenol, 2,4 - diaminophenol, p-benzylaminophenol, hydroquinone, tolu-

hydroquinone, phenylhydroquinone, 4'-methylphenylhydroquinone, etc. It is also contemplated to employ a plurality of auxiliary or accelerating developing agents, such as a 3-pyrazolidone developing agent and a benzenoid developing agent, as disclosed in U.S. Pat. No. 3,039,869, issued June 19, 1962. As examples of suitable combinations of auxiliary developing agents, mention may be made of 1-phenyl-3-pyrazolidone in combination with p-benzylaminophenol and 1 - phenyl-3-pyrazolidone in combination with 2,5 - bis-ethyleneimino-hydroquinone. Such auxiliary developing agents may be employed in the liquid processing composition or they may be initially incorporated, at least in part, in one or more permeable strata of the film unit. It may be noted that at least a portion of the dye developer oxidized during development may be oxidized and immobilized as a result of a reaction, e.g., an energy-transfer reaction, with the oxidation product of an oxidized auxiliary developing agent, the latter developing agent being oxidized by the development of exposed silver halide. Such a reaction of oxidized developing agent with unoxidized dye developer would regenerate the auxiliary developing agent for further reaction with the exposed silver halide.

In addition, development may be desirably effected in the presence of an onium compound, particularly a quaternary ammonium compound, in accordance with the processes disclosed in U.S. Pat. No. 3,173,786.

The support layers referred to may comprise any of the various types of conventional rigid or flexible supports, for example, glass, paper, metal, and polymeric films of both synthetic types and those derived from naturally occurring products. Suitable materials include paper; aluminum; polymethacrylic acid, methyl and ethylesters; vinyl chloride polymers; polyvinyl acetal; polyamides such as nylon; polyesters such as polymeric films derived from ethylene glycol terephthalic acid and cellulose derivatives such as cellulose acetate, triacetate, nitrate, propionate, butyrate, acetate-propionate, or acetate-butyrate.

It will be understood that silver halides of varying halide concentrations may be advantageously employed and that the silver halide emulsions employed may be sensitized chemically and optically by any of the accepted procedures.

While a rupturable container provides a convenient means for spreading a liquid processing composition between layers of a film unit whereby to permit the processing to be carried out with a camera apparatus, the practices of this invention may be otherwise effected. For example, a photosensitive element, after exposure in suitable apparatus and while preventing further exposure thereafter to actinic light, may be removed from such apparatus and permeated with the liquid processing composition, as by coating the composition on said photosensitive element or otherwise wetting said element with the composition, following which the permeated, exposed photosensitive element, still without additional exposure to actinic light, is brought into contact with the image-receiving element for image formation in the manner heretofore described.

In examples of this specification, percentages of components are given by weight unless otherwise indicated.

Throughout the specification and claims, the expression "superposing" has been used. This expression is intended to cover the arrangement of two layers in overlying relation to each other either in face-to-face contact or in separated condition and including between them at least one layer or stratum of a material which may be a viscous liquid.

Since certain changes may be made in the above products, compositions and processes without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. In a process for forming a photographic image which comprises the step of developing an exposed photosensitive

21

element containing a silver halide emulsion with an aqueous alkaline processing composition, the improvement which comprises conducting said process in the presence of an effective concentration of a hydrolyzable antifoggant precursor comprising an antifoggant nucleus possessing a deactivating group which is removed by hydrolysis at a temperature-dependent rate upon being contacted with said processing composition, independent of exposure and development.

2. The process of claim 1 wherein said antifoggant precursor is represented by the formula:



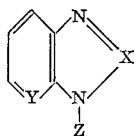
wherein: A is an antifoggant nucleus possessing fog inhibiting properties on said silver halide emulsion; and Z is an antifoggant deactivating moiety which masks an active site of said antifoggant nucleus and is adapted to be removed upon contact with said processing composition, at a temperature-dependent rate.

3. The process of claim 2 wherein said antifoggant precursor is represented by the formula:



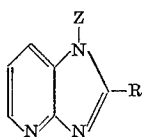
wherein: Z is an alkaline processing composition hydrolyzable antifoggant deactivating group and F is the nonmetallic atoms necessary to complete a heterocyclic antifoggant nucleus.

4. The process of claim 3 wherein said antifoggant precursor is represented by the formula:



wherein: Y is C—H or nitrogen; X is nitrogen or C—R, where R is hydrogen or lower alkyl, i.e., containing less than six carbon atoms; and Z is an alkaline processing composition hydrolyzable antifoggant deactivating group.

5. The process of claim 4 wherein said antifoggant precursor is represented by the formula:



wherein: R is a hydrogen or lower alkyl group; and Z is an alkaline processing composition hydrolyzable antifoggant deactivating group.

6. The process of claim 5 wherein said process is conducted at a temperature within the range of about 50° to 100° F.

7. The process of claim 5 wherein said Z is an acyl or a β -acylalkylene group.

8. The process of claim 5 wherein said alkali hydrolyzable antifoggant precursor is 6-bromo-3-(4'-hexadecane-sulfonamido benzoyl)-5-methyl-4-azabenzimidazole.

9. The process of claim 5 which includes the steps of developing said exposed photosensitive element with an aqueous alkaline diffusion transfer processing composition forming thereby an imagewise distribution of image-forming components in said photosensitive element as a function of the point-to-point degree of exposure thereof and transferring at least part of said imagewise distribution by diffusion to a contiguous image-receiving layer to provide thereto a photographic diffusion transfer image.

10. The process of claim 9 wherein said image-forming components comprise soluble silver complex.

11. The process of claim 9 wherein said image-forming components comprise image-forming materials.

22

12. The process of claim 10 wherein said color image-forming components comprise at least one dye which is a silver halide developing agent.

13. The process of claim 12 which includes, in combination, the steps of exposing a photosensitive element which comprises at least two selectively sensitized silver halide emulsion layers each having a dye of predetermined color associated therewith, which dye is a silver halide development of the latent images contained in each of said tating said exposed photosensitive element with an aqueous alkaline processing composition and effecting thereby hydrolytic removal of said Z moiety from said antifoggant precursor as a function of processing temperature and development of the latent images contained in each of said silver halide emulsions, immobilizing the dye associated with each of said emulsions as a result of said development and forming thereby an imagewise distribution of mobile dye as a function of the point-to-point degree of exposure thereof, and transferring, by imbibition, at least a portion of each of said image wise distributions of mobile dye to a superposed image-receiving element to provide thereto a multicolor dye transfer image.

14. The process of claim 13 which includes, in combination, the steps of exposing a photosensitive element comprising blue-sensitive, green-sensitive and red-sensitive gelatino silver halide emulsion layers mounted on a common support, each of said blue-sensitive, green-sensitive and red-sensitive silver halide emulsion layer having associated therewith, respectively, yellow, magenta and cyan dyes, each of said dyes being a silver halide developing agent soluble and diffusible in alkali; contacting said exposed photosensitive element with an aqueous alkaline processing composition effecting thereby hydrolytic removal of said Z moiety from said antifoggant precursor as a function of processing temperature and development of the latent image contained in each silver halide emulsion; immobilizing said yellow magenta and cyan dye as a function of development of their respective associated silver halide emulsion forming thereby an imagewise distribution of mobile yellow, magenta and cyan dye; and transferring, by imbibition, at least a portion of each of said imagewise distributions of mobile dye to a superposed image-receiving element to provide thereto a multicolor dye transfer image.

15. The process of claim 14 wherein said antifoggant precursor is 6-bromo-3-(4'-hexadecane-sulmonamido benzoyl)-5-methyl-4-azabenzimidazole.

16. The process of claim 14, wherein said process is conducted at a temperature within the range of about 50° to 100° F.

17. As a product, photosensitive element which comprises a support layer carrying a photosensitive silver halide emulsion and having associated therewith a hydrolyzable antifoggant precursor of the formula A—Z, where A is an antifoggant nucleus of the antifoggant A—H and Z is an antifoggant deactivating group, said antifoggant precursor being capable of releasing antifoggant at a temperature-dependent rate independent of exposure and development.

18. The product of claim 17 wherein said antifoggant precursor is represented by the formula:

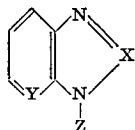


wherein Z is an alkaline processing composition hydrolyzable antifoggant deactivating group and F is the nonmetallic atoms necessary to complete a heterocyclic antifoggant nucleus.

19. The product of claim 18 wherein said antifoggant precursor is represented by the formula: A—Z, wherein A comprises an antifoggant nucleus possessing fog inhibiting properties on said silver halide emulsion and Z is a moiety which deactivates the fog inhibiting properties of said antifoggant nucleus and is adapted to be removed by hydrolysis upon contact with an alkaline processing composition.

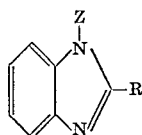
23

20. The product of claim 19 wherein said antifoggant precursor is represented by the formula:



wherein: Y is C—H or nitrogen; X is nitrogen or C—R, where R is hydrogen or lower alkyl, and Z is an alkaline processing composition hydrolyzable antifoggant deactivating group.

21. The product of claim 20 wherein said antifoggant precursor is represented by the formula:



wherein: R is a hydrogen or lower alkyl group; and Z is an alkaline processing composition hydrolyzable antifoggant deactivating group.

22. The product of claim 21 wherein said Z is an acyl or β -acylalkalene group.

23. The product of claim 22 wherein said hydrolyzable antifoggant precursor is 6-bromo-3-(4'-hexadecanesulfonamido-benzoyl)-5-methyl-4-azabenzimidazole.

24. The product of claim 21 wherein said silver halide emulsion has a dye, which dye is a silver halide developing agent associated therewith.

25. The product of claim 24 wherein said dye is disposed in a separate layer intermediate said silver halide emulsion and said support.

26. The product of claim 24 wherein said support layer carries on one surface at least two selectively sensitized silver halide emulsion layers each having a dye which dye is a silver halide developing agent of predetermined color associated therewith.

27. The product of claim 26 wherein each of said selectively sensitized photosensitive emulsion layers has predominant spectral sensitivity to separate regions of the spectrum and the dye associated with each of said emulsion layers possesses a spectral absorption range substantially

24

complementary to the predominant ensitivity range of its associated emulsion layer.

28. The product of claim 27 wherein said photosensitive silver halide emulsion layers comprise, in sequence, a red-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer and a blue-sensitive silver halide emulsion layer, having associated therewith, respectively, cyan, magenta and yellow dyes, each of said dyes being silver halide developing agents.

29. The product of claim 21 which includes a diffusion transfer image-receiving element affixed at least one edge of said photosensitive element.

30. The product of claim 29 which includes a rupturable container retaining an aqueous alkaline processing composition affixed one edge of one of said photosensitive and said image-receiving elements and adapted upon rupture to distribute its contents intermediate said photosensitive element and said image-receiving element upon superpositioning of said elements.

31. The product of claim 27 wherein said antifoggant precursor is dispersed in a silver halide emulsion layer of the photosensitive element.

32. The product of claim 29 wherein said antifoggant precursor is dispersed in a layer on the image-receiving element.

33. The product of claim 28 wherein said hydrolyzable antifoggant precursor is 6-bromo-3-(4-hexadecanesulfonamido-benzoyl)-5-methyl-4-azabenzimidazole.

References Cited

UNITED STATES PATENTS

3,148,062	9/1964	Whitmore, et al.	96—55
3,227,554	1/1966	Barr, et al.	96—55
3,364,022	1/1968	Barr	96—3
3,379,529	4/1968	Porter, et al.	96—36
3,455,686	1/1969	Farney, et al.	96—3
3,473,924	10/1969	Rogers	96—29

NORMAN G. TORCHIN, Primary Examiner

A. T. SURO PICO, Assistant Examiner

U.S. Cl. X.R.

96—66.5, 29

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,575,699 Dated April 20, 1971

Inventor(s) Stanley M. Bloom and Howard G. Rogers

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Claim 11, line 2, after "comprise" insert --color--.

Claim 13, line 6, "velopment of the latent images contain in each of said" should be --veloping agent and is soluble and diffusible, in alkali, con- --.

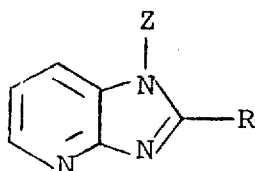
Claim 17, line 1, after "product," insert --a--.

Claim 18, line 1, delete "18." and substitute therefor --: delete "17" and substitute therefor --18--.

Claim 19, line 1, delete "19." and substitute therefor --: delete "18" and substitute therefor --17--.

Claim 21, line 3, cancel the formula and substitute therefor

--



-- .

Claim 27, line 6, "ensitivity" should be --sensitivity--.

Signed and sealed this 21st day of November 1972.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents