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ANTISTATIC PHOTOGRAPHIC FILM

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ABSTRACT OF THE DISCLOSURE

Antistatic agents for use with film-forming organic binders comprising the condensation product of an alkylene oxide having from 2 to 4 carbon atoms with 2,4,7,9-tetramethyl-5-decyne 4,7-diol, said condensation product having a molecular weight of at least 300.

The present invention relates in general to photography and in particular to photographic film materials possessed of superior antistatic properties, as well as to the provision of novel compositions for such purposes.

One of the problems frequently encountered both in the manufacture and use of photographic film elements relates to the pronounced and highly objectionable tendency of such elements to acquire as well as to accumulate intolerable quantities of static electricity. The level of static build-up is unavoidably influenced to a great extent by the conditions employed during the manufacture of the film base, i.e., the sheet materials serving as the support for the emulsion layer as well as the coating operations associated with the subsequent deposition of one or more layers upon such film base, e.g., subbing layers, light-sensitive layers, etc. The generation of static electrical charges can also occur to a significant extent as a result of trimming and packaging operations, by manipulation of the film element in camera mechanisms and particularly, motion picture cameras, cameras utilized for X-ray fluorography, i.e., wherein a sequence of exposures is taken in rapid succession.

The significance of the foregoing phenomena can be made readily evident by reference to the following discussion. As is well known, in the manufacture of multilayer photographic film elements, a film base is coated on one or both sides with for example, a subbing composition usually comprising a dispersion of gelatin in a suitable solvent or solvent mixture, the latter serving to facilitate the adherence or anchorage of subsequently applied layers, e.g., photosensitive, non-curling; antihalation layers, and the like. When such a laminate is wound into a tight curl and subsequently unwound, considerable static electricity is generated and spark discharges are likely to occur. The foregoing phenomena is invariably manifested following development of the exposed film in the form of black streaks, lines, or other irregularities which tend to create a fog pattern throughout the entire emulsion layer. In general, such spurious density deposits become more pronounced as the sensitivity and thus speed of the film material is increased. Consequently, the provision of more efficient sensitizing agent has made incumbent upon the film processor the inclusion in the film element of one or more substances which abate, or otherwise, retard the tendency of such film to accumulate such static charge or alternatively, a substance which is essentially an electrolyte or possesses hygroscopic properties in order to impart

conductivity to the film element and thereby expedite dissipation of such static charges before their accumulation leads to local electrical discharges. It will be readily appreciated that the aforementioned spurious density deposits are objectionable, not only from the standpoint of quality, or reproduction but, more importantly, can be dangerously misleading as would be the case, for example, with medical X-ray films. It is of critical importance with respect to the latter materials that the image obtained constitute a reliable and unimpeachable record of the information recorded. Even the slightest departures of the emulsion material from optimum sensitometric characteristics, as well as any tendency of the film to reflect static charge built-up in the form of spurious density deposits may lead to serious consequences.

Despite the efforts of prior art investigators to devise film-manufacturing techniques, as well as coating methods which would tend to minimize or suppress any possibility of static charge build-up, such problems have nevertheless persisted to challenge film-manufacturing and processing technology. For example, it is often found that the fugitive effects directly attributable to static charge build-up are very much in evidence as a result of mere contact of the film with the gate of the film projector or other parts of the apparatus which the film may frictionally engage during its course of travel through the projector device.

Concomitant with the provision of silver halide emulsions possessed of unusually high photographic speed, has been a corresponding intensification of the antistatic problem. Many of the film materials currently available commercially and specifically and beneficially adapted for use in connection with high speed photoreproduction techniques involve, as required processing, the use of high activity photographic processing solutions, e.g., developer, fixer, etc. As will be recognized, even the slightest tendency of the photographic film element to accumulate static charge will practically, without exception, result in the formation of irregularities in the image-recording emulsion, i.e., defects of the type described hereinbefore. Successful negotiation of the antistatic problem has correspondingly tended to circumscribe severely the emulsion manufacturer's scope of operations with respect to the choice of the ingredients to be included in the emulsion as well as non-sensitized layers of the photographic film element.

In an effort to overcome, or otherwise alleviate the problems associated with static electricity build-up on photographic films, considerable industrial activity has centered around the research and development of substances which could be conveniently included in one or more of the layers present on the photographic film, such substances possessing the singular property of promoting static charge dissipation, or otherwise augmenting the ability of the film element to resist static build-up. In general, such compounds function to reduce the resistivity, i.e., to impart conductivity to the film element and thus to expedite static electricity dissipation prior to discharge and spot exposure of the emulsion. According to recognized practice, such substances are most effectively provided in the form of a film-forming composition utilizing a suitable organic binder material, e.g., resin, colloid, etc., for direct application to the photographic film base as a backing layer. Thus the antistatic compound may be included as a component of an antihalation and/or anticurl, the latter being provided on the opposite side of the film base material, i.e., opposite the light-sensitive emulsion side. Despite the fact that the vast majority of the antistatic compounds thus far promulgated in the art for the aforedescribed purposes have led to significant reductions in antistatic build-up, as well as residual charge retention, the overall improvement realized thereby has nevertheless been somewhat marginal in the aggregate. The sub-optimum effects of such compounds in this connection results primarily from their tendency to otherwise deleteriously affect the photographic film element. In ideal terms, it is imperative that the antistatic compound in no way detract from the strength of adhesion requisite to firm bonding of the backing layer to the film base. Failure in this regard inevitably leads to undesired separation of the backing layer from the film base. This phenomenon often referred to in the art as "dry peel" undesirably characterizes a considerable number of the antistatic compounds heretofore provided. It is likewise of critical importance that the antistatic compound exhibit absolutely no tendency to generate, or otherwise contribute, to the formation of foam in post-exposure processing solutions and particularly those solutions agitated with gas bursts. Quite obviously the existence of foam tends to vitiate any possibility of achieving uniform and intimate contacting of the photographic processing solution with exposed emulsion layer. Again, the emergence of high speed processing has correspondingly rigidified the requirements in this respect. In addition to the aforedescribed desiderata, it is of considerable importance that the antistatic substance be devoid of any tendency to adversely affect the physical appearance of the emulsion layer, e.g., to cause matting, streaking, etc. Furthermore, it is of equal importance that the antistatic compound be totally inert with respect to the sensitometric properties of the photographic film and thus display absolutely no "photoactivity." Despite the relatively vast number of compounds provided in the art for purposes of imparting optimum antistatic behavior to photographic film elements, such compounds are nevertheless invariably found to be deficient in one or more of the aforedescribed aspects. Thus, the use of such compounds usually necessitates resort to the use of additional auxiliary ingredients designed to compensate for the shortcomings of such antistatic agents, e.g., antifoaming agents, antifoggants, sensitizing agents, adhesion promoters and the like. Such corrective procedures can obviously be quite costly, if not prohibitive.

In accordance with the discovery forming the basis of the present invention, it has been ascertained that the use of a rather specific and delimited class of acetylenic diol derivatives makes possible the provision of backing layers for photographic film elements having outstanding antistatic properties, said compounds being totally devoid of any tendency to deleteriously affect the sensitometric properties of the emulsion layer.

Thus, a primary object of the present invention resides in the provision of improved antistatic compositions wherein the foregoing and related disadvantages are eliminated or at least mitigated to a substantial extent.

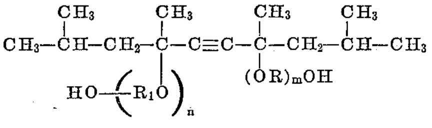
Another object of the present invention resides in the provision of improved film-forming antistatic compositions capable of ready deposition to photographic film base materials in the form of firmly-bonded layers.

A further object of the present invention resides in the provision of film-forming antistatic compositions which are totally devoid of any tendency to detract from the sensitometric properties of photographic elements provided with the same.

A still further object of the present invention resides in the provision of improved antistatic compositions which may be employed to advantage in the preparation of antihalation and anti-curl backing layers for photographic film elements.

Other objects and advantages of the present invention will become 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 antistatic compositions comprising (a) a film forming organic binder, i.e., protective colloid, and (b) an antistatic compound comprising the condensation product of an alkylene oxide with 2,4,7,9-tetramethyl-5-decyne 4,7-diol said condensation products corresponding to the following structural formula:

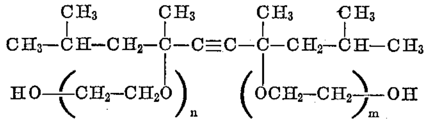


$$\mathrm{CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{HO-(R_1O)_n}{|}}{C}}-C\equiv C-\overset{\overset{CH_3}{|}}{\underset{\underset{(OR)_mOH}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_3}$$

wherein *m* and *n* together represent integers such as to provide a molecular weight within the range of from about 300 to about 150,000 or more, and wherein R and R_1 represent alkylene of 2–4 carbon atoms, e.g., ethylene-propylene, etc.

Particularly beneficial results are found to obtain in accordance with the present invention wherein R and R_1 in the above formula represent ethylene, such products corresponding to the following structural formula:

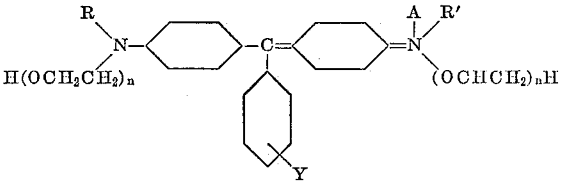
(II)



$$\mathrm{CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{HO-(CH_2-CH_2O)_n}{|}}{C}}-C\equiv C-\overset{\overset{CH_3}{|}}{\underset{\underset{(OCH_2-CH_2)_m-OH}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_3}$$

The products included within the ambit of the above depicted structural formulae may be readily prepared by merely condensing the butyne diol compound with an alkylene oxide according to the method of reacting aliphatic alcohols with alkylene oxides described in U.S. Pat. 1,970,578.

The tertiary, acetylenic diol-alkylene oxide condensates of the present invention are found to provide synergistic improvement when applied as a backing layer on photographic film elements whether the latter be intended for antistatic, or anti-curl purposes, or, alternatively, in the event such backing layer be intended to perform an antihalation function. Accordingly, the film-forming binder may be either of a permanent or temporary nature. In the latter case, resin materials are selected which, though water-insoluble, nevertheless exhibit ready solubility in aqueous alkaline media thus assuring ready removal of the backing layer during post-exposure processing, e.g., developer immersion. Should an antihalation utility be contemplated for the backing layer, the antistatic agent composition will be provided with one or more of the dyestuff materials customarily employed in the art for such purposes. In this connection, reference is made to the dyestuffs described, for example, in U.S. Pats. 1,805,404; 2,036,546; 2,150,695; 2,282,890; 2,304,946; 2,598,660; 2,606,833; 3,264,108; etc. Although any of the afore-referenced dyestuff materials may be employed to advantage in the practice of the present invention salient advantage has nevertheless been determined to obtain with antihalation dyestuffs of the type described in U.S. Pat. 2,598,660, such dyestuffs corresponding to the following structural formula:



wherein *n* represents an integer from 2 to 10 inclusive, Y represents a substituent selected from hydrogen, lower alkyl, halogen, nitro, sulfo, carboxy, carbalkoxy and alkoxy, and A represents an anion of a strong mineral acid, or, alternatively, an internal linkage wherein Y represents sulfo or carboxy, and wherein R and R′ represent lower alkyl, e.g., methyl, ethyl, propyl, etc.; hydroxyalkyl, and omega hydroxypolyoxyalkyl.

The aforementioned dyestuffs are found to present particular advantage in that they are readily and easily decolorized as a concomitant of photographic processing and furthermore, exhibit highly favorable solubility characteristics, i.e., can be readily dissolved away from the antihalation layer in the normal course of post-exposure processing, i.e., developing, fixing, washing, etc.

The film-forming binder component of the backing layer coating composition conventionally termed protective colloid may be selected from any of those well-known in the art for such purposes, with the selection of a particular one being determined largely by the ultimate character contemplated for the backing layer, i.e., whether permanent or transitory, as previously mentioned. In the latter case, any of the water-insoluble, alkali-soluble resin film formers may be used with specific representatives including, for example, copolymers of alkyl methacrylates and methacrylic acid; the carboxy resinic lactones, the polyvinyl phthalates, the polyvinyl acetate phthalates, and the ethyl cellulose phthalates. Other suitable resins include the cellulose organic acid esters containing dicarboxylic acid groups such as cellulose acetate phthalate, cellulose acetate maleate, cellulose acetate succinate, cellulose acetate propionate phthalate, cellulose acetate propionate maleate, and cellulose acetate propionate succinate. The above-enumerated resins and their method of preparation are well known in the art, being extensively described in the literature, both patent and otherwise.

In those instances wherein the backing layer is to be of a permanent nature, it is preferred practice, in accordance with the present invention, to employ as the film-forming binder, a composition comprising at least 50–50% gelation with the remainder comprising, for example, a synthetic polymeric substance of the type hereinbefore mentioned.

In order to assure the obtention of optimum results, it is advisable to employ the polyoxyalkylenated butyne diol antistatic compound in concentrations ranging from about 2% to about 10% by weight, based on the weight, of film-forming binder e.g., gelatin, with a range of 3–6% being particularly preferred. In any event, it will be understood that the antistatic agent, apart from the requirement of being present in amounts sufficient to yield the desired conductive character to the backing layer, is not of critical importance to the realization of the advantages described herein. Thus, it will be envisaged that particular circumstances and requirements of the processor may dictate departures from the aforestated range.

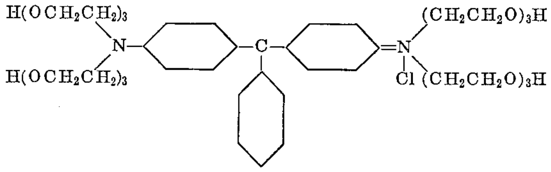
Other ingredients, strictly of an optional nature, which may be included in the backing layer coating composition for purposes of augmenting adhesion strength, stability and the like, include, for example, hardening agents, e.g., formaldehyde, glyoxal, mucochloric acid, etc., coating aids such as saponin or other materials promulgated in the art for such purposes. Again, it must be emphasized that nothing critical attends the selection of the latter-mentioned ingredients, their identity and use being common knowledge in the art. At this point, it should be stressed that the antistatic agents of the present invention possess the highly desirable property of relatively unlimited compatibility with the vast majority of compounds promulgated in the art for the preparation of photographic film backing layer compositions, whether such be intended for use as an antihalation, anti-curl or other purposes.

The film base materials to which the antistatic compositions of the present invention may be applied encompass a wide variety of substances including, for example, cellulose organic esters such as cellulose acetate, or cellulose nitrate; film-forming polymeric materials such as polyvinyl chloride; polyamides; polyesters such as those obtained by the condensation reaction of a dicarboxylic acid with a dihydric alcohol; polycarbonates, and the like.

The advantage made possible by the present invention will be made manifest by reference to the following examples. However, it will be understood that such examples were given for purposes of illustration only, and are not to be considered as necessarily constituting a limitation on the present invention.

EXAMPLE I

An antihalation coating composition of the type conventionally employed in the photographic arts as a backing layer for light-sensitive photographic elements is prepared by adding to 10 liters of an aqueous gelatin solution (10% gelatin), 10 gms. of saponin as coating aid, 10 gms. of formaldehyde (hardening agent) and 16 gms. of the antihalation dyestuff described in Example 1 of U.S. Pat. 2,598,660, said dyestuff having the following structural formula:



4 - [p - bis(8 - hydroxy - 3,6 - dioxaoctyl)amino-α - phenylbenzylidene] - 2,5 - cyclohexadienylidene - [bis(8 - hydroxy-3,6-dioxaoctyl)]imonium chloride.

The composition is adjusted to a pH of 5.6 in order to achieve most effective dye strength. The coating composition thus obtained is divided into three parts identified as (a), (b) and (c) respectively. Part (a) is coated onto one side of a cellulose acetate photographic film base by conventional techniques and serves as the control sample. To part (b), is added 3% based on gelatin solids, of a condensation product of Formula II given hereinbefore, said product comprising the reaction product of 10 mols of ethylene oxide with 2,4,7,9-tetramethyl-5-decyne 4,7-diol. The latter product is available commercially under the trade name designation Surfynol 465. The composition so constituted is thereafter coated onto a cellulose acetate photographic film base. To part (c) is added 3% based on gelatin solids, of a condensation product of Formula II above, comprising the reaction product of 30 mols of ethylene oxide with 2,4,7,9-tetramethyl-5-decyne 4,7-diol. The latter product is available commercially under the trade name designation Surfynol 485. The composition thus prepared is likewise applied to a photographic film base. Each of the coated samples, after drying, is conditioned in an atmosphere of 50% relative humidity for a period of 12 hours. Resistivity measurements of the coatings are then made by the common parallel electrode technique. The results obtained are itemized in the following table:

TABLE I

	Ohms
Control—part (a)	150×10^3
Sample containing Surfynol 465—part (b)	25×10^3
Sample containing Surfynol 485—part (c)	24×10^3

As the above data makes manifestly clear, the antistatic compounds of the present invention make possible at least a five-fold decrease in resistivity of the photographic film base when compared to the control sample. The significant increase in conductivity of such layers allows any static charge accumulated by photographic elements coated therewith to be uniformly dissipated to the extent that only negligible residual charge remains with the correlative advantage that deleterious effects upon the quality of image photoreproduction which would otherwise obtain as a direct result of the presence of such static charge, are completely eliminated.

EXAMPLE II

Example I is repeated except that each of the coated film base materials identified as (a), (b) and (c) respectively, is further provided on the side opposite the backing layer with a conventional photographic silver halide emulsion in gelatin containing 4% silver iodide and 96% silver bromide. After drying, each of the samples is exposed in a Type 1–B Sensitometer and developed in a photographic developer of the following composition:

	Grams
Metol	1.5
Sodium sulfite, anhydrous	45.0
Sodium bisulfite	1.0
Hydroquinone	3.0
Sodium carbonate, monohydrated	6.8
Potassium bromide	.8
Water to make 1.0 liter.	

An inspection of sample (a) reveals the existence of a rather high population of spurious density deposits, or other irregularities which detract considerably from the overall appearance of the final image. In contradistinction, the prints obtained with samples (b) and (c) respectively, are completely devoid of such fugitive density deposits whether in the form of streaks, lines, or other irregularities. In addition, no evidence of emulsion fog is detected. It is also observed that the backing layer exhibits absolutely no tendency to separate from the photographic film base, i.e., is firmly-bonded to such film base, despite continued subjection to the post-exposure processing media, e.g., developer, fixer, etc. Moreover, the objectionable foaming tendency characterizing so many of the antistatic agents heretofore provided in the art, is in no way evident, and thus a highly efficient degree of solution, e.g., developer, contact with the photographic emulsion is attained.

Results similar to those described above are obtained when the procedures exemplified are repeated but wherein the gelatin is replaced totally or partly with other film-forming organic binders either hydrophilic or hydrophobic in nature. In those instances wherein water-insoluble, alkaline-soluble resinous materials are employed, the backing layer is of course temporary in nature. Despite the presence of anti-halation dyestuffs, the backing layer may be permanently affixed so long as such dyestuffs be readily convertible to a colorless, or leuco form so as not to interfere with viewing or projection of the reproduced image.

The present invention has been disclosed with respect to certain preferred embodiments thereof, and there will become obvious to persons skilled in the art, various 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 photographic element comprising a film base coated on one side with a light-sensitive gelatino-silver halide emulsion and on the opposite side of said film base a backing layer comprising (a) a film-forming organic binder and (b) an antistatic compound consisting essentially of the condensation product of an alkylene oxide having from 2–4 carbon atoms with 2,4,7,9-tetramethyl-5-decyne 4,7-diol, said condensation product having a molecular weight of at least 300.

2. A photographic element as defined in claim **1** wherein the alkylene oxide component of the antistatic compound is ethylene oxide.

3. A photographic element as defined in claim **1** wherein the film-forming organic binder of the backing layer is gelatin.

4. A photographic element as defined in claim **1** wherein the backing layer further contains an antihalation dyestuff.

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RONALD H. SMITH, Primary Examiner

U.S. Cl. X.R.

96—87 A; 106—125, 137