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## ANTISTATIC PHOTOGRAPHIC FILM

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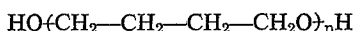
Int. Cl. G03c 1/82

U.S. Cl. 96-84

6 Claims

## ABSTRACT OF THE DISCLOSURE

An antistatic composition and a photographic film element containing said antistatic composition, comprising (a) a film-forming organic binder and (b) an antistatic compound comprising a polyether glycol of the following structural formula:



wherein  $n$  represents a positive integer sufficient to provide a molecular weight within the range of from about 650 to about 2000.

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 condition 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. Thus, as will be evident, the accumulation of static electrical charges can result from almost any operation, whereby as an incident thereto, the photographic film element is caused to come into contact with a dissimilar surface, whether due to handling, the nature of the rollers employed in the coating machinery, etc.

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 multi-layer 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, noncurling; 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 is increased. Consequently, the provision of more efficient sensitizing agents has made incumbent upon the film processor the inclusion in the film element of one

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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 of 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 build-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 buildup 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 buildup. 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. In general, the antistatic compound may be employed to greater or lesser advantage in either the sensitized emulsion layer, an intermediate, auxiliary layer, e.g., subbing layer or as a component of an outer layer, e.g., antiabrasion layer. In many instances, the antistatic compound may be utilized to exceptional advantage in the form of a backing layer disposed on a photographic film base surface opposite to that carrying the light-sensitive layer or layers. According to the latter expedient, the antistatic agent is most effectively

provided in the form of a film-forming composition employing a suitable film-forming, organic binder material, e.g., resin, colloid, etc., and thus is in a form suitable for direct application to the photographic film base.

Despite the fact that the vast majority of the antistatic compounds thus far promulgated in the art for the afore-described purposes have led to significant reductions in antistatic buildup 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.

The problems encountered have perhaps been most severe in those instances wherein the antistatic compound is designed primarily for direct use in the light-sensitive emulsion layer. As will be readily appreciated, it is imperative that the antistatic agent contemplated for such use be substantially inert with respect to sensitometric characteristics of the emulsion, i.e., exhibit negligible tendency to unfavorably affect such properties as, contrast, speed, density and the like. However, a significant number of the antistatic agents heretofore provided are uniformly characterized in exhibiting a rather pronounced photoactive behavior. For example, it has been ascertained that many of the antistatic agents derived from polyethylene glycols tend to create severe fogging problems as well as other undesired effects. In order to avoid such shortcomings, it has become recognized practice to confine the use of such antistatic compounds to one or more of the non-sensitized layers present on the photographic element. However, such procedures have proved to be only partly remedial since their fugitive "photoactivity" is often manifested in connection with the photographic development operation, such condition being often referred to as "development fog." In ideal terms, it is essential that the antistatic compound not only be devoid of any significant degree of photoactive behavior or any other property which would tend to preclude its use in a light-sensitive emulsion layer but in addition, in no way detract from the strength of adhesion requisite to firm-bonding with the photographic film base in those instances where applied in the form of a backing layer. Failure in this regard inevitably leads to undesired separation of the backing layer from the film base, this phenomenon being often referred to in the art as "dry peel." 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 the 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 utmost 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. The importance of the latter factor correspondingly emphasizes the requirement that the antistatic agent exhibit relatively unlimited compatibility with the remaining ingredients of the coating composition in question and especially where such composition is intended for use as the light-sensitive emulsion layer.

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 and particularly in those instances involving the use of the film under low humidity conditions. Thus, the efficacious use of such compounds usually imposes the additional requirement that auxiliary ingredients, designed to compensate for the

shortcomings of such antistatic agents, e.g., antifoaming agents, antifoggants, sensitizing agents, adhesion promoters and the like be included. 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 polyether glycols makes possible the obtention of photographic film elements possessed of superior antistatic properties without regard to the particular situs of such compounds, i.e., whether included in a light-sensitive and/or non-sensitized, auxiliary layer, such compounds being totally devoid of any tendency to deleteriously affect the sensitometric properties of the film element.

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.

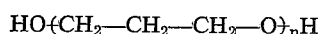
Another object of the present invention resides in the provision of improved antistatic compounds which are readily compatible with the various ingredients conventionally employed in the preparation of sensitized and non-sensitized coating compositions designed for use in the fabrication of photographic film elements.

A further object of the present invention resides in the provision of antistatic compounds which in no way adversely affect the sensitometric properties of light-sensitive photographic emulsions whether included in the light-sensitive emulsion per se or alternatively in one or more auxiliary, non-sensitized layers.

A still further object of the present invention resides in the provision of antistatic compounds, compositions containing same as well as photographic elements fabricated therewith having superior antistatic properties and especially under conditions of low humidity.

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 improved antistatic compounds comprising polytetramethylene ether glycols of the following structural formula:



wherein  $n$  represents a positive integer sufficient to provide a molecular weight within the range of from about 650 to about 2,000.

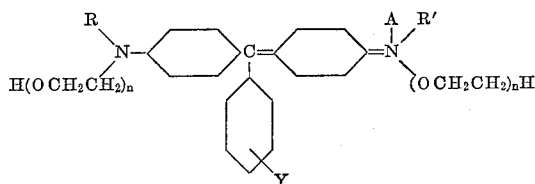
The compounds encompassed by the above structural formula which are derivatives of tetrahydrofuran are readily available commercially from the Quaker Oats Company under the trade name designation "QQ" Polymegs.

The antistatic compounds of the present invention are beneficially adapted for use in the light-sensitive emulsion layer and/or one or more auxiliary layer of the type conventionally provided on multilayer photographic elements. Such compounds are especially desirable since they exhibit sufficient compatibility with the wide variety of film-forming organic binder materials customarily utilized in the preparation of both sensitized and non-sensitized layers, whether such film-forming material be hydrophilic or hydrophobic in nature. Consequently, any necessity for the use of special auxiliary ingredients whereby to facilitate the obtention of a homogeneous and uniform dispersion is completely obviated. Thus, the particular layer-forming composition may be constituted either wholly or partly of gelatin. In the latter case, a predetermined portion of the gelatin is replaced by a different film-forming organic binder according to techniques well known in the art. In any event, the processor may exercise wide discretion in selecting the ingredients which comprise such layers without fear of encountering compatibility problems.

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In order to assure optimum results, it is advisable to employ the polytetramethylene ether glycols in concentrations ranging from about 2% to about 15% by weight based upon the total weight of film-forming binder, e.g., gelatin with a range of 4-10% 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 photographic element, 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 aforesaid range.

Significant improvement in antistatic behavior can likewise be obtained by the use of the polytetramethylene ether glycol as an additive to a backing layer composition 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:



where  $n$  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 resins film formers may be used with specific representatives including, for example, copolymers of alkyl methacrylates and methacrylic acid, the carboxy

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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 50-60% gelatin with the remainder comprising for example a synthetic polymeric substance of the type hereinbefore mentioned.

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 of natural origin, as well as any of the synthetic 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.

The synergistic improvement attending the use of the antistatic compounds described herein are noted to obtain to particular advantage when such compounds are included as ingredients of a surface layer, i.e., as the outermost layer on the emulsion side of the photographic element. When proceeding according to this embodiment, it is in general advantageous to employ as the film-forming organic binder, i.e., protective colloid, a composition containing significant quantities of gelatin. Again, the concentration of antistatic agent is preferably maintained within the range hereinbefore specified. The employment of the antistatic agent in a surface layer presents the singular advantage that maximum resistance to both static charge acquisition and accumulation is centered in that portion of the photographic element most likely to be subjected to frictional contact with charge-imparting environments, whether as a result of handling, packaging, manipulation in various camera devices, etc. Significant advantages can likewise be realized by adding the antistatic agent to 2 or more of the layers present on the photographic element. For example, if the final film product be contemplated for usage which would inherently involve extensive frictional contact, e.g., cine type film or any other film material likely to be subjected to rapid sequential exposure, it may well be advisable to include the antistatic agent not only in a gelatin surface layer, but alternatively in a backing layer which may be applied as previously mentioned as an antistatic backwash, anti-curl or anti-halation layer in order to assure maximum suppression of static charge buildup and retention. Further embodiments of the present invention contemplate the inclusion of the antistatic agent in an intermediate, non-sensitized layer, such as, a subbing layer. The efficacy of a particular manner of proceeding will of course be controlled primarily by the severity of the antistatic problem to be negotiated.

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 advantages made possible by the present invention will be made manifest by reference to the following ex-

amples. 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

A cellulose acetate support is coated on both sides with a conventional gelatino-silver halide emulsion of the X-ray type. To each of said light-sensitive coatings is applied an anti-abrasion layer comprising a 2% gelatin solution (aqueous) containing a gelatin-hardening agent (formaldehyde), a spreading agent (saponin) and a matte agent.

A second sample of cellulose acetate film base is similarly coated except that the gelatin anti-abrasion layer in each case contains in addition, 10% by weight based on dry gelatin of a polytetramethylene ether glycol of the formula given hereinbefore having a molecular weight of about 650. The latter product is commercially available from the Quaker Oats Company under the trade name designation "QQ" Polymeg 620. Each of the film strips thus prepared is divided into 10 strips measuring  $1\frac{1}{16}$  inches wide and 10 inches in length. All of the film strips are conditioned at a relative humidity of 23% for a period of approximately 12 hours. Each of the strips is thereafter rubbed in total darkness with a nylon pad in such manner as to generate static electricity in the film. Immediately thereafter, each of the samples is 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.       |       |

followed by fixing, washing and drying.

An examination of the developed film strips serving as control, i.e., not containing the polytetramethylene ether glycol antistatic agent, reveals the existence of a rather high population of spurious density deposits or other irregularities in the form of black streaks, specks, lines or various other patterns in the otherwise clear emulsion. In contradistinction, each of the film strips provided with the polytetramethylene ether glycol is totally devoid of anything which resembles static markings. Of equal significance is the observation that the photographic emulsion exhibited no fog.

#### EXAMPLE II

Example I is repeated except that the antistatic charge buildup and retention test with each of the film strips is carried out by subjecting same to vigorous frictional engagement with the fingers in rubbing fashion. Each of the film strips so treated is thereafter developed, fixed and washed in the manner explained in Example I. The results obtained are similar to those described in Example I namely, each of the film strips provided with the polytetramethylene ether glycol antistatic agent is totally devoid of static markings in contradistinction to the control samples which exhibited numerous density deposits varying from light to medium in severity.

#### EXAMPLE III

Example I is repeated except that the molecular weight of the polytetramethylene ether glycol employed is approximately 1,000. As with the preceding examples, the film strips containing the antistatic agent are totally devoid of static markings as compared to the control samples which are highly offensive in this regard.

#### EXAMPLE IV

Example II is repeated except that the antistatic agent

in each case is that described in Example III. Again, the results obtained establish clearly the superior antistatic properties of the polytetramethylene ether glycol-containing film strips.

#### EXAMPLE V

A series of film strips is prepared in the manner described in Example I, except that the gelatin anti-abrasion layer is omitted. A further series of film strips is prepared utilizing the identical gelatino-silver halide X-ray emulsion but further containing about 5% by weight, based upon the weight of dry gelatin, of the polytetramethylene ether glycol of Example I. Each of the film strips thus prepared is humidity-conditioned as described in Example I and exposed in a Type I-B Sensitometer and thereafter developed, fixed, washed and dried in the manner previously described. A visual examination of each of the print-samples reveals the total absence of fogging with respect to those emulsion samples containing the polytetramethylene ether glycol antistatic compound. Moreover, such samples revealed no static markings despite the frictional contact attending the readying of such samples for exposure, i.e., handling, insertion, into the exposure apparatus, etc.

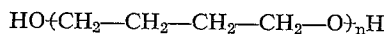
Results similar to those described above are obtained when the general procedures outlined in the foregoing examples are repeated but wherein the polytetramethylene ether glycol antistatic agent is incorporated into an antihalation backing layer and subbing layer respectively. In each case, the processed film samples displayed no static markings following development despite subjection to repeated frictional contact due to handling and processing.

It will be understood that the photographic film element in question may be adapted to the production of black and white or color reproduction. With respect to the latter, it has been ascertained that the antistatic compound described herein in no way interfere or otherwise affect color development processing whether the color coupling component employed be present in one or more light-sensitive emulsions or alternatively in the developer. Since the polytetramethylene ether glycol compounds are readily compatible with color coupling materials, film elements containing same are beneficially adapted to either mode of color processing.

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 film element comprising a film base having coated thereon at least one light-sensitive gelatino-silver halide emulsion layer said element containing in a film-forming organic binder layer thereon an antistatic compound comprising a polyether glycol of the following structural formula:



wherein  $n$  represents a positive integer sufficient to provide a molecular weight within the range of from about 650 to about 2000.

2. A photographic element according to claim 1, wherein said antistatic compound is present in a silver halide emulsion layer.

3. A photographic element according to claim 1, wherein said antistatic compound is present in a surface layer.

4. A photographic element according to claim 1, wherein said antistatic compound is present in a backing layer positioned on the opposite side of said film base.

5. A photographic element according to claim 4, wherein said backing layer comprises an antihalation layer.

6. A photographic element according to claim 4, wherein said backing layer comprises an anticurl layer.

(References on following page)

References Cited

UNITED STATES PATENTS

|           |        |                |          |
|-----------|--------|----------------|----------|
| 1,757,482 | 5/1930 | Seel           | 96—114.2 |
| 2,423,549 | 7/1947 | Blake et al.   | 96—107   |
| 2,716,062 | 8/1955 | Carroll et al. | 96—107   |
| 2,995,444 | 8/1961 | Dersch         | 96—114   |
| 3,052,544 | 9/1962 | Dersch         | 96—114   |

FOREIGN PATENTS

602,795 8/1960 Canada 96—87

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U.S. Cl. X.R.

96—87, 114.2