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GELATIN SILVER HALIDE EMULSION PLASTICIZED WITH DICARBOXYLIC ACID ESTERS

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This invention concerns the incorporation in coating and impregnating compositions of an agent designed to improve the characteristics of paper, and paper and film coatings. More particularly, this invention concerns dimensionally stabilizing paper, plasticizing gelatino emulsions and coatings, reducing foam in spumous materials, and improving the electrification properties of paper and film.

Three of the problems which have plagued the photographic industry with respect to coating photographic base have been the tendency for gelatin and other similar materials to foam due to the air which becomes entrained in handling mixtures of these materials, the tendency of emulsion layers to curl and crack in low humidities due to the brittleness of the emulsion layers, and the tendency of paper and film to become statically charged and to discharge across a photographic emulsion causing static streaks.

Various methods have been suggested to meet the problem of foaming including passing solutions containing gelatin under a vacuum in order to remove entrained air, adding certain wetting agents in an effort to reduce the surface tension of the gelatin to permit air to escape, and the like. Various methods have been used in an attempt to reduce the curl of photographic prints such as immersing the finished prints in solutions or steaming the back of the paper. Certain compositions have been added to lower the electrical surface resistivities of the paper and film in order to reduce the static charge built up in the paper webs and film as they pass through various operations such as emulsion coating, rewinding, slitting, chopping and the like. For instance, British Patent 709,555 describes the use of long chain fatty acid partial esters of aliphatic polyhydric alcohols. Glycerin has been used to plasticize photographic emulsions. The above operations using conventional methods have required the use of different compositions for accomplishing each of these purposes and, consequently, it has been desired to fined a simple means of solving all three problems with a single chemical composition.

I have discovered that a certain ester of a glycol ether can be used as an anti-foaming agent for gelatin and other spumous materials, as a plasticizer for gelatin used in coating paper for photographic purposes, as a plasticizer in gelatino photographic emulsions and as an agent for lowering the surface resistivities and correspondingly reducing the tendency of paper and film to build up static charges.

An object of this invention is to provide a process for reducing foaming of gelatin emulsions, for stabilizing paper and for improving the electrification properties of paper and film using a single chemical composition. Another object of this invention is to stabilize photographic paper by reducing the curl and emulsion cracking. A further object of this invention is to provide an anti-foaming agent for gelatin and other spumous materials. An additional object is to provide a method of improving

the electrification properties of paper and film. A further object is to provide a gelatin plasticizer.

The above objects may be accomplished by using a composition of matter prepared as described in column 3, lines 9–43 by esterification of succinic acid with a mixture of 2(2-ethoxy ethoxy) ethanol and ethylene glycol. This mixture of reaction products is intended when reference is made herein to bis(ethoxy diethylene glycol) succinate.

By substituting dibasic acids selected from the class consisting of succinic, adipic, and phthalic acids and by substituting diethylene glycol monoalkyl ethers in which the alkyl group may be lower alkyl such as ethyl, propyl or butyl, other reaction products mixtures may be obtained which are also operative in my invention.

To use this material as an anti-foaming agent, the bis (ethoxy diethylene glycol) succinate is added to emulsions or dispersions containing gelatin vehicles in which entrained air causes foaming. For instance, when baryta dispersions containing gelatin are drawn from the making kettles into the holding kettles at the coating machines, or into the coating pans, or are recirculated by pumps in the coating pans, a considerable quantity of foam develops. If foaming is extensive and carries over into the coated layer, small craters appear as the entrained air escapes during drying.

The bis (ethoxy diethylene glycol) succinate can be added in the making kettle or at some other point prior to coating. However, the addition of this material may be made most conveniently in the making kettle, at which point it acts to reduce foam in the subsequent operations.

Bis (ethoxy diethylene glycol) succinate may be used to reduce curl and emulsion cracking in photographic papers by adding it to the baryta coating when the coating composition is prepared in the making kettles. In this way the pigment layer is plasticized and the stresses and strains of both the emulsion layer on top of the pigment layer and the paper base beneath the pigment layer are lessened. Bis (ethoxy diethylene glycol) succinate is compatible with mineral pigment dispersions, with the gelatin and is also photographically inert. In the event that the clay layer has not been plasticized by incorporating it in the coating, a subsequent treatment may be given to the paper to accomplish this purpose. The paper may be immersed in a solution of bis (ethoxy diethylene glycol) succinate in order to incorporate this material in the paper base as well as in the pigment layer, in this way also stabilizing the paper against curl.

The electrification properties of paper are improved by the addition of bis (ethoxy diethylene glycol) succinate in the paper coating, and the tendency of the static charge to build up is decreased. When a web of paper travels at a relatively high speed on mechanical equipment involving carrying rolls in contact with the paper, a static charge of electricity builds up until a sufficient potential is obtained to cause an electrical discharge. The magnitude of the static charge increases with decreasing relative humidity, and increasing electrical resistance of the paper.

The build up of static charges in paper webs is always objectionable; however, in the case of photographic papers, the discharge of static electricity during operations such as, emulsion coatings, rewinding, slitting, chopping and the like can fog light-sensitive emulsion layers. Although bis (ethoxy diethylene glycol) succinate can be incorporated in the coating composition, it may also be applied by immersing the paper in a solution in ethanol, water, or similar solvent.

The agents which I have described such as bis (ethoxy diethylene glycol) succinate, may be used as plasticizers in various kinds of photographic emulsions. In addition to being useful in non-sensitized emulsions, they may also be used in positive speed emulsions, high speed negative

emulsions, X-ray emulsions, graphic are films, etc. If used with sensitizing dyes they may be added to the emulsion before or after the dyes are added. Various silver salts may be used as the sensitive salt, such as silver bromide, silver iodide, silver chloride or mixed silver halides. Various other types of addenda such as stabilizers, anti-foggants, and the like may be used with these plasticizers.

The preferred composition of matter which is used in my invention is easily prepared by the simple esterification of available organic chemicals. The following preparation, using succinic acid as the dibasic acid, illustrates the process of forming these compounds.

A one liter, 2 neck ground glass, round bottom flask was charged with 205 grams of a mixture of diethylene glycol monoethyl ether and ethylene glycol in a molar ratio of 1.2:1, 85 grams (0.72 mols) of succinic acid, 200 ml. of benzene and 0.1 gram of p-toluene sulfonic acid as a catalyst. The flask was equipped with a Dean-Clark separator for the azeotropic removal of water using total reflux. The reaction mixture was refluxed until 92–94% of the theoretical amount of water was collected based on the succinic acid. Ten grams of sodium carbonate were then added to neutralize the mixture. After removing the carbonate by filtration and washing the filter with a small quantity of benzene to remove adhering esters, the mixture was concentrated, then extracted with benzene, and vacuum distilled.

The resulting mixture was found to contain materials other than the esters of ethylene glycol and of diethylene glycol monoethyl ether, inasmuch as polymerization of some of the reaction products took place.

The preferred composition of matter may be obtained by refluxing a dibasic acid selected from the group consisting of succinic, adipic and phthalic acids with a mixture of 30–25% by weight ethylene glycol and 70–75% by weight diethylene glycol monoalkyl ether having the following formula:

$$CH_3(CH_2)_nOCH_2CH_2OCH_2CH_2OH$$

in which n is an integer of from 1 to 3 with the removal of water until about 90% of the theoretical amount is removed based on the esterification of the dibasic acid. This composition of matter may be added to a photographic film emulsion in an amount of 30–150% by weight based on the amount of gelatin in the emulsion.

The following examples are intended to illustrate but not to limit my invention:

Example I

Using a pigment dispersion containing one part gelatin to approximately 10 parts pigment, considerable foam developed in the holding kettles as the coating mixture was being drawn from the making kettles. Using a pigment dispersion containing one part of my preferred composition of matter as described above to one part gelatin, one part gelatin to approximately 10 parts pigment, no foam developed in the holding kettles or in the coating pan.

Example II

A sample of paper containing a beater size of stearate soap, gelatin and starch was conditioned to equilibrium with 42% relative humidity and coated as follows:

Part A was given a tub size of 1 pound of gelatin per 3 gallons of water. Part B was coated with 15% of my preferred composition of matter as described in column 3, lines 9–43 and 1 pound of gelatin per 3 gallons of water. These two samples were sensitized with a high contrast recording type emulsion and were then slit into 35 mm. width rolls for electric tests.

The following electrification characteristics were tested: Surface resistivities at three relative humidities, electrification characteristics in contact with a polished stainless steel roller, electrification characteristics in contact with a Micarta (phenol-formaldehyde resin) roller, and electrification curves in contact with a cloth covered metal roller. The results of the tests showed that the effectiveness of the bis (ethoxy diethylene glycol) increased as the concentration increased.

Example III

To 470 grams of a photographic emulsion containing light sensitive chloro-bromide silver salts and 8.5% gelatin by weight, sufficient of my preferred composition of matter as described in column 3, lines 9–43, was added to equal 50%, 100%, and 150% of the gelatin in the emulsion. Sufficient water was added to maintain the percent solids equal in each emulsion part, and to result in equal solids laydown on each part during coating. This emulsion was coated on glossy single weight projection paper carrying a baryta-gelatin coating.

Bis (Ethoxy Diethylene Glycol) Succinate Added, grams	Water Added, grams	Cracks per inch	Preprocess Curl [2]	
			18% R.H.	18% after 70%
20	40	0	0.8	7.0
40	20	0	0.5	3.4
60	None	0	0.1	1.4
None	60	13	2.3	9.6

Example IV

My preferred composition of matter as described in column 3, lines 9–43, was added to a high speed gelatino-silver bromide emulsion which was then coated on a cellulose acetate support. Portions of this film were tested for tackiness as compared with similar portions of a film to which has been added glycerin as a plasticizer with the following results:

Plasticizer	Concentration, percent	Degree of Tackiness at 80% RH
Glycerin	0	none.
Do	4	trace.
Do	9	slight.
Do	16	bad.
Bis (Ethoxy Diethylene Glycol) Succinate	0	none.
Do	4	none.
Do	8	trace.
Do	16	none.

Bis (ethoxy diethylene glycol) succinate was found to have little effect on the tackiness produced when as much as 16% was added to the film as compared with glycerin, which is a well known plasticizer for photographic emulsions.

I have found that the concentration of bis (ethoxy diethylene glycol) succinate when used as a plasticizer is preferably equal to the weight of the gelatin vehicle in the pigment coating formulas, but ½ to 1½ times the amount of gelatin may be used. When used to reduce the electrical resistivity of paper, a concentration of 15% by weight in the paper coating is preferred, but 5–30% may be used. As a dispersant of foam an amount equal to the gelatin in the pigment coating composition is preferred, but ½ to 1½ times that amount may be employed.

I also prefer to add an amount of bis (ethoxy diethylene glycol) succinate equal to the gelatin used in the pigment coating mixture, but a range of ½ to 1½ times may be used. This material may be incorporated into the coated paper or into uncoated paper by applying the bis (ethoxy diethylene glycol) succinate in an after treatment by immersing the paper in a solution of a concentration of from 5% to 30% based on the total weight of paper treated. When used in a tub size along with gelatin, the concentration may range from 5% to 30% of the total solution used. When used as a plasticizer in a

photographic emulsion 30–150% by weight of the gelatin can be used.

When the bis (ethoxy diethylene glycol) succinate is added as the coating compositions are first made up, this material has an opportunity to perform each of its functions. It can reduce foam in the coating composition during the handling of the coating through successive operations of pumping to the coating pan, flowing on the paper and the like. It also can plasticize the pigment coating after it has been placed on the paper and reduce stress and strain between the emulsion layer which is coated over the pigment layer and the paper base beneath the pigment layer. At the same time the bis (ethoxy diethylene glycol) succinate also serves to reduce the electrical resistivity of the paper and lower the tendency of the paper to build up a static charge due to passing the paper over rollers and the like. When used with photographic paper, bis (ethoxy diethylene glycol) succinate has a particularly beneficial property in that it reduces static charges which can fog an emulsion with a discharge either during coating operations or operations following the coating.

Post-processing curl of photographic prints may be reduced by soaking the photographic print in a solution of bis (ethoxy diethylene glycol) succinate. Although various concentrations may be used, we prefer to soak the prints from 1 to 10 minutes in a concentration of from 5 to 30% by weight of the solution.

Various other esters of glycol ethers may also be used, although the preferred ester of a glycol ether is bis (ethoxy diethylene glycol) succinate. Others which may be used include bis (ethoxy diethylene glycol) adipate, bis (butoxy diethylene glycol) adipate, bis(butoxy diethylene glycol) phthalate, bis (ethoxy diethylene glycol) phthalate, and bis (butoxy diethylene glycol) succinate.

Certain modifications may be made and these are intended to be included within the scope of my invention. For instance, mixtures of the diethylene glycol monoalkyl ether and ethylene glycol may contain as much as 50 percent ethylene glycol or may contain only a few percent. In addition, for some purposes, the reaction products of esterifying the dibasic acid such as succinic acid, may be used without distilling the mixture of reaction products. Normally, for photographic emulsions such distillation is desirable but for other applications such as the plasticization of paper, or the use in paper coatings where extreme purity is unnecessary, commercial grades of the ethylene glycol monoalkyl ether which normally contain ethylene glycol, may be used to form the reaction products which I have found can be used for the purposes disclosed herein.

It is believed that the reaction mixtures which may be obtained by esterifying the dibasic acids with the diethylene glycol monoalkyl ether or by a mixture of the diethylene glycol monoalkyl ether and ethylene glycol contain unreacted diethylene glycol monoalkyl ether, ethylene glycol and various esters of the dibasic acid as well as polymerization products which are formed from these esters. However, nothing herein is intended to limit my invention to this particular theory of operation, but on the contrary, it is intended that the reaction products formed by esterifying a dibasic acid with either diethylene glycol monoalkyl ether or with a mixture of this ether and ethylene glycol be included in the scope of this invention.

Since these compositions are soluble in water, we prefer to use water as a solvent. However, other solvents may be used such as ethanol, methanol, and the like. Bis (ethoxy diethylene glycol) succinate may also be incorporated in the final bath following the final washing of the prints in photographic processing.

This application is a continuation-in-part of U.S. patent application Serial No. 532,756, filed September 6, 1955.

I claim:

1. A photographic emulsion containing light-sensitive silver halide salts, and a composition of matter obtained by refluxing about 1 mol of succinic acid with about 3 mols of a mixture of 30–25% by weight ethylene glycol and 70–75% by weight diethylene glycol monoethyl ether with the removal of water until about 90% of the theoretical amount is removed based on the esterification of the succinic acid.

2. A photographic gelatino-silver halide emulsion containing 30–150% by weight based on the gelatin content of a composition of matter obtained by refluxing about 1 mol of succinic acid with about 3 mols of a mixture of 30–25% by weight ethylene glycol and 70–75% by weight diethylene glycol monoethyl ether with the removal of water until about 90% of the theoretical amount is removed based on the esterification of the succinic acid.

3. A gelatino-silver halide emulsion containing 10–150% by weight based on the gelatin content of a composition of matter obtained by refluxing about 1 mol of a dibasic acid selected from the group consisting of succinic, adipic, and phthalic acids with about 3 mols of a mixture of 30–25% by weight ethylene glycol and 70–75% by weight diethylene glycol monoalkyl ether having the following formula:

$$CH_3(CH_2)_nOCH_2CH_2OCH_2CH_2OH$$

in which n is an integer of from 1 to 3 with the removal of water until about 90% of the theoretical amount is removed based on the esterification of the dibasic acid.

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