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WATER SPOT PREVENTION IN PHOTOGRAPHIC FILM

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This invention relates to the processing of photographic film and particularly to a method for the prevention of "water spots" caused during the drying of the film.

The rapid processing of photographic film requires quick drying of the negative after developing and fixing. This accelerated drying may be accomplished by directing blasts of warm, dry air against both faces of the gelatin film. During the drying, water often drains from the film in an irregular manner, clinging to both the emulsion and base sides in drops, streaks or uneven patterns. Small droplets of water will often remain on the surface of the negative even after careful wiping. If a partially drained or incompletely wiped negative is subjected to vigorous drying conditions as, for example, hot air blasts or intense radiant heat, the areas under the drops of water will dry much more slowly than the surrounding film. Such uneven drying results in the formation of stresses in the film and causes it to shrink unevenly, changing the density of the silver image. Even when surplus water is removed from the emulsion side of the film, if drops of water remain on the base side, drying of the emulsion immediately opposite the water spots is retarded and drying marks may result.

It is, therefore, an object of the present invention to provide a method for preventing the water spotting occasioned by the rapid drying of photographic film.

The use of anionic wetting agents as water spot preventers has already been proposed. Muehler et al. in U. S. Patent 2,367,516 discloses the use of a condensation product of a naphthalene sulfonic acid and formaldehyde. Anionic wetting agents ionize in the rinse bath yielding a negative ion which is surface active. However, the presence of metallic ions, such as calcium, found in hard water, and aluminum, which is carried over from the fixing bath, causes precipitation of the metal salt of the wetting agent, thus destroying the effectiveness of the wetting agent and causing the formation of an objectionable scum residue.

Our invention resides in a method of water spot prevention using wetting agents of a type which will not form insoluble precipitates in the presence of metallic ions commonly present in the wash bath. More particularly, we have discovered that non-ionizing, or non-ionic, wetting agents are satisfactory for the prevention of water spots. We have found, further, that excellent results are obtained through the use of mixtures of non-ionic wetting agents and anionic or cationic wetting agents, resulting in highly satisfactory drying without accompanying water spot formation.

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Non-ionic wetting agents which are especially advantageous according to our invention include, among others, those falling in the following classes:

1. Partial esters of polyhydric alcohols with long chain fatty acids.

EXAMPLES

Long chain fatty acid partial esters of hexitol anhydrides. The hexitol anhydrides include sorbitans and sorbides, mannitans and mannides.

Anhydrohexitol partial oleates.

Hexitan partial fatty acid ester.

2. Esters of water-soluble hydroxyalkyl ethers of polyhydric alcohols with long chain carboxylic acids.

EXAMPLES

Polyoxyalkylene derivatives of hexitol anhydride partial long chain fatty acid esters.

3. Polyethers, polyether alcohols and their esters.

EXAMPLES

Aryl alkyl polyether alcohol.

Polyether.

Other suitable non-ionic wetting agents include non-ionic fatty acid condensates, and surface-active waxes.

These non-ionic wetting agents differ materially from organic solvents, such as alcohols, ethers, etc., which are occasionally mentioned for the drying of films. The organic solvents must be used in substantially full strength, whereas the abovementioned non-ionic wetting agents are normally employed in concentrations under 1.0% to promote the wetting of aqueous solutions.

Anionic wetting agents which may be used in conjunction with the non-ionic wetting agents are many in number. Of particular value are those disclosed in Muehler et al. U. S. Patent 2,367,516, particularly the condensation product of an aldehyde and a naphthalene sulfonic acid, neutralized to form the alkali metal salt; and the esters of sulfo-succinic acid, such as the dioctyl ester, dihexyl ester, and diamyl ester.

Non-ionic wetting agents may be satisfactorily employed with or without the addition of an anionic secondary wetting agent. We prefer to use the non-ionic wetting agents in concentration ranging from 0.01 to 1.0%. Glycerine may be added to reduce the tendency of the film to curl during drying.

The following examples illustrate solutions containing non-ionic wetting agents in accordance with the teachings of our invention:

Example 1

Aryl alkyl polyether alcohol	cc.	1
Water to	cc.	1000

Film and plates bathed in this solution have been found to dry without defects, while prints immersed in the bath before ferrotyping obtained more perfect contact, resulting in improved gloss and freedom from unglazed spots. No precipitate occurred on exhaustion under conditions such that traces of alum fixing bath were carried into this solution.

Example 2

An aqueous solution designed primarily for drying film consists of:

Sorbitammonooleate polyalkylene derivative	cc.	2
Water to	cc.	1000

35-mm. negative film immersed in this solution for 60 seconds was found to drain smoothly and dry without defects, while a control drained irregularly and the drops remaining on the surface caused spots of varying density on the dried film.

Alcohols have frequently been employed to dry photographic films and plates, causing more rapid drying than otherwise obtained, especially when the emulsion is swollen. Isopropyl alcohol is preferable to methyl and ethyl alcohols in that it does not attack the film base. However, isopropyl alcohol often drains irregularly from the surface of the film and, under forced drying conditions, may leave streaks and spots. We have discovered that the addition of a non-ionic wetting agent corrects this tendency and causes smooth draining.

Example 3

Isopropyl alcohol	cc.	750
Alkyl aryl polyether alcohol	cc.	1
Water	cc.	250

This mixture was found to drain smoothly from the film, whereas in the absence of the alkyl aryl polyether alcohol, only very irregular draining occurred.

While non-ionic agents may be used in the absence of a secondary wetting agent, we have found that many non-ionic wetting agents, when used alone, have a pronounced foaming tendency resulting in the formation of a very tenacious persistent foam, the removal of which requires careful wiping of the film. The addition of a secondary wetting agent of the anionic type, which in itself is insufficiently powerful to produce the desired draining effect, will cause the foam to be much less persistent without affecting the wetting properties of the solution. Such secondary agents are normally used in concentrations of from 0.02 to 1.0%.

The further addition of an hydroxy acid to the solution containing primary and secondary wetting agents may also be advisable in order to prevent precipitation of the secondary, anionic wetting agent by the metal salts likely to be present. Suitable organic hydroxy acids include citric, gluconic, lactic, tartaric, etc. The alkali metal salts and the ammonium salts of these acids are also satisfactory. The hydroxy acids are normally employed in concentrations of 0.01 to 0.5%.

The following examples illustrate rinsing solutions containing mixtures of non-ionic and anionic wetting agents:

Example 4

The following solution has been found of value in producing high gloss on ferrotyped prints:

Glycerine	cc.	100
Sorbitan oleate polyalkalene derivative	cc.	1
Condensation product of formaldehyde and a naphthalene sulfonic acid neutralized to form the alkali metal salt	gram	1
Lactic acid (85%)	cc.	0.6
Water to	cc.	1000

Example 5

The following stock solution has been found to dry film with complete freedom from defects, and to resist precipitation by hard water and alum contamination up to 0.5 gram of potassium alum per liter:

Alkyl aryl polyether alcohol	cc.	200
Condensation product of formaldehyde and a naphthalene sulfonic acid neutralized to form the alkali metal salt	grams	200
Sodium citrate	do	50
Water to	cc.	1000

For use, dilute 1 part with 200 parts of water.

Non-ionic wetting agents may be mixed with cationic wetting agents to provide rinse baths having a very small foaming tendency. Cationic wetting agents which may be used include quaternary ammonium salt such as the dimethyl alkyl amine oxides, and an oxazoline salt. Phosphonium salts of the long-chain type are also suitable cationic wetting agents.

Example 6

Alkyl aryl polyether alcohol	cc.	1
Dimethyl alkyl alkyl amine oxide (25%)	cc.	0.5
Water to	cc.	1000

This combination has the advantage of less foaming tendency than either agent used alone, while the tendency of the dimethyl alkyl amine oxide to precipitate with anions is greatly reduced.

Certain of the quaternary ammonium salts, when added to rinse baths containing non-ionic wetting agents, protect the non-ionic wetting agent against fungus or bacterial growth. A particularly effective salt of this type is diisobutyl-phenoxyethoxyethyl - dimethyl - benzylammonium chloride. Other organic or inorganic fungicides may also be employed.

Example 7

Sorbitammono-oleate polyalkylene derivative	cc.	1
Diisobutyl-phenoxyethoxyethyl-dimethyl-benzylammonium chloride	cc.	2
Water to	cc.	1000

This composition has the advantage of less foaming tendency than either agent used alone. The mixture is stable against precipitation by most ions, and the presence of diisobutyl-phenoxyethoxyethyl - dimethyl - benzylammonium chloride protects the sorbitammono-oleate polyalkylene derivative against biological growth.

It is apparent that various modifications may be made without departing from our invention as claimed. The quantities given in the above examples, while advantageous, are not critical.

Other ingredients may be added, for example, to harden and lubricate the dried film, improving its resistance to abrasion on handling. Thus, formaldehyde, diacetyl and other carbonyl compounds increase the hardening, while cineole and other oils which are soluble in the bath can be used for lubrication. Non-ionic, cationic and anionic wetting agents other than those specifically mentioned are to be considered within the scope of our invention.

What we claim and desire to secure by U. S. Letters Patent is:

1. The method of preventing water spots on photographic film during drying which comprises treating a developed, fixed and washed silver halide photographic film, with a solution containing a non-ionic wetting agent selected from the class consisting of partial esters of polyhydric alcohols with long-chain fatty acids, esters of water-soluble hydrooxyalkyl ethers of polyhydric alcohols with long-chain carboxylic acids, and polyethers, polyether alcohols, and their esters, and drying the film while containing a residue of said wetting agent.

2. The method of preventing water spots on photographic film during drying which comprises treating a developed, fixed and washed silver halide photographic film, with a solution containing less than 1.0% of a non-ionic wetting agent selected from the class consisting of partial esters of polyhydric alcohols with long-chain fatty acids, esters of water-soluble hydroxyalkyl ethers of polyhydric alcohols with long-chain carboxylic acids, and polyethers, polyether alcohols, and their esters, and drying the film while containing a residue of said wetting agent.

3. The method of preventing water spots on photographic film during drying which comprises treating a developed, fixed and washed silver halide photographic film, with a solution containing a non-ionic wetting agent consisting of an aryl alkyl polyether alcohol, and drying the film while containing a residue of said wetting agent.

4. The method of preventing water spots on photographic film during drying which comprises

treating a developed, fixed and washed silver halide photographic film, with a solution containing a non-ionic wetting agent consisting of a polyoxyalkylene derivative of hexitol anhydride partial long-chain fatty acid esters, and drying the film while containing a residue of said wetting agent.

5. The method of preventing water spots on photographic film during drying which comprises treating a developed, fixed and washed silver halide photographic film with a solution containing a polyoxyalkylene derivative of hexitol anhydride partial long-chain fatty acid esters and diisobutylphenoxyethoxyethyl - dimethyl - benzylammonium chloride, and drying the film while containing a residue of said derivative and said chloride.

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