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2,490,760

WATER SPOT PREVENTION IN PHOTOGRAPHIC FILM

Richard W. Henn and John I. Crabtree, Rochester, N. Y., assignors to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

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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 an aldehyde and a naphthalene sulfonic acid. 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 cation-active, or cationic, wetting agents are satisfactory for the prevention of water spots. We have found, further, that excellent results are obtained through the use of a

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mixture of a cationic wetting agent and an anionic wetting agent.

Examples of cationic wetting agents which may be used according to our invention are quaternary ammonium compounds, phosphonium salts, and betaine derivatives. Suitable cationic wetting agents, commercially available include dimethyl alkyl amine oxides; a mixture of higher alkyl dimethyl benzyl ammonium chlorides; cetyl dimethyl benzyl ammonium chloride; fatty acid salts of substituted oxazoline; and a long-chain phosphonium salt.

Suitable anionic wetting agents are many in number. Of particular value are those disclosed in Muehler et al. U. S. Patent 2,367,516, already described, and the esters of sulfo-succinic acid, such as the dioctyl, dihexyl, and diamyl.

Cationic wetting agents may be satisfactorily employed with or without the addition of an anionic secondary wetting agent. We prefer to use the cationic wetting agents in concentrations ranging from 0.01 to 1.0 per cent. 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

The following stock solution was prepared:

	Cc.
Dimethyl alkyl amine oxide, 20% solution	15
Glycerine	1000

For use this was diluted:

	Parts
Stock solution	1
Water	9

Prints bathed in this solution before ferrotyping produced not only higher gloss and freedom from unglazed spots, but also were free from cracks, oyster-shell markings, and excessive curl. The solution was also found of value for drying unbacked Panchromatic, negative film, draining smoothly from the surface and reducing the curl otherwise obtained when dried under low humidity conditions.

Example 2

The following drying solution was prepared:

	Cc.
Long-chain phosphonium salt	2
Water, 400 P. P. M. CaCO ₃ hardness	1000

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This solution remained clear whereas most of the wetting agents described for drying film previous to this invention, would be very cloudy and precipitate. A high-speed, negative film bathed in this solution drained freely and without defects or noticeable residue, while film washed in water of this hardness without the wetting agent drained very irregularly and a residue of salts was deposited where the drops evaporated.

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 appear to 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 cationic wetting agent corrects this tendency and causes smooth draining.

Example 3

	Cc.
Isopropyl alcohol.....	1000
Dimethyl alkyl amine oxide, 20% solution..	2
Formalin (40% formaldehyde).....	10
Eucalyptus oil.....	2.5

The above solution was found to produce uniform and fairly rapid drying of the film and to yield a hardened, lubricated surface which resisted abrasion.

While cationic wetting agents may be used in the absence of a secondary wetting agent, we have found that many cationic 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 per cent.

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 anionic secondary 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 example illustrates a rinsing solution containing a mixture of cationic and anionic wetting agents.

Example 4

A solution of dimethyl alkylamine oxide was found to foam excessively and the foam persisted on standing. The following modification was then prepared, which formed much less persistent foam, yet retained the ability of the dimethyl alkylamine oxide to dry the film without defects.

A 20% aqueous solution of a dimethyl alkylamine oxide.....cc..	2
The diamyl ester of sodium sulfosuccinic acid.....gm..	1
Water to.....cc..	1000

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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. Cationic and anionic wetting agents other than those specifically mentioned are to be considered within the scope of our invention.

We claim:

1. The method of preventing water spots on gelatino silver halide emulsion films during drying which comprises developing, fixing and washing said film, treating said film with a solution containing a cationic wetting agent consisting of a dimethyl alkyl amine oxide, and drying said film while containing a residue of said wetting agent.

2. The method of preventing water spots on gelatino silver halide emulsion film during drying which comprises developing, fixing and washing said film, treating said film with a solution containing a cationic wetting agent consisting of a dimethyl alkyl amine oxide, and an anionic wetting agent, and drying said film while containing a residue of said wetting agents.

3. The method of preventing water spots on gelatino silver halide emulsion films during drying which comprises developing, fixing and washing said film, treating said film with a solution containing a cationic wetting agent consisting of a dimethyl alkyl amine oxide and an anionic wetting agent consisting of a diamyl ester of sodium sulfosuccinic acid, and drying said film while containing a residue of said wetting agents.

4. The method of preventing water spots on gelatino silver halide emulsion films during drying which comprises developing, fixing and washing said film, treating said film with a solution containing a cationic wetting agent consisting of a dimethyl alkyl amine oxide, isopropyl alcohol, formaldehyde and a lubricating oil, and drying said film while containing a residue of said wetting agent.

RICHARD W. HENN.
JOHN I. CRABTREE.

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