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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 drying of the film.

In processing photographic film such as roll film and sheet film, it is customary to dry the film after development and fixing either by subjecting it to an elevated temperature or a current of air or both. When the excess water has not been well removed from the film this accelerated drying treatment frequently causes the formation of so-called "water spots" or physically distorted areas in the emulsion or gelatin layers which are objectionable in later viewing or printing of the film.

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.

In order to overcome this water spotting tendency obtained in the rapid drying of processed photographic film, we have tried the use of various surface active agents in baths in which the film is immersed after development, fixing, and washing. We have found that whereas some wetting and dispersing agents have little or no effect in preventing water spotting, others are especially useful for this purpose. Many wetting agents were found to give excessive foam and leave behind undesirable residues on the film which required careful rinsing or squeegeeing for their removal. Thus the compounds marketed under the names Aerosol AY and Aerosol MA which are respectively the diamyl and dihexyl esters of sodium sulfosuccinic acid, when used over a wide range of concentrations, were not satisfactory for these reasons and also because they possessed lower effectiveness as water spot preventatives. We have found, however, that the sulfonated naphthalene wetting and dispersing agents such as the isopropyl naphthalene sulfonates and condensation products of aldehydes and naphthalene sulfonic acids are especially effective in preventing water spotting. The agents which we propose to use are those sold under the trade name Aerosol OS which is the sodium salt of an isopropyl naphthalene sulfonic acid, and Tamol NNO, which is believed to be a condensation product of formaldehyde and a naphthalene sulfonic acid neutralized so as to form the alkali metal salt.

The alkali metal salts of alkyl naphthalene sulfonic acids are sold by the American Cyanamid and Chemical Corporation under various trade

names. Sulfonated isopropyl naphthalenes are sold under the trade names Aerosol OS, Vatsol OS and Aquarex. Either the mono-, the di-, or the tri-isopropyl naphthalene sulfonates may be used but the tri-isopropyl compound gives more foam than the others. Alkyl naphthalene sulfonates having similar properties for our purpose are marketed by the Ciba Co., Inc., as Invadine N; E. I. Du Pont de Nemours & Co., as Alkanol B, Alkanol E, and Alkanol SA; the General Dyestuff Corporation as Corekal A, Nekal A, and Nekal BX; and by the National Aniline and Chemical Corporation as Naccasol A.

The Tamols are sold by Rohm & Haas Company. They are believed to be condensation products of an aldehyde such as formaldehyde with naphthalene sulfonic acids by Ullmann "Enzyklopädie der technischen Chemie," 2nd. Auflage (1930), 5. Band, pages 84 and 686 and H. Wagner, "Chemiker Zeitung," vol. 46 (1922), page 801. The specific product Tamol NNO, which was used in our tests, is a relatively neutral amorphous solid having no odor. When dissolved in water at low concentrations, it gives an essentially clear colorless solution without odor which does not decompose with standing. More concentrated solutions have a slight yellowish color. A solution of Tamol NNO does not readily foam even with a high degree of agitation and the foam, if any, breaks almost instantaneously. Condensation products of formaldehyde and naphthalene sulfonic acid such as Tamol N, (see H. Wagner, Chemiker Zeitung, vol. 46 (1922), page 801) and products known as Neradol N marketed by the I. G. Farbenindustrie, A. G., when completely neutralized (Ullmann, Enzyklopädie der technischen Chemie, 2nd Auflage (1930) 5. Band, page 686) are believed to have properties similar to those of Tamol NNO which is a neutralized product. Neradol ND marketed by the I. G. Farbenindustrie, A. G. is said to consist of completely neutralized Neradol N by G. Grasser, "Synthetic Tannins" (translated by F. G. A. Enna) (1922) Crosby Lockwood & Son, London, page 91. Compare also E. Wolesensky, Technologic Papers of the Bureau of Standards 20: (1925-26) Paper No. 302, pages 11 and 16.

In our method of testing the water spot preventing agents the films used were given a flash exposure such that a low density was obtained. They were developed in the usual Elon hydroquinone developer, fixed in a hypo fixing bath containing acetic acid, boric acid and potassium alum for 15 minutes, and washed about 20 min-

utes. Immediately after washing, the films were bathed in solutions of the wetting agents under examination for from 1 to 10 minutes, drained a few seconds or squeegeed and then dried. The films were dried in a current of air at 100°-130° F., and the results determined by observation.

The results of our tests indicated that when the film was bathed in a solution of Aerosol OS at a concentration of from 0.5 to 3 grams per liter for from 2 to 10 minutes and rinsed for a few minutes in plain water, the use of a subsequent squeegeeing step was optional. Water spotting was effectively prevented. If the concentration was increased to about 5 grams per liter, the squeegeeing operation was desirable to prevent the formation of a residue of the wetting agent on the film. Likewise in the case of Tamol NNO where the concentration was greater than 2 or 3 grams per liter it was found desirable to squeegee the film in order to prevent the formation of a residue. In general, the agents which we propose to use may be incorporated in water in a concentration of from 0.5 gram to 5 grams per liter. More or less than these amounts may be used but, in general, a lower amount will not be effective and a higher amount will necessitate careful squeegeeing in order to prevent residue formation on the film.

The following table indicates typical results which we have obtained:

Wetting agent	Concentration	Time of treatment	Additional treatment	Results and remarks
	Per cent	Minutes		
None.....				"Streamers" ¹ formed.
Do.....			Squeegeed.....	Excessive water spotting.
Aerosol OS.....	0.1	2	do.....	No spots; no residue.
Do.....	0.1	2	None.....	Do.
Do.....	0.05	2	Squeegeed.....	A few spots.
Do.....	0.05	2	None.....	No spots.
Tamol NNO.....	0.2	2	Squeegeed.....	Do.
Do.....	0.2	2	None.....	No spots; residue.
Do.....	0.1	2	Squeegeed.....	No spots; no residue.
Do.....	0.1	2	None.....	Do.
Do.....	0.05	2	Squeegeed.....	Do.
Do.....	0.05	2	None.....	Do.

¹ Long water marks produced by streaks of water.

It will be understood that our water spot preventing agents may be used on film such as roll film or cut sheet film, motion picture film and glass plates, and also on photographic paper.

The results of our experiments indicate that both Aerosol OS and the Tamol were similar in activity as far as water spot formation was concerned. The Tamol was found to be preferable in some cases but both Aerosol OS and the Tamol are satisfactory. It was found that solutions of Tamol NNO did not foam as readily as solutions of Aerosol OS nor to the same degree and the Tamol NNO solutions were essentially colorless

and clear whereas solutions of Aerosol OS were slightly turbid.

It is considered that the compounds herein described as suitable for preventing water spots in the drying of film may be packaged as a dry powder or in concentrated solution form for the preparation of dilute solutions for use according to the method herein described. Either the alkali metal sulfonates or the sulfonic acids may be packaged but in the case of the acids, either mixed with the material or in a separate compartment, an alkali metal salt of a relatively weak acid or acid salt such as sodium borates, citrates, or acetate, or an alkali hydroxide such as sodium hydroxide may be included in sufficient quantity to completely react with the sulfonic acid groups.

It will be understood that the examples and modifications described herein are illustrative only and that our invention is to be taken as limited only by the scope of the appended claims.

We claim:

1. The method of preventing water spots on photographic film during drying, which comprises treating the film, after development, fixing, and washing, in a solution of a sulfonated naphthalene selected from the group consisting of an alkyl naphthalene sulfonate and condensation products of an aldehyde and a naphthalene sulfonic acid, and then drying said film.

2. The method of preventing water spots on photographic film during drying, which comprises treating the film, after development, fixing, and washing, in a solution of an isopropyl naphthalene sulfonate, and then drying said film.

3. The method of preventing water spots on photographic film during drying, which comprises treating the film, after development, fixing, and washing, in a solution of a condensation product of an aldehyde and a naphthalene sulfonic acid, and then drying said film.

4. The method of preventing water spots on photographic film during drying, which comprises treating the film, after development, fixing, and washing, in a solution of an isopropyl-naphthalene sulfonate of about 0.1% concentration for about two minutes, and then drying said film.

5. The method of preventing water spots on photographic film during drying, which comprises treating the film, after development, fixing, and washing, in a solution of a neutralized condensation product of formaldehyde and a naphthalene sulfonic acid having a concentration of about 0.1% for about two minutes, and then drying said film.

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