

## UNITED STATES PATENT OFFICE

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## STABILIZATION OF PHOTOGRAPHIC GLYOXAL HARDENING SOLUTIONS WITH WATER SOLUBLE BORON COMPOUNDS

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This invention relates to stabilized glyoxal hardening solutions and to a method of preparing the same.

In the processing of gelatino silver halide emulsions, particularly in color film, it is the practice to treat the emulsions with a hardening compound so as to reduce the tendency of the gelatin to soften or distend during processing of the photographic material containing the gelatino silver halide emulsions, particularly at temperatures higher than those specified for processing the particular photographic material. Compounds which have been used for hardening gelatin in silver halide emulsions are alum, potassium chrome alum, and aliphatic aldehydes, such as formaldehyde, hydroxyaldehydes, acrolein, and the like. Of these, formaldehyde has been extensively employed in view of its cheapness and commercial availability. Although formaldehyde is satisfactory as a hardening agent, it possesses the undesirable property of producing fog, desensitization or change of contrast when used prior to the development step.

Within recent years, glyoxal has attained prominence as a hardening agent for photographic gelatino silver halide emulsions. Aqueous alkaline solutions of glyoxal are suitable for the hardening of color film prior to rapid processing at elevated temperatures. If treatment with such a solution is omitted, excessive swelling and reticulation of the emulsion layer or layers occurs. Alkaline glyoxal hardening solutions, however, are unstable. The pH falls on standing, possibly due to the oxidation of the glyoxal to glyoxylic and/or oxalic acid, and the solution becomes ineffective as a hardener. The useful life of an alkaline glyoxal solution containing an alkali metal carbonate as the alkali is approximately 6 hours, and as the solution ages, the reduced hardening causes not only reticulation but also a change in film speed and color balance.

Accordingly, it is an object of the present invention to provide stabilized alkaline glyoxal hardening solutions.

A further object is to stabilize such alkaline solutions by the addition of water soluble boron compounds in stabilizing amounts.

Other objects and advantages will appear hereinafter from the following description.

We have found that the foregoing objects are readily accomplished by the addition of a stabilizing amount of a water soluble boron compound to alkaline glyoxal hardener solutions. Alkaline glyoxal hardener solutions generally

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consist of 0.04 to 2% of glyoxal of low formaldehyde content and 0.1 to 3.0% of an alkali metal carbonate, such as sodium, potassium, or lithium carbonate, or equivalent amounts of their hydrates, per liter of water with or without the presence of other adjuvants. Such solutions may contain, if desired, 0.03 to 0.06% of a water softener compound, such as, for example, sodium hexametaphosphate, ethylenediamine-tetraacetic acid and its alkali salts, sodium gluconate, the sodium salt of glucoheptonic acid, and the like, 1.0 to 6.0% of an alkali metal sulfate, such as sodium or potassium sulfate, and 0.001 to 0.1% of an azole, such as 2-mercapto-benzimidazole, phenylmercaptotetrazole, 2-mercaptobenzothiazole, benzotriazole, 6-nitrobenzimidazole and the like. A small quantity of formaldehyde may be added for stain reducing purposes, if desired.

The purpose of the water softener compound is to prevent sludging in case soft or distilled water is not available. The alkali metal carbonate or any other strong alkali is added for the purpose of establishing a pH which accelerates the hardening action of the glyoxal on the gelatin. Optimum results are obtained within a pH range extending from 9 to 11. The alkali metal sulfate is believed to reduce swelling of the gelatin so that the hardener may work more efficiently. The azole reduces the fogging tendency of the glyoxal alone or in the presence of small amounts of formaldehyde.

Some of the water soluble boron compounds which have been found to be suitable as stabilizing agents for the alkaline glyoxal prehardening solutions, include boron acids and their water soluble salts, e. g., borax, sodium metaborate, sodium perborate, orthoboric acid, and polyboric acids, such as those characterized by the formulae  $H_3B_4O_9$ ,  $H_4B_6O_{11}$  and  $H_2B_{10}O_{16}$  as well as organic derivatives of boric acid, such as benzylboric acid,  $C_7H_7B(OH)_2$  or ethyl boric acid,  $C_2H_5B(OH)_2$ , and the like.

The stabilizing proportions of boron compounds to be added to the solution may vary from 0.5 gram to 20 grams per liter of alkaline glyoxal solution. The addition of these proportions or higher, since they are not critical, causes no adverse effect upon the film speed and stabilizes or preserves the solution for at least 24 hours. With tap water as the solvent for the solution, the keeping quality is enhanced by 18 to 20 additional hours. The boron compounds not only stabilize the hardening action, but also reduce to a minimum the detrimental effects of the use

of an aged and unstabilized hardener on photographic speed and color balance. In order to better disclose the invention, the following examples are furnished, it being understood that these examples are illustrative only and are not intended to limit the scope of the invention.

#### Example I

A glyoxal solution was prepared according to the following composition:

Sodium hexametaphosphate	grams	0.5
Sodium perborate	do	2.0
Sodium carbonate (monohydrate)	do	9.0
Sodium sulfate	do	25.0
Benzotriazole	do	0.3
38% aqueous glyoxal solution	mls	6.0
Water to make 1 liter.		

The above hardening solution when used for 2 minutes at 80° F. prior to development and subsequent processing, hardens a multilayer color film sufficiently to permit rapid processing at the same high temperature instead of the normally recommended temperature of 68° F. without affecting the speed and color balance of the film.

The color film used had three light sensitive layers which were sensitized to the blue, green, and red regions of the spectrum respectively. Each layer contained color formers fast to diffusion, and capable of yielding upon color development with an aromatic primary amino developing agent, dye images complementary in color to the color for which the layer was sensitized.

The exposed and hardened color film was developed for 6 minutes in a black and white (first) developer, shortstopped for 1 minute, washed for 2 minutes, given a second (reversal) exposure, color developed for 4 minutes in a suitable color developer, shortstopped for 30 seconds, bleached for 1¼ minutes, fixed for 2 minutes, and washed for 1½ minutes.

The total processing time was cut from the conventional 86 minutes to less than 20 minutes. The advantage of hardening the exposed film prior to development is that customary intermediate hardening treatments can be omitted. The processing time is also reversed by virtue of higher processing temperatures.

#### Example II

Example I was repeated with the exception that 2.0 grams of sodium metaborate were used in place of 2.0 grams of sodium perborate.

#### Example III

Example I was repeated with the exception that 5.0 grams of borax were used in place of 2.0 grams of sodium perborate.

#### Example IV

Example I was repeated with the exception

that 1.0 gram of boric acid was used in place of 2.0 grams of sodium perborate.

In all four instances, the addition of the water soluble boron compounds extended the useful life of the hardener solution to at least 24 hours, whereas a hardener solution containing no such compounds became utterly useless after 6 hours.

While we have disclosed the preferred methods of our invention, it will be readily apparent to those skilled in the art that many changes and variations may be made in the proportions of the hardening solution without departing from the spirit thereof. The scope of the invention is, therefore, to be limited solely by the appended claims.

#### We claim:

1. An alkaline glyoxal hardening solution for photographic film, comprising 0.04 to 2.0% of glyoxal, an amount of alkali sufficient to establish a pH range extending from 9 to 11, and a stabilizing amount of a compound selected from the class consisting of boron acids and the water soluble salts thereof.

2. An alkaline glyoxal hardening solution comprising 0.1 to 3.0% of alkali metal carbonate, 0.04 to 2.0% of glyoxal, and a stabilizing amount of sodium perborate.

3. An alkaline glyoxal prehardening solution comprising 0.1 to 3.0% of alkali metal carbonate, 0.04 to 2.0% of glyoxal, and a stabilizing amount of borax.

4. An alkaline glyoxal prehardening solution comprising 0.1 to 3.0% of alkali metal carbonate, 0.04 to 2% of glyoxal, and a stabilizing amount of boric acid.

5. An alkaline glyoxal prehardening solution comprising 0.3 to 3.0% of alkali metal carbonate, 0.04 to 2.0% of glyoxal, and a stabilizing amount of sodium metaborate.

6. An alkaline glyoxal hardening solution for photographic film comprising 0.1 to 3% of alkali metal carbonate, 0.04 to 2.0% of glyoxal, and a stabilizing amount of a compound selected from the class consisting of boron acids and the water soluble salts thereof.

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