Patented Dec. 11, 1951 2,578,075

UNITED STATES PATENT OFFICE

2,578,075

BROWNPRINT FIXING COMPOSITION CONTAINING ALKALI THIOSULFATE, ALKALI OXALATE, AND A SURFACE ACTIVE WETTING AGENT

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No Drawing. Application June 18, 1949, Serial No. 100,093

7 Claims. (Cl. 95—88)

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This invention relates to a new brownprint fixing composition and process. It is a continuation in part of copending application, Serial No. 597,719, filed June 5, 1945, now abandoned.

Brownprints, also known in the trade as "sepia" and "Van Dyke" prints, are produced by coating on a base material, usually paper, a composition containing a light-sensitive ferric salt of an organic acid, such as the citrate or oxalate, a soluble silver salt, such as silver nitrate, and a salt that will act as a solvent for the ferrous salts that are eventually formed. This latter salt usually is an alkali salt of a polycarboxylic acid, such as the sodium, potassium, or ammonium salts of oxalic acid. The most active of these are the oxalates but they have a limited compatability with the silver nitrate and their use in a sensitizing coating composition is therefore restricted to relatively small amounts when in the same solution.

When used, the sensitized sheet is exposed to actinic light under a tracing or the like for the purpose of producing a negative print. The action of the light on the exposed areas reduces the trivalent ferric iron to the bivalent ferrous form, which when dissolved in situ by the alkali salt of an organic acid, reduces the silver nitrate to give a brownish image of silver. After exposure it is the custom to wash the print in water. This "wash" puts the alkali salt of an organic acid into solution so that the reaction mentioned may take place. Thereafter the sheet is fixed with a solution of hypo (sodium thiosulfate) to dissolve the unexposed silver salts, and then given a final wash in water.

Under conditions of unhurried washing and fixing schedules, good prints with stable white areas are readily obtainable from coatings of this type. However, modern continuous printing machines have such high powered lights that only very short exposures are required with correspondingly curtailed washing and fixing operations. Brownprints made in this manner were often found to have lines and other unexposed areas that were discolored or that became discolored after a short time. I have found this discoloration to be due primarily to undissolved iron salts although silver salts were present in minute amounts.

The present invention provides an improved fixing composition and solution thereof which will rapidly remove both iron salts, whether in ferric or ferrous condition, and silver salts, thus making for a permanent print with clean whites and dense images.

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The present invention also provides an improved fixing process in which the brownprint is subjected to the new fixing solution.

The improved composition and process are adapted for use according to the common tub washing and fixing procedure but particular advantages are derived when they are used on fast continuous printing machines.

In the new fixing composition an alkali oxalate is used together with the customary hypo (sodium thiosulfate), or other alkali thiosulfate, the alkali oxalate acting in a twofold capacity. It is a powerful solvent for undissolved ferric and ferrous iron salts that remain on the sheet after the first water wash and it also permits the use of an increased concentration of hypo by retarding the bleaching effect that strong solutions of the latter would ordinarily have on the image. For example, by dissolving four ounces of potassium oxalate and four ounces of hypo (sodium thiosulfate) in one gallon of water, a solution was obtained which produced, when used in place of the usual hypo fixing solution, a print having better and more permanent whites with improved density and image color.

The fixing composition and process are materially and advantageously improved by also including in the composition a suitable surface active wetting agent, for example, modified sodium lauryl sulfate. The addition of such a wetting agent was found to speed up the solvent and fixing action of the solution containing hypo and oxalate to such an extent that the amounts of these agents could be very materially reduced, e. g., 2 ounces of potassium oxalate plus 2 ounces of hypo, plus 10 grams of the wetting agent giving similar results to those obtained with 4 ounces of potassium oxalate and 4 ounces of hypo per gallon of water when the wetting agent was not included.

While the composition can be prepared in the form of a solution, it is advantageously prepared in the form of a dry composition, which can be packaged and shipped and stored and used by adding it to water to form the fixing solution. In such a composition the hypo is advantageously used in the form of the anhydrous salt. The use of ordinary hypo containing 5 mols. of water of crystallization is not well adapted for admixture, e. g., with potassium oxalate because of the tendency of the water to cause the composition to form a sludge. By using the anhydrous hypo a satisfactory dry composition can readily be prepared.

While sodium and potassium oxalates may be

used, ammonium oxalate is particularly advantageous for use in the new composition. Although ammonium oxalate is much less soluble than the potassium salt, it nevertheless has a sufficient solubility for use according to the present invention.

The following approximate proportions have been found to be particularly advantageous especially for one commercial type of brownprint paper:

	Per cent
Anhydrous sodium thiosulfate	32
Ammonium oxalate	60
Wetting agent (e. g. modified sodium lauryl sulfate)	8

However, the proportions may be varied within the following limits to still produce an effective fixing composition.

	Per cent
Anhydrous alkali thiosulfate	20 to 60
Alkali oxalate	80 to 30
Wetting agent	0 to 10

The proportions which are chosen within the above ranges may to some extent be dependent on the particular brownprint paper with which the fixing solution is intended to be used. This is true because commercial brownprint papers do not all have the same proportion of light reducible ferric salt to soluble silver salt and consequently, a composition having a different proportion of ammonium oxalate to sodium thiosulfate than that given in the specific example may be somewhat more effective for certain brownprint papers. It would be a relatively simple matter to determine the best proportions for any particular brownprint material.

The dry composition can readily be made and packaged, shipped and stored. In order to make the new fixing solution the composition is dissolved in water in the proportions of e. g., 4 ounces per gallon. Due to the hydrolysis of the sodium and ammonium salts, the water solution will be non-acid and in fact somewhat alkaline in nature.

The procedure for forming brownprints making use of the new fixing solution may be described as follows:

The brownprint sheet coated with a ferric salt and a soluble silver salt is exposed to light through an original or master to reduce the ferric salt to a ferrous salt in the light struck areas. The sheet is then washed with water to develop the image by allowing the ferrous ions to reduce the soluble silver salt to metallic silver and by dissolving the major portion of the excess salts from the sheet. Then the sheet is subjected to the new fixing solution which fixes the print by removing any remaining silver salts and iron salts from the unexposed areas. The sheet is then given a final water wash to remove the fixing salt and the iron and silver salts dissolved thereby.

When my solution is used in place of the customary straight hypo fixing solution a much more rapid and thorough washing out of unexposed salts is accomplished with the result that cleaner whites are obtained in a shorter time. If the old standard washing and fixing scheduled of 2 to 3 minutes first water washing, 1 to 2 minutes in fixing solution and ½ to 1 minute of final water wash is followed, the new fixing solution will effect removal of all unexposed iron and silver salts so that the masked portions of the print will have the same permanent whiteness as the paper stock. A

straight hypo fixing solution does not accomplish this result particularly on the more retentive, transparentized or "treated" papers; hypo being a solvent for the unexposed silver salts only, does not remove the iron salts.

It is an advantage of the present invention that it facilitates the more rapid removal of unexposed iron and silver salts from the brownprint process papers. While giving noticeably better results even in the old fashioned tub washing and fixing procedure, the new composition is particularly designed and advantageously used in high speed printing machines that operate on a relatively short washing and fixing schedule. Another advantage presented by the present invention is the tendency to overcome any bleaching difficulties that arise when a printer attempts to compensate for the short fixing time by unduly increasing the concentration of his fixing salts.

The new composition is advantageously prepared in the form of a dry composition containing anhydrous hypo, the alkali oxalate and wetting agent, mixed together in proper proportions and packaged in packages of suitable size, such that, e. g., 1 pound may be dissolved in 4 gallons of water or 4 ounces dissolved in 1 gallon of water to give the "fixing solution."

The new fixing solutions can, however, be made by adding each of the individual agents in suitable proportions to water or by combining two of the agents together, e. g., the ammonium oxalate and wetting agent in proper proportions and adding these and the hypo to form the fixing solution.

The wetting agent used should be one which is compatible with the hypo and oxalate and while different wetting agents can be used the alkali metal salts of sulfated higher alcohols appear to be particularly advantageous.

Thus other dry wetting agents such as hydrocarbon sodium sulfonate, sodium alkyl sulfates, principally sodium lauryl sulfate, iso propyl naphthalene sodium sulfonate, sodium salt of sulfated monoglyceride, and sodium salt of the oleic acid amide of sulfonated ethyl alcohol, may be used. In addition to these, many other wetting agents can be used where the original container permits a fluid condition for the developer or where the ingredients are individually added to the solution which is to be the fixing solution. A typical fluid wetting agent is a solution of sodium sulfate derivative of 3,9-diethyl tridecanol-6.

From the standpoint of the fixing process it will be seen that the present invention enables standard apparatus and procedure to be followed, using the new fixing solution in place of hypo; and that the process is particularly advantageous for use in high speed machines and as a high speed fixing process.

What is claimed is:

1. An anhydrous composition for forming a brownprint fixing solution by the addition of water thereto consisting essentially of from 20 to 60% of anhydrous alkali thiosulfate, from 80 to 30% of alkali oxalate and from 0 to 10% of a dry surface active wetting agent compatible therewith.

2. A composition for forming a brownprint fixing solution by the addition of water thereto consisting essentially of from 20 to 60% of sodium thiosulfate, from 80 to 30% of alkali oxalate and from 0 to 10% of a dry surface active wetting agent compatible therewith.

3. An anhydrous composition for forming a brownprint fixing solution by the addition of water thereto consisting essentially of approximately 32% anhydrous sodium thiosulfate, 60% ammonium oxalate and 8% modified sodium lauryl sulfate surface active wetting agent.

4. An improved brownprint fixing solution consisting essentially of from 20 to 60% of alkali thiosulfate, from 80 to 30% of alkali oxalate and from 0 to 10% of a surface active wetting agent compatible therewith dissolved in water in the proportion of approximately 4 ounces of the specified three ingredients in their indicated proportions to one gallon of water.

5. A composition for forming a brownprint fixing solution by the addition of water thereto consisting essentially of from 20 to 60% of anhydrous alkali thiosulfate, from 80 to 30% of alkali oxalate and from 0 to 10% of a modified sodium lauryl sulfate surface active wetting agent.

6. A composition for forming a brownprint fixing solution by the addition of water thereto consisting essentially of from 20 to 60% of anhydrous alkali thiosulfate, from 80 to 30% of alkali oxalate and from 0 to 10% of a surface active wetting agent selected from the group consisting of alkali salts of sulfated higher alcohols, hydrocarbon alkali sulfonates, alkali salts of sulfated mono-glycerides and alkali salts of the oleic acid amide of sulfonated ethyl alcohol.

7. An improved brownprint fixing solution consisting essentially of from 20 to 60% of alkali thiosulfate, from 80 to 30% of alkali oxalate and from 0 to 10% of a surface active wetting agent selected from the group consisting of alkali salts

of sulfated higher alcohols, hydrocarbon alkali sulfonates, alkali salts of sulfated mono-glycerides and alkali salts of the oleic acid amide of sulfonated ethyl alcohol dissolved in water in the proportion of approximately 4 ounces of the specified three ingredients in their indicated proportions to one gallon of water.

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