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REMOVAL OF MEASLE SPOTS IN PAPER BASE REVERSAL PRINT MATERIAL

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This invention relates generally to color photography and more particularly to a novel process for the processing of reversal print material on a paper base so as to obtain finished prints substantially free of undesirable colorless areas.

The production of color prints by reversal techniques is very well known in the photographic art and is a popular manner for obtaining color prints. The reversal process involves exposing a film comprising at least one silver halide emulsion layer containing a color coupler to light, developing with a first developer, washing, subjecting the film to a second exposure, developing with a color developer, bleaching, fixing and drying so as to obtain a finished positive print.

The finished print produced by the prior art reversal processes was generally of good quality and no particular problem arose when the base upon which the emulsion was coated was a non-porous material such as glass. However, when the reversal print material was on a paper base, the workers in the art were faced with the problem of the appearance of small colorless areas, commonly referred to as "measles," on the finished print. It is immediately obvious that these measles detract from the quality of the finished print and, in some cases, their presence necessitated starting the reversal process anew with the obvious risk that the finished product would again be unsuitable.

Numerous theories were advanced for the appearance of measles on paper based reversal print materials but the most commonly accepted explanation is that minute portions of the first developer are entrapped or absorbed by the fibers of the paper base and that the entrapped first developer reacts with the subsequently applied alkaline color developer. The reaction of the entrapped first developer with the color developer is believed to involve competition with the color developing agents resulting in leaving many small uncolored areas in the finished print.

Many attemps were made by the prior art workers to eliminate the undesirable measles but none of the proposed solutions was completely satisfactory. The prior art solutions included the use of longer wash times and the use of various alkaline, acid or neutral salt solution baths after the first development. Although these treatments reduced the number of measles, they failed to completely eliminate them.

Therefore, it is the object of this invention to provide a novel proces for treating a paper base reversal print material so as to substantially eliminate measle spots.

It is another object of this invention to provide a novel process for the substantial elimination of measle spots from paper base reversal print materials, said process being capable of yielding a finished print of a high degree of quality.

It has now been discovered that the above object can be obtained by treating the paper base reversal print material with an oxidizing bath after the first development.

The oxidizing baths of the instant invention consist of weak aqueous solutions of sodium or potassium perchlorate, nitrate, perborate or chlorate. The concentration of the sodium or potassium salt should be from about 1 to about 5% by weight.

As has heretofore been pointed out, the instant invention resides in treating a paper base reversal print material with a weak oxidizing bath after first development and then carrying out the conventional reversal techniques.

The following table will illustrate the treating steps necessary for the production of a reversal print:

TABLE I

Steps	Prior Art	Present
1	First developer	First developer.
2	Wash	Wash.
3	Second exposure	Oxidizing bath.
4	Color developer	Wash.
5	Wash	Second exposure.
6	Bleach	Color developer.
7	Wash	Wash.
8	Fix	Bleach.
9	Wash	Wash.
10	Dry	Fix.
11		Wash.
12		Dry.

The duration of the oxidizing bath treatment is not critical and can vary over a wide range. However, it has been discovered that a 5 to 10 minute treatment is sufficient in the ordinary case.

It is to be understood that this invention resides in the introduction of an oxidizing bath treatment after first development in a conventional reversal process and not in any specific light sensitive emulsion first developer, color developer, bleach or fixer. These materials are very well known in the art and are all operable in the process of the instant invention.

Particularly useful color films for the instant reversal process comprise a paper base having coated thereon at least two silver halide layers which have been sensitized to particular regions of the spectrum. Typical films include a red sensitive silver halide emulsion layer which gives a cyan image due to a phenolic coupler, a green sensitive layer which gives a magenta image due to a pyrazolone coupler and a blue sensitive layer which gives a yellow image due to a coupler which has an open chain containing a ketomethylene group.

The first developers are conventional black and white developers and the most common are polyhydroxybenzenes, e.g., hydroquinone, catechol, pyrogallol, and N-substituted amino-phenols, e.g., N-ethylaminophenol and N-methylaminophenol; to which can be added various salts such as potassium bromide, sodium thiocyanate, sodium sulfite and sodium carbonate.

The color developers are also conventional and the most common ones are derivatives of p-phenylenediamine and p-aminophenol such as N,N-dimethyl-p-phenylene diamine and N-ethyl-p-aminophenol.

The bleaching solutions employed in conventional reversal techniques are also well known and a common one is an aqueous solution of potassium dichromate and sulfuric acid. Other developers, fixers and bleaches are disclosed in U.S. Patents 2,553,498 and 2,572,903. It is to be understood that this invention is not limited to the above specific formulations since they are mentioned by way of example only.

The following example will illustrate the novel process of this invention:

A conventional film comprising a silver halide emulsion containing 1-phenyl-3-methyl-5-pyrazolone as a color coupler is coated on a paper base and given a pattern exposure to light. After development with a conventional hydroquinone developer and washing, the film is treated for 10 minutes at 75° F. with 1% by weight aqueous solution of sodium perchlorate. After the sodium perchlo-

rate treatment the film is treated in the following manner:

(1) Washed for 5 minutes;

(2) Given a second exposure;

(3) Developed with a N,N-diethyl-p-phenylenediamine color developer;

(4) Washed;

(5) Bleached with a solution consisting of:

Potassium dichromate	grams	9.4
Sulfuric acid	cc	12.0
Water to make	liter	1.0

(6) Washed;

(7) Fixed;

(8) Washed;

(9) Dried.

Numerous variations of the above invention will occur to skilled workers in the art and it is not intended that the invention be limited except as necessitated by the appended claims.

What is claimed is:

1. In the process for producing reversal prints wherein an exposed color film comprising a silver halide emulsion coated on a paper base is treated with a first developer, given a second exposure, treated with a color developer, bleached and fixed, the improvement which comprises treating said film with an aqueous solution of 1 to 5% by weight of a salt selected from the group consisting of sodium perchlorate, potassium perchlorate, sodium nitrate, potassium nitrate, sodium perborate, potassium perborate, sodium chlorate and potassium chlorate after said treatment with said first developer and before the color developer treatment.

2. The process of claim 1 wherein the salt is sodium perchlorate.

3. The process of claim 1 wherein the salt is potassium perchlorate.

4. The process of claim 1 wherein the salt is potassium nitrate.

5. The process of claim 1 wherein the salt is sodium nitrate.

6. The process of claim 1 wherein the salt is sodium perborate.

7. The process of claim 1 wherein the salt is potassium perborate.

8. The process of claim 1 wherein the salt is potassium chlorate.

9. The process of claim 1 wherein the salt is sodium chlorate.

References Cited by the Examiner

UNITED STATES PATENTS

2,393,027	1/1946	Doerr	96—22

FOREIGN PATENTS

802,275	10/1958	Great Britain.

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