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STABILIZATION OF PHOTOGRAPHIC
PRINTS WITH THIOPHENOLS

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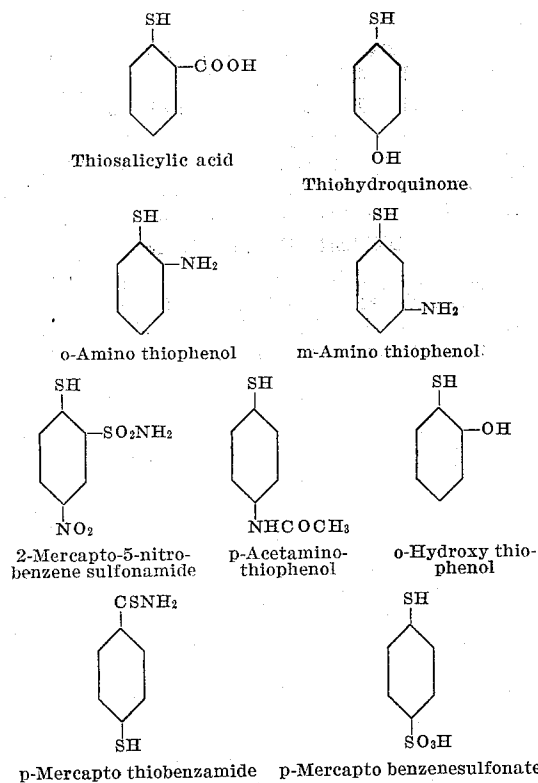
5 Claims. (Cl. 95—88)

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This invention relates to photography and particularly to the rapid processing of photographic materials.

In Yackel U. S. application Ser. No. 594,589, filed May 18, 1945, a rapid processing method is described which involves the use of stabilizing agents such as potassium thiocyanate, sodium sulfate, thiourea, etc. The photographic prints are developed in the usual way and are then treated with a solution of the potassium thiocyanate or other stabilizing agent after which they are dried without washing. This produces a stable photographic print and materially reduces the time necessary for processing the exposed emulsion.

I have now found that exposed and developed photographic emulsions may be stabilized by treating them with a solution of a thiophenol such as thiophenol itself or a substituted thiophenol. The thiophenol may be one which contains one or more benzene nuclei and may be substituted with groups such as $-\text{COOH}$, $-\text{NH}_2$, $-\text{OH}$, $-\text{SH}$, $-\text{SO}_3\text{H}$, $-\text{CSNH}_2$, $-\text{SO}_2\text{NH}_2$. The following compounds may, for example, be used according to my invention.



According to my invention a silver halide emulsion preferably a gelatino silver halide emulsion

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is exposed in the usual way and is then developed in the customary silver halide developing agent. If the emulsion is coated on a paper or other porous support, it is desirable to moisten the surface of the emulsion with a sponge, a rubber roll or other applicator wet with developing solution so that the paper support is not soaked with the developing solution.

After development has taken place, the excess developing agent on the surface of the print is removed by any convenient means such as a squeegee and the print is treated with the thiophenol stabilizing solution. The purpose of the stabilizing agent is to make the undeveloped silver halide remaining in the print substantially incapable of further photosensitivity. The silver compound produced by the stabilizing agent should be light-colored or transparent so that it does not interfere with the view or printing of the final image. Solutions containing thiohydroquinone produce a bright yellow silver salt while thiosalicylic acid produces a colorless silver salt.

Stabilization of a photographic print according to my process consists in exposing a photographic paper to a negative followed by development in the following solution diluted 1 part of developer to two parts of water.

	Grams
Monomethyl-p-amino phenol sulfate	3.1
Sodium sulfite (desiccated)	45
Hydroquinone	12
Sodium carbonate (desiccated)	67.5
Potassium bromide	1.9
Water to 1 liter.	

After development for from 5 to 60 seconds, the print is treated in an acetic acid stop bath for 5 seconds and bathed for 15 seconds to 15 minutes in the stabilizing solution. Prints treated in this way were stable to sunlight, heat and humidity without printing-out or fading. The following examples illustrate stabilizing solutions which may be used.

<i>Example 1</i>	
Thiosalicylic acid	grams 30
Ammonium citrate	do 60
Ammonium hydroxide	ml 60
Water	liter 1

<i>Example 2</i>	
Thiohydroquinone	grams 10
Alcohol	ml 250
Acetic acid	ml 20
Water	liter 1

<i>Example 3</i>	
Ortho amino thiophenol	grams 10
Acetic acid	ml 20
Water	liter 1

Example 4

Meta amino thiophenol	grams	10
Acetic acid	ml	20
Water	liter	1

The stabilizing solutions may contain one or more of the thiophenol stabilizing agents as well as various buffer salts and solvents to help solubilizing the various compounds. Hardening agents such as Formalin, glyoxal, zirconium salts, potassium alum, chrome alum, ammonium molybdate, etc., may also be incorporated in the solutions. Auric chloride or other chloride of a metal below silver and above osmium in the electromotive series may be added to the stabilizing bath as described in Brice application Ser. No. 624,570, filed October 25, 1945, now Pat. No. 2,448,857, September 7, 1948.

It will be apparent that my invention may be used either with positive emulsions such as are used on photographic papers or on negative film emulsions. It is generally necessary to use hardened emulsions according to my invention. Positive emulsions such as those employed on photographic papers are generally hardened and no further hardening treatment is required. However, in the case of certain negative film emulsions, the emulsion must be hardened before or during stabilizing according to my invention.

Although the emulsion may be immersed in the developing and stabilizing solutions, I prefer merely to moisten the surface of the emulsion with these solutions except in the case of films. Thus in the case of paper supports, the support does not become wet and the drying time is then greatly reduced.

It will be apparent from the foregoing description of my invention that all or a major part of the silver remains in the emulsion after stabilizing treatment. This differs from the customary fixing and washing in which the intent is to remove the residual silver halide from the emulsion.

I claim:

1. A rapid process for the formation of an image in a hardened silver halide photographic layer which comprises exposing said layer, developing it with a silver halide developing agent to form a silver image and immediately thereafter stabilizing it by treatment with a solution of a thiophenol only until the silver halide has been substantially completely converted to a complex with said thiophenol, leaving said complex in said layer and drying said stabilized image without any further treatment.

2. A rapid process for the formation of an

image in a hardened silver halide photographic layer which comprises exposing said layer, developing it with a silver halide developing agent to form a silver image and immediately thereafter stabilizing it by treatment with a solution of thiosalicylic acid only until the silver halide has been substantially completely converted to a complex with thiosalicylic acid, leaving said complex in said layer and drying said stabilized image without any further treatment.

3. A rapid process for the formation of an image in a hardened silver halide photographic layer which comprises exposing said layer, developing it with a silver halide developing agent to form a silver image and immediately thereafter stabilizing it by treatment with a solution of thiohydroquinone only until the silver halide has been substantially completely converted to a complex with thiohydroquinone, leaving said complex in said layer and drying said stabilized image without any further treatment.

4. A rapid process for the formation of an image in a hardened silver halide photographic layer which comprises exposing said layer, developing it with a silver halide developing agent to form a silver image and immediately thereafter stabilizing it by treatment with a thiophenol in the presence of a silver salt of a metal below silver and above osmium in the electromotive series and drying said stabilized image without any further treatment.

5. A rapid process for the formation of an image in a hardened silver halide photographic layer which comprises exposing said layer, developing it with a silver halide developing agent to form a silver image and immediately thereafter stabilizing it by treatment with a thiophenol in the presence of auric chloride and drying said stabilized image without any further treatment.

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