This invention relates to a method of stabilizing photographic emulsions.

As is known, photographic emulsions are relatively delicate and on storage under unfavourable conditions may deteriorate quickly.

The deterioration may take several forms, such as discolouration of the emulsion, a decrease in its sensitivity to light, marked increase in the amount of chemical fog produced on development of the emulsion or undesirable changes of gradation of the final image.

Hereofore many compounds of different types have been suggested as additions to photographic materials for the purpose of rendering them less liable to deterioration and alterations of properties and quality on storage, without impairing their normal photographic qualities; such additions include quinine, quinidine, secondary or tertiary aromatic or aromatic aliphatic amines and thio-pyrazolones, also imidazoles and similar compounds which form silver salts whose solubility does not exceed that of silver chloride.

In the specification of my pending application Serial No. 63,451, filed February 11, 1936, I have described a method of stabilizing photographic materials by treatment of the material with a 2-thiol-4-hydroxy-pyrimidine or its alkyl, aryl or aralkyl substitution derivatives or a tautomeric compound or an alkali metal or ammonium salt thereof.

Such compounds are 6-membered ring compounds of the following general formula:—

\[
\begin{array}{c}
\text{R}1 \text{C} = \text{O} \\
\text{R}2 \text{C} = \text{N} \\
\text{O} \text{C} = \text{N} \\
\text{H} \text{S} \text{O} \\
\end{array}
\]

where R1 and R2 may be alkyl, aryl or aralkyl groups or parts of an arylene group. The utility of such compounds is believed to be due to the presence of the system:

\[
\begin{array}{c}
\text{N} \text{C} = \text{N} \\
\text{O} \text{C} = \text{N} \\
\text{H} \text{S} \text{O} \\
\end{array}
\]

It has now been found that the 6-membered ring compounds containing the following system:

\[
\begin{array}{c}
\text{N} \text{C} = \text{N} \\
\text{O} \text{C} = \text{N} \\
\text{N} \text{H} \text{O} \\
\end{array}
\]

that is, 2-amino-4-hydroxy-pyrimidine

\[
\begin{array}{c}
\text{H} \text{C} = \text{N} \\
\text{H} \text{O} \\
\end{array}
\]

and its alkyl, aryl, aralkyl and arylene substitution derivatives, their tautomeric compounds and salts of such compounds also have a very beneficial effect in stabilizing photographic emulsions.

Accordingly this invention comprises a method of stabilizing photographic materials which include a light sensitive silver halide gelatine emulsion consisting in treating the said material with a compound comprising 2-amino-4-hydroxy-pyrimidine or one of its alkyl, aryl, aralkyl or arylene substitution derivatives or one of their tautomeric compounds or one of their salts. If a salt is employed it may be salt of either tautomeric form, and whilst in general it is preferable to employ the alkali metal salts on account of their solubility other salts such as the silver salts may be used.

Examples of substitution derivatives of 2-amino-4-hydroxy-pyrimidine which may be employed are as follows:

- 6-methyl-2-amino-4-hydroxy-pyrimidine

\[
\begin{array}{c}
\text{C} \text{O} \\
\text{H} \text{C} = \text{N} \\
\text{N} \text{H} \text{N} \text{H} \\
\end{array}
\]

- Benzoyle guanidine (2-amino-4-hydroxy-5,6-benzyopyrimidine)

\[
\begin{array}{c}
\text{C} \text{O} \\
\text{C} \text{H} = \text{N} \\
\text{O} \text{H} \\
\end{array}
\]

- 2-amino-4-hydroxy-6-benzyl-6-methyl-pyrimidine

\[
\begin{array}{c}
\text{C} \text{O} \\
\text{C} \text{H} = \text{N} \\
\text{O} \text{H} \\
\end{array}
\]

- 2-amino-4-hydroxy-6-phenyl-pyrimidine

\[
\begin{array}{c}
\text{C} \text{O} \\
\text{C} \text{H} = \text{N} \\
\text{O} \text{H} \\
\end{array}
\]

The compounds may be incorporated in the emulsion, or they may be incorporated in the support, or in an intermediate layer between the sensitive emulsion and the support, such as the baryta coating commonly employed in photographic papers, or they may be incorporated in a further protective layer coated on the emulsion surface, or the otherwise finished photographic material may be bathed in a solution of the compound.

Again the wrapping materials and the like which may come into contact with the photographic material may also be treated with the
compounds, either by incorporation or bathing. It is found that photographic materials treated in accordance with this invention show marked improvement in keeping properties particularly with regard to the reduction in the tendency to form chemical fog on development and the maintenance of speed on storage and the qualities of the materials remain more constant.

Photographic materials treated according to the present invention also show improvement in the depth of blacks produced on development.

The compounds may conveniently be added to the silver halide emulsion just prior to coating in the proportion of about 1 to 10 ccs. of a 1% solution per pound of emulsion.

The following examples illustrate the manner in which the invention may be carried into effect and they also show the results obtained by treating the photographic materials.

EXAMPLE I

Three sets of photographic paper A, B and C were made up by coating with a normal washed bromide emulsion. The samples A were made with a normal washed bromide emulsion without any addition, the samples B with the same emulsion and with the addition of 1 c.c. of a 10% aqueous solution of 2-amino-4-hydroxy-pyrimidine per pound of emulsion the addition being made just prior to coating, and the samples C with the same bromide emulsion and with the addition of 10 ccs. of a 10% aqueous solution of 2-amino-4-hydroxy-pyrimidine per pound of emulsion, again the addition being made just prior to the coating.

Three samples from each set were developed without exposure and under similar conditions in a standard metal hydroquinone developer as normally used for bromide emulsions, one sample from each set being developed for two minutes at 80°F. another for four minutes at 65°F. and the third for two minutes at 65°F. The samples were then examined in a standard reflection densitometer and the fog densities or amount of blackening produced in them measured.

Another three samples from each set were then incubated for 10 days at a temperature of 115°F. and a relative humidity of 65%. These samples were then developed under similar conditions to the other samples and examined in the standard reflection densitometer.

The results of these tests are given in the following table:

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount of 10% aqueous solution of 2-amino-4-hydroxy-pyrimidine per lb. of emulsion</th>
<th>Fog of unincubated sample</th>
<th>Fog of incubated sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>None</td>
<td>0.61</td>
<td>0.23</td>
</tr>
<tr>
<td>A2</td>
<td>None</td>
<td>0.61</td>
<td>0.23</td>
</tr>
<tr>
<td>A3</td>
<td>None</td>
<td>0.61</td>
<td>0.23</td>
</tr>
<tr>
<td>B1</td>
<td>1</td>
<td>0.61</td>
<td>0.61</td>
</tr>
<tr>
<td>B2</td>
<td>1</td>
<td>0.61</td>
<td>0.61</td>
</tr>
<tr>
<td>B3</td>
<td>1</td>
<td>0.61</td>
<td>0.61</td>
</tr>
<tr>
<td>C1</td>
<td>10</td>
<td>0.61</td>
<td>0.61</td>
</tr>
<tr>
<td>C2</td>
<td>10</td>
<td>0.61</td>
<td>0.61</td>
</tr>
<tr>
<td>C3</td>
<td>10</td>
<td>0.61</td>
<td>0.61</td>
</tr>
<tr>
<td>A4</td>
<td>None</td>
<td>0.61</td>
<td>0.61</td>
</tr>
<tr>
<td>B4</td>
<td>None</td>
<td>0.61</td>
<td>0.61</td>
</tr>
<tr>
<td>C4</td>
<td>None</td>
<td>0.61</td>
<td>0.61</td>
</tr>
<tr>
<td>A5</td>
<td>None</td>
<td>0.61</td>
<td>0.61</td>
</tr>
<tr>
<td>A6</td>
<td>None</td>
<td>0.61</td>
<td>0.61</td>
</tr>
<tr>
<td>B6</td>
<td>None</td>
<td>0.61</td>
<td>0.61</td>
</tr>
<tr>
<td>C6</td>
<td>None</td>
<td>0.61</td>
<td>0.61</td>
</tr>
</tbody>
</table>

I claim:

1. A photographic material having a fog inhibiting compound selected from the group consisting of 2-amino-4-hydroxy-pyrimidine, the alkyl, aryl, aralkyl and arylene substituted 2-amino-4-hydroxy-pyrimidines and their tautomeric compounds and their salts in intimate contact with a light sensitive silver halide gelatine emulsion.

2. A photographic material having a fog inhibiting compound selected from the group consisting of 2-amino-4-hydroxy-pyrimidine, the alkyl, aryl, aralkyl and arylene substituted 2-amino-4-hydroxy-pyrimidines their tautomeric compounds and their salts incorporated in a light sensitive silver halide gelatine emulsion.

3. A photographic emulsion comprising a silver halide gelatine emulsion having incorporated therein as a fog inhibiting agent, a small proportion of 2-amino-4-hydroxy-pyrimidine.

4. A photographic emulsion comprising a silver halide gelatine emulsion having incorporated therein as a fog inhibiting agent a small proportion of 6-methyl-2-amino-4-hydroxy-pyrimidine.

5. A photographic emulsion comprising a silver halide gelatine emulsion having incorporated therein as a fog inhibiting agent a small proportion of benzoylguanidine.

6. A photographic material having a fog inhibiting compound selected from the group consisting of 2-amino-4-hydroxy-pyrimidine, the alkyl, aryl, aralkyl and arylene substituted 2-amino-4-hydroxy-pyrimidines their tautomeric compounds, and their salts in fog inhibiting relationship with a light sensitive silver halide gelatine emulsion.

JOHN DAVID KENDALL.