This invention relates to photographic silver halide emulsions the spectral sensitivity of which has been modified by means of symmetrical or unsymmetrical carbocyanines containing an alkoxyl or substituted alkoxyl group at the central carbon atom of the trimethylene chain.

According to the French Patent No. 743,639 it has been proposed to sensitize photographic emulsions by means of compounds considered as meso-alkoxyl substituted carbocyanines and manufactured by condensation of quaternary cyclonammonium salts, which contain a reactive methyl group, with tetraalkyl orthocarboxylic esters in the presence of piperidine or non-volatile alkalies as condensation agent. Carbocya

nine dyestuffs produced by the same process are described as suitable sensitizers of photographic emulsions by Piprianow, Systnik and Systsch in Chem. Zentr. I., 1936, page 4654, who also agree as to the formation of meso-alkoxyl substituted carbocya-

mine dyestuffs during the condensation. This assumption, however, has been found to be wrong.

As explained hereinafter, no meso-alkoxyl substituted carbocyanines but the known meso-alkyl substituted carbocyanines are formed when using tetraalkyl orthocarboxylic esters in the presence of piperidine or non-volatile alkalies. This explains the assumption of the identity of the influence of the \(-\text{CH}_n\) and \(-\text{O-CH}_n\) substituents in the meso-position of the carbocyanines as erroneously described by Piprianow et al.

It is an object of the present invention to provide photographic silver halide emulsions the spectral sensitivity of which has been modified by incorporating therein a heretofore unknown meso-alkoxyl carbocyanine dyestuff.

A further object of our present invention is to provide photographic single or multi-layer material comprising a light-sensitive silver halide emulsion layer containing a heretofore unknown carbocyanine dyestuff.

Further objects will become apparent from the following description.

We have found that these objects are accomplished by incorporating in a photographic silver halide emulsion one of the meso-alkoxyl substituted carbocyanines which have an unexpected strong capacity for sensitizing photographic emulsions. These meso-alkoxyl substituted carbocyanines correspond to the following formula:

\[
\begin{align*}
\text{R} & \quad \text{Y} \\
\text{O} & \quad \text{CH} = \quad \text{O} \\
\text{C} & \quad \text{OH} = \quad \text{C} \\
\text{X} & \quad \text{OH} \\
\end{align*}
\]

wherein Y and Z are the same or different non-metallic atoms necessary to complete a 5- or 6-membered N-containing heterocyclic nucleus including a substituted nucleus and a nucleus fused to another nucleus or to a ring system, \(\text{R}\) is alkyl, substituted alkyl; \(\text{R}', \text{R}''\) are the same or different alkyl, substituted alkyl, aryl or arakyl groups, and \(\text{X}\) is an acid residue.

These carbocyanines are obtained by causing 2-(beta-methyl-beta-alkoxyl-vinyl)-cyclusonium salts of the general formula:

\[
\begin{align*}
\text{R} & \quad \text{N} \\
\text{C} & \quad \text{OH} = \quad \text{C} \\
\text{OH} & \quad \text{OH} \\
\end{align*}
\]

to react, as described in the copending application Spec. No. 755,228, filed June 17, 1947, by Leo Arnold Van den Broeke et al., now Patent No. 2,557,806, with a heterocyclic quaternary salt usable for cyanine condensations and containing an atom group capable of reacting with the CH5 group of the 2-(beta-methyl-beta-alkoxy-vinyl)-cyclonammonium salts.

Compared with the corresponding alkyl substituted dyestuffs, the meso-alkoxyl dyestuffs of our invention obtained in this way possess an absorption maximum which is shifted towards the short wave region. This means that the meso-alkoxyl carbocyanines may be used for green or blue sensitized photographic emulsions whereas the corresponding carbocyanines bearing in meso-position the known substituents are panchromatic sensitizers.
Some specific examples illustrating our invention are given hereinafter.

**Example 1**
A meso-alkoxyl carbocyanine usable as blue sensitizer of the probable formula:

![Chemical structure](image)

has a sensitizing maximum at 505 μm, the maximum of the corresponding meso-methyl carbocyanine being at 560 μm.

**Example 2**
A blue sensitizer of the probable formula:

![Chemical structure](image)

has a sensitizing maximum at 530 μm, the maximum of the corresponding meso-methyl carbocyanine being at 575 μm.

The following examples show alkoxyl substituted carbocyanines suitable for orthochromatic sensitizing of silver halide emulsions.

**Example 3**
The sensitizer of the formula:

![Chemical structure](image)

has a sensitizing maximum at 530 μm, the maximum of the corresponding meso-methyl carbocyanine being at 590 μm.

**Example 4**
The sensitizer of the formula:

![Chemical structure](image)

has a sensitizing maximum at 530 μm, the maximum of the corresponding meso-methyl carbocyanine being at 600 μm.

**Example 5**
The sensitizer of the formula:

![Chemical structure](image)

has a sensitizing maximum at 510 μm.

**Example 6**
The sensitizer of the formula:

![Chemical structure](image)

has a sensitizing maximum at 520 μm, the maximum of the corresponding meso-ethyl carbocyanine being at 630 μm.

For panchromatic sensitizing carbocyanine dyestuffs may be used which contain nuclei, such as quinoline and naphthothiazole which cause these dyes to absorb longer wave lengths and whereby some of these dyestuffs spontaneously cause a second sensitizing maximum.

**Example 7**
The sensitizer of the formula:

![Chemical structure](image)

has a sensitizing maximum at 645 to 650 μm (second maximum).

The alkoxyl substituted carbocyanines according to the present invention are also most suitable for use in combination with other sensitizers whereby often a strong sensitizing effect is obtained. In this respect the supersensitizing, for instance, of pseudocyanines is especially important. The dyestuffs used to suit now for the supersensitizing of pseudocyanines in the ortho region generally had a too high red-sensitiveness whereas the dyestuffs without this disadvantage are inferior supersensitizers. The compounds according to this invention overcome all of these disadvantages.

**Example 8**
An excellent orthochromatic supersensitizing effect is obtained by combining the dyestuff of Example 3 with the known quinopseudocyanine ethyl bromide.

It will be apparent that the above examples are illustrative of a few adaptations of the invention which is not limited to the embodiments and examples disclosed. For instance, it is to be understood that the dyestuffs of our invention may be used either alone or in combination with other colored sensitizing or supersensitizing substances either for sensitizing or supersensitizing films, plates and papers.

We claim:
1. A light-sensitive photographic silver halide emulsion containing both 3,3"-dimethyl-meso-methoxyl-thia-carbocyanine bromide and quinopseudocyanine ethyl bromide.
2. A light-sensitive photographic silver halide emulsion containing a dyestuff selected from the group consisting of meso-alkoxyl substituted
symmetrical and unsymmetrical carbocyanines of the following general formula:

\[
\begin{array}{c}
\text{OR} \\
\text{R'} \\
\text{R''} \\
\end{array}
\]

wherein Y and Z are non-metallic atoms necessary to complete a heterocyclic N-containing nucleus, R, R' and R'' are alkyl, and X is an acid residue, and a 2,2'-cyanine in order to obtain a supersensitizing effect.

MARCEL ADAM SCHOUWENAARS.
LEO ARNOLD VAN DE STRATE.
OSCAR HENDRIK VAN DEN BROELE.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Number</th>
<th>Name</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,066,966</td>
<td>Dieterle et al.</td>
<td>Jan. 5, 1937</td>
</tr>
<tr>
<td>2,156,464</td>
<td>Schulz</td>
<td>May 2, 1939</td>
</tr>
<tr>
<td>2,166,938</td>
<td>Carroll</td>
<td>July 25, 1939</td>
</tr>
</tbody>
</table>

FOREIGN PATENTS

<table>
<thead>
<tr>
<th>Number</th>
<th>Country</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>42,245</td>
<td>France</td>
<td>Mar. 21, 1933</td>
</tr>
<tr>
<td>42,256</td>
<td>France</td>
<td>Mar. 28, 1933</td>
</tr>
</tbody>
</table>