This invention relates to the developing of images produced by the diazotype process, and particularly to the so-called "dry" developing process.

The diazotype process of reproducing images has been extensively used in the past, and involves reacting a light-sensitive diazonium compound with at least one azo dye coupler to produce a deeply colored azo dye from substantially colorless or only very slightly colored starting materials. The sensitivity of the diazonium compound is such that when exposed to light of the proper wave length and of sufficient intensity, it is decomposed or chemically changed so that it is no longer capable of forming deeply colored material. Wave lengths between about 3,400 and about 4,100 Angstroms are generally the most effective. However, the dye formation is essentially an aqueous phase reaction and requires a definite pH or degree of alkalinity in the absence of which it will not take place.

It has been accordingly found suitable to provide a support such as a paper sheet, a sensitized stratum containing a mixture of one or more diazonium compounds and one or more couplers, but not in the alkalinity or pH range required for color formation, then expose the stratum to an optical image to be reproduced, and develop the image by treating the exposed stratum to bring it to the conditions suitable for color formation. Those parts of the stratum which correspond to the light parts of the image become deacycated by the light so that little or no color is formed during the development, depending upon the light gradation. The darker parts of the image however, at least partially protect the correspondingly positioned stratum against deactivation by the light so that color is developed in accordance with the image.

If the development is effected by the application of an aqueous solution of alkaline material, it becomes necessary to provide special liquid treating apparatus and also delay the final handling of the developed copy until the stratum and its carrier are again dried.

In an attempt to avoid the difficulties resulting from wetting a so-called "dry" process has been evolved with gaseous moist ammonia applied to the stratum as the developing agent. Any wetting of the stratum is thereby reduced to insignificance. There still remains the difficulty of providing special developing chambers as well as the moist ammonia gas which is extremely annoying in the event of its liberation outside the development chamber. Not only does the ammonia have a choking effect on people even in small quantities, but it may spoil stored diazotype copying sheets by causing premature color formation.

Attempts have been made in the past to incorporate developing agents in the sensitized stratum but in such condition that they do not cause development until heated or steamed. Although such techniques can be made to operate, they have been found unsatisfactory in that the useful storage life of the sensitized stratum is severely shortened, color formation taking place gradually even without the application of heat or steam. As a result it becomes necessary, if such processes are used, to make sure the sensitized material is relatively fresh, even a few weeks storage being too long in many cases. It is accordingly a principal object of the invention to provide an improved diazotype image development technique which does not have the above and other disadvantages.

A further object of the invention is the provision of an improved development process, as well as development media and compositions, in which the development has the advantages of the so-called "dry" type as well as further advantages with respect to ease of treatment.

The above as well as other objects of the invention will be more readily understood from the following description of embodiments thereof, reference being had to the accompanying drawings wherein:

Figure 1 is a perspective view of the improved color-developing material of the invention ready for use, and

Figure 2 is a side view of one technique for practicing the improved developing process of the invention.

According to the present invention the color-developing material is a hydrophilic wax-like material having a melting point between about 20 and 150 degrees centigrade and having the desired color-developing ability when molten. This composition can be carried in the form of a layer by a carrier support such as a sheet of paper and applied to an exposed sensitized diazotype copying stratum. By melting the color-developing layer, it becomes transferred to or wets the diazotype stratum by reason of its hydrophilic property and thereby causes development of the image. The development is simple and neat, and can even be effected with an ordinary household type flatiron.

As preferred examples of the novel color-developing material of the invention, wax-like hydrophilic materials have been found to be
3 extremely effective. By wax-like (or waxy) is
meant an amorphous or microcrystalline struc-
ture and a melting point of between about 20 and
150 degrees centigrade. A hydrophilic character
is defined as the property of having an affinity
for water, usually accompanied by appreciable
solubility in or miscibility with aqueous phases.
Examples of suitable wax-like hydrophilic mate-
rals are the solid polyethylene glycols and solid
alkaline soaps of fatty acids, particularly those acids
having from about 12 to 22 carbon atoms per
molecule.

Polyethylene glycols are polymerization prod-
ucts of ethylene glycol. When the polymeriza-
tion is extensive enough, the products are solid
and quite similar to wax, being commercially
known under the trade name "Carbowax." Such
material by itself has no color-developing abili-
ity. However it will readily transfer to a sen-
sitized diazotype layer when applied to it in
molten condition, and when a color-developing
agent is incorporated with it, will cause the de-
velopment of color as desired. For best results,
the color-developing agent should be dissolved or
dispersed in the polyethylene glycol. Sodium
acetate is an effective agent for this purpose but
its solubility and efficacy are increased by also
including urea in the mixture. Urea alone is readily miscible with the polyethylene
glycol when both are molten, but the color-
developing ability is greatly improved by the pre-
20

ence of a salt of a base with a weak acid.

4 Without limiting the invention, one example of a highly satisfactory color developing material
is as follows:

<table>
<thead>
<tr>
<th>Parts by weight</th>
</tr>
</thead>
</table>
| Polyethylene glycol having an average molec-
| ular weight of about 3000 and | 20 |
| Urea | 10 |
| Sodium acetate (CH₃COONa·3H₂O) | 15 |
| H₂O | 10 |

The above ingredients are mixed and heated
till the glycol melts and the urea and sodium ac-
etate are completely dissolved. Upon cooling to
room temperature, the mixture solidifies to a uni-
form wax-like product.

30 The mixture is exceedingly effective even when the urea and the sodium acetate content are each
as low as 5 per cent by weight. The water con-
tent may be reduced to insignificance without appreciably affecting the operation. Concentra-
tion of urea and sodium acetate higher than
those shown in the example may also be used,
being limited only by the melting point range
given above, and the loss of amorphous or wax-
like characteristic. Other salts may be used in
place of the sodium acetate. Thus any of the
alkali metal acetates or alkali earth acetates are
substantial equivalents. Other metal acetates
are also suitable but not quite so effective. In-
stead of the acetate, the salt of a different weak
acid such as oxalate, formic, propionic or other
fatty acid is also effective.

When the color-developing mixture is molten,
the mixture appears to be sufficiently
alkaline with or without the urea to provide
vigorous development of color. This alkalinity
is indicated by a pH of at least about 8 or higher,
when molten. Although the development of
color may be started at pH as low as 5, the high-
er pH or alkalinity is needed to at least partially
neutralize the excess acidity used to protect the
diazotype from premature coloring.

5

As another example of color-developing ma-
terial, the following composition has also been
found to be highly satisfactory:

<table>
<thead>
<tr>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium stearate soap</td>
</tr>
<tr>
<td>Urea</td>
</tr>
</tbody>
</table>

The two ingredients are melted together and
stirred producing a completely miscible combina-
tion. Upon cooling, the melt solidifies to a wax-
like product resembling the original soap. Where
the soap is sufficiently alkaline by itself the urea
may be omitted. Apparently at the elevated
color-developing temperature, the urea hydro-
ylizes in the presence of the other materials to
increase the alkalinity and the color-developing
action. With other proportions of the ingredi-
ents, complete miscibility when molten may not
result, but by thoroughly dispersing the two
phases and then solidifying, a satisfactory color-
developing material is produced. Suitable soaps
are not limited to the stearates, but include all
the fatty acids having between about 12 and 22
carbon atoms per molecule either saturated or
unsaturated. Any alkali metal salt of such an
acid is effective.

Figure 1 shows a color-developing member 10
exemplifying the invention. The member con-
sists of a sheet 12 of porous material such as
paper, and a layer 14 of wax-like hydrophilic ma-
terial such as described in the examples carried
by the sheet. Although shown as a coating layer,
all or part of the layer 14 may be impregnated
within the sheet 12. The member is readily pre-
bared by any standard paper-waxing or coating
technique, the only changes necessary being to as-
sure a liberal amount of the composition on the
sheet. About 5 grams or more per square foot
of carrier has been found very effective. The
member of Figure 1 may also be made by merely
dipping the sheet 12 in the molten color-develop-
ing composition, then withdrawing and cooling.

Figure 2 shows a convenient developing tech-
nique according to the invention. The sensitized
and exposed diazotype paper with the diazotype
coating, shown at 22, is placed on a support 24,
the developing member 10 superimposed over it,
and a hot pressing member 26 pressed down over
the developing member 10. The developing mix-
ture rapidly melts and the color development is
rapidly completed, so that the pressing member
26 can be rapidly shifted about into pressing en-
gagement with the carrier 16 over all the por-
tions of the image. Not more than a few seconds
is needed. The developing sheet 16 may then be
readily peeled away from contact with the diazo-
type 20 before or after cooling.

With the compositions of the invention no sub-
squent drying of the diazotype print is necessary.
The developing material is not watery and does
not have to be removed from the print even if
present in substantial excess. The alkalinity at
room temperature is low enough to not appreci-
ably affect the diazotype color or the paper
sheet 20, even over prolonged periods. The poly-
ethylene glycol-sodium acetate-urea-water mix-
ture is especially inert.

The present invention can be used to develop
diazotypes whether or not they have all the neces-
sary coupler compounds incorporated with the
sensitized stratum that is exposed to the image
being copied. Thus in some types of diazo-
type, the sensitive stratum is prepared with-
out couplers, and has only a light-sensitive di-
azonium compound such as p-diethylamino ben-
ene diazonium chloride usually in the form of a
double salt with zinc chloride. A small amount
of acidic material such as aluminum sulphate
may also be incorporated. With such strata, the
color developing compositions of the invention
include one or more phenolic azo dye couplers
such as phloroglucinol or resorcinal, which react
with the diazonium compound when the pH is
sufficiently raised, to form the intense dye color.
About 1 to 5 percent of coupler compound by
weight in the developer is sufficient.

Other diazonium compounds and couplers may
also be used inasmuch as they can all be de
veloped in accordance with the present invention.
A feature of the invention is the fact that the
prepared developing mixes and mixes are
quite stable and have an extremely long shelf
life. Paper coated with any of the mixtures has
been found to be fully as active after a year’s
storage, as when freshly prepared. Even devel-
oper mixes including coupler compounds are rela-
tively stable notwithstanding some alkalinity,
apparently not only because the alkalinity is low
but also because the mixture is stored as a solid
in which form its reactivity is low.

While several exemplifications of the invention
have been indicated and described above, it will
be apparent to those skilled in the art that other
modifications may be made without departing
from the scope of the invention, as set forth in
the appended claims.

What is claimed is:
1. In a process of developing an image in a
stratum by chemical reaction between a light-
sensitive diazonium compound and an azo dye
coupler, in an alkaline medium, the step of apply-
ing the alkali required for said developing process
incorporated in a solid film of a hydrophilic,
waxy material having a melting point between
about 20° and about 150° C. and heating said
material to cause said waxy material to melt and
thereby to at least partially transfer said alkali
to said stratum to react with the substances
thereof to develop the image.

2. The combination as defined by claim 1 in
which said waxy material is applied in the form
of a coating carried by a carrier member.

3. The process as defined by claim 1 in which
said alkali comprises a water-soluble salt of a
strong base with a weak acid.

4. The process as defined by claim 1 in which
said alkali is essentially a water-soluble alkali
metal soap of a fatty acid.

5. The process as defined by claim 1 in which
said alkali includes urea and a water-soluble salt
of a strong base with a weak acid.

6. The process as defined by claim 1 in which
the composition applied to said stratum com-
prises a mixture of a hydrophilic wax, water, and
a water-soluble salt of a strong base and a weak
acid.

7. The process as defined by claim 1 in which
the composition applied to said stratum com-
prises a solid solution of water, a polyethylene
glycol wax, urea and a water soluble salt of a
strong base and a weak acid.

8. The process as defined by claim 1 in which
the composition applied to said stratum com-
prises a solid solution of water, a polyethylene
glycol wax, urea and sodium acetate.

9. In a process of developing an image in a
stratum by chemical reaction between a light-
sensitive diazonium compound and an azo dye
coupler, in an alkaline medium, the steps of ap-
plying the alkali required for said process incor-
porated in a layer of a hydrophilic, waxy material
having a melting point of about 20° to about
150° C. supported on a sheet of paper, and apply-
ing heat to said layer to cause it to melt and
thereby to at least partially transfer said alkali
to said stratum to react with the substances
thereof to develop the image.

10. A process according to claim 9 in which
said heat is applied by pressing said sheet of paper
against said stratum with a hot member.

References Cited 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>2,085,938</td>
<td>Russell</td>
<td>Oct. 12, 1937</td>
</tr>
<tr>
<td>2,117,189</td>
<td>Sus</td>
<td>Oct. 8, 1940</td>
</tr>
<tr>
<td>2,228,562</td>
<td>Dieterle</td>
<td>Jan. 14, 1941</td>
</tr>
<tr>
<td>2,284,236</td>
<td>Smith</td>
<td>May 26, 1942</td>
</tr>
<tr>
<td>2,313,288</td>
<td>Barde</td>
<td>Mar. 9, 1943</td>
</tr>
<tr>
<td>2,388,654</td>
<td>Yackel</td>
<td>Nov. 13, 1945</td>
</tr>
<tr>
<td>2,500,617</td>
<td>Steans</td>
<td>Apr. 24, 1950</td>
</tr>
</tbody>
</table>