This invention relates to the art of dyes and 
yielding. It relates more particularly to a new 
class of vat assistants and to vat dye liquors or 
pastes and vat dyeing processes, especially print-
paste and printing processes comprising or 
employing such assistants, by means of which 
yieldings or prints of excellent fastness, depth, and 
brilliance may be obtained.

As is well known, vat dyes are water-insoluble 
solids and when used to dye textile fibers, they 
are ordinarily converted to a water-soluble 
(leuco) form (as by treatment with a reducing 
agent such as sodium hydroxysulfito or formalde-
hyde sulfoxylate and potassium carbonate). In 
this form they are taken up by the fibers and are 
then rendered insoluble by an oxidizing or fixing 
treatment.

The printing process for dyeing textile fabrics 
generally involves applying a so-called printing 
paste to the fabric in the form of a design (for 
example by means of a screen, a stencil, or an 
embossed roll) and subsequently subjecting the 
printed fabric to further treatment to fix the dye 
upon the fibers.

Usually vat dye printing pastes contain, in ad-
dition to the vat dye, potential reducing agents,— 
substances which in themselves do not reduce 
the vat dye under the conditions of the printing 
operation but which upon application of heat 
with or without steam are capable of reducing 
the vat dye to the soluble leuco form. A mixture 
of sodium formaldehyde sulfoxylate and potas-
sium carbonate is usually used as this reducing 
agent. The printing paste also ordinarily con-
tains substances which promote the reduction 
of the dye or the absorption of the reduced com-
ponent by textile fibers, and suitable gums or 
thickeners. In some cases, as in printing with 
difficulty reducible vat dyes, the vat dye in the 
printing paste is subjected to a preliminary re-
duction before applying the printing paste to 
the fabric.

The heat treatment above referred to, ordi-
narily designated “aging”, usually comprises sub-
jecting the printed fabric to a short treatment 
with wet (saturated) steam while excluding 
oxigen, e. g., air, whereby the vat dye is reduced 
the leuco form or its reduction is rendered 
more complete. This causes the dye to be ab-
sorbed more completely by the fiber.

After application of the printing paste to the 
fabric, and aging when this is employed, the 
fabric is subjected to an oxidizing treatment by 
passing it through an atmosphere containing 
an oxidizing agent, e. g. air, or through a bath 
containing an oxidizing agent, e. g. a bath con-
taining acetic acid and sodium dichromate. This 
oxidizing treatment converts the reduced vat dye 
compound back to the insoluble form upon the 
fiber. The fabric bearing the oxidized print is 
then washed, soaped, and rinsed, or otherwise 
suitably finished.

Vat dyes, when printed on textile fabrics with 
the aid of alkali-metal hydroxides, carbonates, or 
bicarbonates, frequently fail to yield full color 
value. This may be attributed to improper fixa-
tion of the dye on the fibers because of varying 
aging conditions or varying physical condition 
of the vat dye printing paste.

In accordance with the present invention, I 
have found that certain aryl ketones, though 
they themselves have no tinctorial power, never-
theless are excellent assistants or adjuvants for 
the application of vat dye stuffs in dyeing proc-
ces involving vat dyes. They are especially 
effective for assisting the conversion of vat dyes 
to their leuco form or for causing more complete 
conversion to this form, and hence they may 
be employed to advantage in all processes involv-
ing such a step. I have found, moreover, that 
vat dye printing pastes containing such com-
pounds as assistants yield fast prints having 
excellent penetration, strength, and brilliance.

The ketones which I employ may be repre-
sented by the formula

\[ R-\text{CO-}R' \]

wherein \( R \) represents an aryl radical of the 
benzene or naphthalene series, especially the 
former, and \( R' \) represents either a carboxyl group 
or a low-molecular alky1, aryl, or aralkyl group, 
and wherein either \( R \) or \( R' \), or both, contain a 
group conferring solubility in water or alkaline 
solutions, for example an —SO_3Me, —COOMe, 
—OMe, or —SMe group, where Me represents 
hydrogen, a metal, an ammonium group, or an 
alkyl- or hydroxy-alkyl-substituted ammonium 
group (thus forming an amine salt). In view of 
their high water-solubility, I prefer to employ 
those ketones, the water-solubility conferring 
group of which is —COOMe or —SO_3Me, the 
latter especially. It will be understood that \( R \) 
and \( R' \) are separate radicals joined only through 
a single C=O group and that either or both 
may contain further substituents, e. g. alkyl-, 
oxo-, mercapto-, halogen-, sulfonate-, carboxy-, 
or amino-groups. As an example of amine salts
may be mentioned the amine salt of 2-benzoylbenzoic acid and diethanolamine.

Examples of the aryl ketones suitable for the purposes of the present invention are the following acids or their salts, for example, their alkylamine and alkylolamine salts and their metal salts, especially their alkali-metal salts; e.g. those of Na and K:

- 2-benzoyl-benzoic acid
- Benzophenone-2-sulfonic acid
- 2-(4-methyl-benzoyl)-benzoic acid
- Benzophenone-2-carboxy-4'-sulfonic acid
- 2-(3-amino-4-chlor-benzoyl)-benzoic acid
- Acetophenone-sulfonic acid
- 2-(4-chlor-benzoyl)-benzoic acid
- 2-Hydroxy-benzoyl-formic acid
- 2-Mercapto-benzoyl-formic acid
- 1-Naphthyl-formic acid
- 2,3,4-Trihydroxybenzophenone
- 3-Benzoyl-phthalic acid
- 2,4-Dihydroxybenzophenone-2'-sulfonic acid
- 2-(Alphanaphthoyl)-benzoic acid
- 2-(2-Hydroxy-4-methyl-5-chlor-benzoyl)-benzoic acid

The vat dye pastes of the present invention are suitable for application to the same types of fibers as ordinary vat printing pastes, for example, natural cellulosic e.g., cotton), regenerated cellulosic, cellulose esters and ethers e.g., the cellulose acetates and nitrates, and natural silk, as well as mixed goods manufactured from such fibers.

The printing pastes of this invention may be prepared in the usual manner with vat dyes of all types including those derived from anthraquinones, indophenols, various indigoid, thioindigoid and indirubin compounds, etc., for example, indanthrones, pyranthrones, flavanthrones, dibenzanthrones, isodibenzanthrones, perylene quinones, anthanthrones, dibenzpyrene quinones, anthrindicarbazoles, naphthacridones, indigo, thioindigo, indirubin, etc. including derivatives thereof, such as their halogen, nitro, sulfur, and
alkoxy derivatives, either in reduced or un-
reduced form. The assistants described are espe-
cially satisfactory with dyes of the indigo and
thioindigo series, however. The following dyes
5 with which the invention may be employed to
advantage are set forth to exemplify the general
applicability of the invention:

<table>
<thead>
<tr>
<th>Dye</th>
<th>C. I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vat Orange R</td>
<td>1217</td>
</tr>
<tr>
<td>10 Tetra brom Indigo</td>
<td>1184</td>
</tr>
<tr>
<td>Indanthrene Blue GCD</td>
<td>1109</td>
</tr>
<tr>
<td>Indanthrene Dark Blue BO</td>
<td>1109</td>
</tr>
<tr>
<td>Pyranthrene</td>
<td>1118</td>
</tr>
<tr>
<td>Pyranthrene</td>
<td>1106</td>
</tr>
<tr>
<td>Indanthrene Golden Orange R</td>
<td>1097</td>
</tr>
<tr>
<td>Indanthrene Scarlet G</td>
<td>1106</td>
</tr>
<tr>
<td>Carbanthrene Blue Green FPD</td>
<td>1173</td>
</tr>
<tr>
<td>Carbanthrene Violet R</td>
<td>1104</td>
</tr>
<tr>
<td>20 Carbanthrene Red Violet 2RX</td>
<td>1161</td>
</tr>
<tr>
<td>21 Carbanthrene Brilliant Green</td>
<td>1121</td>
</tr>
<tr>
<td>22 Vat Red Violet RH</td>
<td>1122</td>
</tr>
<tr>
<td>23 Vat Scarlet G</td>
<td>1228</td>
</tr>
<tr>
<td>25 Brilliant Indigo B</td>
<td>1183</td>
</tr>
<tr>
<td>26 Brilliant Indigo 4G</td>
<td>1189</td>
</tr>
<tr>
<td>Dinaphthyl-thioindigo</td>
<td>1250</td>
</tr>
</tbody>
</table>

The dye pastes or printing pastes of the present
invention, of course, may contain the usual ad-
tions, among which may be mentioned acid
reagents, e.g. alkali-metal hydroxides, carbonates,
or bicarbonates, reducing agents, e.g. alkali-
metal-hydrosulphites or alkali-metal-formalde-
hyde-sulfoxylates, and suitable thickening agents,
e.g. starch, dextrin, mucilage, glue, British gum,
gum arabic, and gum tragacanth. They may con-
tain as well as the aryl ketones herein de-
scribed assistants, such as glycerine, alcohols,
ethers or amines, or hydrotrropic reagents (as
defined in my copending application Serial No. 673,531, filed May 26, 1933).

The application and development of printing
pastes of the present invention may be effected
in the customary manner for applying vat dye
printing pastes.

The following examples will serve to illustrate
the invention. Proportions are given as parts
by weight.

**Example 1**—1 part of sodium 2-benzoyl-ben-
zoate is dissolved in 19 parts of a dye stuff paste
containing 11.5% Vat Orange R (the remainder of the paste being mainly water, which may con-
tain in addition a dispersing agent (leukenol)
and/or glycerine). The resultant paste is in-
trarily mixed with 80 parts of a reducing paste
which is prepared by mixing 52 parts of a starch
(British gum) tragacanth thickening paste (e.g.
2 parts cornstarch, 10 parts British gum, 2 parts
5% tragacanth (solution), and 38 parts water).
15 parts potassium carbonate, 16 parts water,
12 parts sodium formaldehyde-sulfoxylate, and 5
parts glycerine.

The printing paste so prepared is applied to
textile fabric, e.g. a woven cotton fabric, in the
usual manner.

The printed fabric is dried, exposed to air-
free steam at about 102° C. for 5 to 5 minutes, and
then furtherly developed to yield a fast orange
dye. The fabric may be printed by passing it through an aqueous bath which
contains acetic acid and sodium dichromate and
which is maintained at a temperature of 60° C.
The developed print is then washed, soaked, rinsed, and dried in the usual manner. The
orange print thus obtained has excellent penetra-
tion, is well-fixed to the fiber, and is ordinarily
15% to 20% stronger than prints obtained by the same procedure, without the sodium 2-benzoyl-benzoate from the printing paste.

**Example 2.—** 1 part of the disodium salt of benzophenone-2-carboxy-4'-sulphonate is dissolved in 19
parts of a dyestuff paste containing 10% tin-
broncmidg (the remainder of the paste being
invert material). The resultant paste is intimately
mixed with 80 parts of a reducing paste prepared
as described in Example 1. This printing paste,
upon application to and development upon a tex-
tile fabric, for example a cotton fabric, yields
prints of superior brilliancy and increased strength over those obtained with a printing
paste lacking the disodium benzophenone-2-car-
boxy-4'-sulfonate but otherwise the same.

**Example 3.—** 200 parts of a dye stuff paste con-
taining 16% Indanthrene Blue GCD (C. I. 11123)
is intimately mixed with 50 parts of the disodium
salt of benzophenone-2-carboxy-4'-sulfonate, 3
parts sodium isopropyl-naphthalene-sulfonate, and
115 parts of soluble dextrin. The homogeneous
mixture thus obtained is spread on the fiber
and ground to the desired fineness. The resultant
powder can be used in the same manner as ordi-

cary vat dyestuff powders for the production of
prints on textiles and, when so applied, yields
prints of high brilliancy and strength.

**Example 4.—** 100 parts of sodium isatinate are
mixed with 120 parts of an aqueous Vat Pink FP
paste containing 15% actual dye solids. The
mixture is evaporated down to 100 parts. This
mixture is then mixed with 400 parts of the
reducing paste described in Example 1. The paste
thus formed may be printed on cotton or other
textile fabric, aged, and developed by the method of
Example 1 yielding a fuller and stronger print
than obtainable with omission of the sodium
isatinate.

It is not necessary that the ketone be intro-
duced as such into the paste but it may be formed
from another compound or other compounds
under the conditions of application and it will
be understood that the invention includes such
formation of the ketone within its scope. Thus,
isatin, when heated in alkaline media forms a salt
of 2-amino-benzoyl-formic acid (isatinic acid), may be employed instead of the sodium
isatinate of Example 4, as in the follow-
ing example.

**Example 5.—** 1 part of isatin is mixed with
19 parts of an aqueous 15% Vat Pink FP paste.
The mixture is evaporated down to 19 parts.
The mixture is then mixed with 76 parts of the
reducing paste described in Example 1. The
paste thus formed may be printed on cotton,
aged, and developed by the method of Example 1.
A fuller and stronger print is obtained than when
the isatin is omitted. Since vat dye prints are
aged by application of heat to the alkaline paste
isatin present is converted to an alkali-metal
isatinate. Accordingly either isatin or isatinic
acid or a soluble isatinate may be used with sub-
stantially the same results.

It will be understood that the vat dye powders
obtained according to the foregoing example
and/or other similarly obtained vat dye prepara-
tions, either in a paste or powder form, and con-
taining the aryl-ketonic bodies as disclosed in
this invention, may also be used for the printing
and dyeing of textile fibers, by the methods ren-
ferred to as dyeing operations, including as such
the pad-dry dyeing method, package dyeing
padding in a reduced vat dye bath, whereby excellent results are obtained. They may also be used for the production of white and/or colored discharge prints.

5 I claim:

1. In the preparation of dyed textile fibers, the step which comprises bringing the fibers into contact with a vat dyestuff and a non-foaming aryl ketone having the general formula

   $R - CO - R'$

   wherein $R$ represents an aryl radical of the benzene or naphthalene series and $R'$ represents a carboxyl group or a low molecular alkyi, aryl, or aralkyl group, and which ketone contains a group conferring solubility in water or alkaline solution.

2. In the preparation of dyed textile fibers, the step which comprises subjecting a vat dyestuff in contact with the fibers to the action of a reducing agent in the presence of a non-foaming aryl ketone having the general formula

   $R - CO - R'$

   wherein $R$ represents an aryl radical of the benzene or naphthalene series and $R'$ represents a carboxyl group or a low molecular alkyi, aryl, or aralkyl group, and which ketone contains a group conferring solubility in water or alkaline solution.

3. In the printing of a textile fabric, the step which comprises applying to the fabric a printing paste comprising a vat dyestuff and a non-foaming aryl ketone having the general formula

   $R - CO - R'$

   wherein $R$ represents an aryl radical of the benzene or naphthalene series and $R'$ represents a carboxyl group or a low molecular alkyi, aryl, or aralkyl group, and which ketone contains a group conferring solubility in water or alkaline solution.

4. The method of producing a printed textile fabric, which comprises printing upon the fabric an alkaline paste comprising a vat dyestuff, a potential reducing agent, and a non-foaming aryl ketone having the general formula

   $R - CO - R'$

   wherein $R$ represents an aryl radical of the benzene or naphthalene series and $R'$ represents a carboxyl group or a low molecular alkyi, aryl, or aralkyl group, and which ketone contains a group conferring solubility in water or alkaline solution.

5. A dyestuff composition comprising a vat dyestuff and a non-foaming aryl ketone having the general formula

   $R - CO - R'$

   wherein $R$ represents an aryl radical of the benzene or naphthalene series and $R'$ represents a carboxyl group or a low molecular alkyi, aryl, or aralkyl group, and which ketone contains a group conferring solubility in water or alkaline solution.

6. A vat dye printing paste comprising a vat dyestuff, a potential reducing agent, and an assistant, dispersed in an alkaline aqueous medium, said assistant comprising a non-foaming aryl ketone having the general formula

   $R - CO - R'$

   wherein $R$ represents an aryl radical of the benzene or naphthalene series and $R'$ represents a carboxyl group or a low molecular alkyi, aryl, or aralkyl group, and which ketone comprises a $-COOMe$ or $-SO_{2}Me$ group, $Me$ representing an alkali-metal.

7. A vat dye powder comprising a vat dyestuff and a solid non-foaming aryl ketone having the general formula

   $R - CO - R'$

   wherein $R$ represents an aryl radical of the benzene or naphthalene series and $R'$ represents a carboxyl group or a low molecular alkyi, aryl, or aralkyl group, and which ketone comprises a $-COOMe$ or $-SO_{2}Me$ group, $Me$ representing an alkali-metal.

8. In the application of a vat dyestuff to textile fibers, the step which comprises subjecting fibers with the vat dyestuff thereon to an aging treatment in the presence of a non-foaming aryl ketone having the general formula

   $R - CO - R'$

   wherein $R$ represents an aryl radical of the benzene or naphthalene series and $R'$ represents a carboxyl group or a low molecular alkyi, aryl, or aralkyl group, and which ketone comprises a $-COOMe$ or $-SO_{2}Me$ group, $Me$ representing an alkali-metal.

9. In the application of a vat dyestuff to textile fibers, the step which comprises bringing the fibers into contact with the vat dyestuff and an aryl ketone having the general formula

   $R - CO - R'$

   wherein $R$ and $R'$ represent aryl radicals of the benzene series, and which ketone comprises an $-SO_{2}Me$ group wherein $Me$ represents hydrogen or a metal.

10. In the preparation of dyed textile fibers, the step which comprises bringing the fibers into contact with a vat dyestuff and a diaryl ketone containing a group conferring solubility in water or alkaline solution.

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