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METHOD FOR CONVERTING CARBON MONOXIDE INTO FORMIC ACID

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Fig. 1

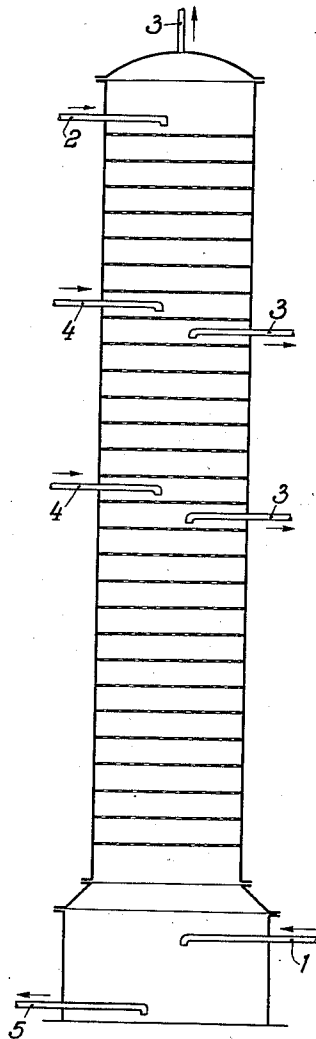
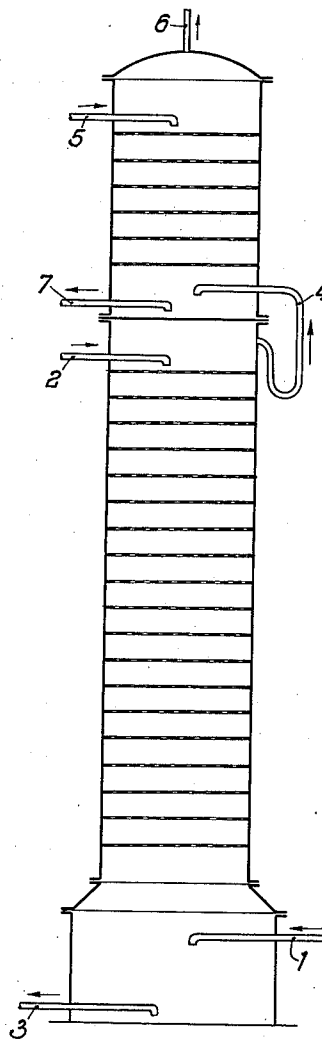


Fig. 2



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METHOD FOR CONVERTING CARBON MON-
OXIDE INTO FORMIC ACID

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10 Claims. (Cl. 260—114)

It is known to make alkyl formates by inter-
action under pressure of carbon monoxide and
water-free alcohols such as, for example, methyl
alcohol, ethyl alcohol or propyl alcohol, in cer-
tain cases in the presence of metal alcoholate. It
has also already been proposed to convert the
alkyl formates prepared in this way into form-
amide and ammonium formate with the aid of
ammonia. From these compounds formic acid
and ammonium sulphate may be obtained by in-
teraction with sulphuric acid. Generally speak-
ing, however, the technical production of formic
acid is carried out almost exclusively by forming
formates from carbon monoxide and alkali or
alkaline earth hydroxides. The formic acid is
then liberated in a second stage from the metal
formates obtained thus by treatment with a
mineral acid, e. g. sulphuric acid and is removed
by distillation. Proposals have already been
made directly to convert carbon monoxide into
formic acid by attachment of water. However,
the difficulties which beset a satisfactory solution
of the problem on these lines are extraordinarily
great (of U. S. Patents Nos. 1,606,394 and 1,895,238
among others).

The present invention relates to a process for
converting carbon monoxide into formic acid, in
which, in contradistinction to the processes usual
at the present time, there is no consumption of
alkali or alkaline earth hydroxide and mineral
acid. As auxiliary substance for carrying out
the process an alcohol is used, such as an alkyl
alcohol (e. g. methyl alcohol, ethyl alcohol) which
is continuously regenerated in the course of the
process and led in circulation. The invention
depends upon preparing alkyl formates in the
manner known per se by the action of carbon
monoxide on alcohols under elevated pressure,
a reaction which is preferably carried out with
use of metal alcoholates as reaction intermedi-
ates. The resulting alkyl formates, preferably
separated from any free alcohol, are then hy-
drolyzed by water, which may have added there-
to an acid as catalyst, into the constituents of the
ester, viz. alcohol and formic acid. The former
is freed from any ester and then interacted with
carbon monoxide and converted into alkyl for-
mate, which is used again in the process, so that
as regards the alcohol the process is cyclic.

It is advantageous to carry out the hydrolysis
of the alkyl formate in several stages, preferably
in so-called column apparatus (such as is used
for separating mixtures of liquids), in counter-
current to the saponifying agent, viz. water or
dilute acids. The hydrolysis must, of course,

be conducted at a temperature which does not
exceed the decomposition temperature of the
free acid. Since the individual reaction com-
ponents are in mutual equilibrium it is also ad-
vantageous to promote the course of the hy-
drolysis by disturbing the equilibrium. This is
advantageously effected by removing the alcohol
formed by the hydrolysis of the ester with the
portions of non-converted ester from the reac-
tion space after one or several stages and sup-
plying fresh ester each time to the following
stage of the column. The rate of reaction may
also be increased by carrying out the ester hy-
drolysis under pressure. The alcohol-ester mix-
ture is separated in a separate column and re-
supplied to the circuit.

The present process has, as compared with the
known processes for making formic acid, the ad-
vantage that no alkali or alkaline earth hydroxide
and sulphuric acid are consumed and that a
chemically pure product of any desired concen-
tration can be obtained in continuous operation
by suitably choosing the structural material for
the plant used for the hydrolysis of the ester.

The process is described below in greater de-
tail with reference to the accompanying draw-
ing, both figures of which show columns suitable
for carrying out the process described.

In Fig. 1 alkyl formates are supplied through
the pipe 1 at the bottom of the column. Water
or diluted acid is supplied at the top at 2 and it
flows through the various bottoms of the col-
umn in countercurrent to the vapours of the
formic acid ester. The alcohol formed by the
hydrolysis is withdrawn, with the portions of
unsaponified ester, through the pipes 3, of which
there may be any desired number, and is further
treated in a separate separating column. Fresh
ester, and if necessary, steam as well, is supplied
each time through the pipes 4. The formic acid
produced is withdrawn at 5.

In Figure 2 the formic acid ester is supplied
through the pipe 1. The vapours of the ester
traverse the column in counter current to the
water supplied at 2. The acid formed is with-
drawn at 3 whilst the alcohol vapours with the
portions of unsaponified ester are led through
the pipe 4 to the second part of the column.
Here the hydrolysis of the ester with suspen-
sions of aluminium, chromium or iron hydroxide
in water, which are supplied at 5, is carried to
completion. The alcohol vapours leave the col-
umn through the pipe 6, and the product of the
second interaction, a solution of aluminium, chro-

mium or iron formate is withdrawn above the separating bottom at 7.

Example 1

5 Ethyl formate, obtained by the action of carbon monoxide on alcohol under pressure in presence of alkali or alkaline earth alcoholate, is separated from alcohol and alcoholate by rectification. 1500 kilograms of this ester are supplied to the column shown in Figure 1 through the pipe 1. The addition of water, which is preheated to about 80° C., is effected at 2. Steam is supplied through the pipes 4 so that a temperature between 80 and 100° C. is maintained throughout the column. The quantity of steam and water supplied altogether to the system amounts to 500 kilograms. The formic acid produced is withdrawn at 5; a quantity of 1000 kilograms is obtained having a strength of 85%. The alcohol, together with the portions of unsaponified ester, escapes in the form of vapour through the pipe 3. This mixture is separated in the known manner into alcohol and ester in a separate column. The alcohol, after being dried, is returned into the ester-producing circuit, whilst the ester is subjected anew to the hydrolysis.

Example 2

30 1200 kilograms of methyl formate which have been obtained in an analogous manner to the ethyl formate of Example 1 are supplied through the pipe 1 under a pressure of 5 atmospheres to the saponifying column shown in Figure 2. 400 kilograms of water which have been heated to about 120° C. are supplied at 2. Through the pipe 3 about 750 kilograms of 90% acid are withdrawn. The vapours of methyl alcohol, unsaponified ester and water are withdrawn at the head of the column and separated from one another by stepwise condensation. The ester is then supplied anew in the form of vapour at the foot of the column. The water arising from the alcohol-water mixture is supplied again to the head of the column. After drying, the alcohol is converted again into methyl formate, by bringing carbon monoxide into reaction with the methanol in known manner.

What I claim is:—

30 1. A method of making formic acid consisting in interacting carbon monoxide with an alcohol under superatmospheric pressure to form an alkyl formate, hydrolyzing the said alkyl for-

mate to formic acid and alcohol, and separating the alcohol and interacting it anew with carbon monoxide for the purpose of making an alkyl formate for the process.

2. A method of making formic acid consisting in interacting carbon monoxide with an alcohol under superatmospheric pressure in the presence of metal alcoholate to form an alkyl formate, hydrolyzing the said alkyl formate to formic acid and alcohol, and separating the alcohol and interacting it anew with carbon monoxide for the purpose of making an alkyl formate for the process.

3. A method of making formic acid consisting in interacting carbon monoxide with an alcohol under superatmospheric pressure to form an alkyl formate, hydrolyzing the said alkyl formate under pressure to formic acid and alcohol, and separating the alcohol and interacting it anew with carbon monoxide for the purpose of making an alkyl formate for the process.

4. A method of making formic acid consisting in interacting carbon monoxide with an alcohol under superatmospheric pressure to form an alkyl formate, hydrolyzing the said alkyl formate to formic acid and alcohol at temperatures below the decomposition temperature of the free acid, and separating the alcohol and interacting it anew with carbon monoxide for the purpose of making an alkyl formate for the process.

5. A method of making formic acid consisting in interacting carbon monoxide with an alcohol under superatmospheric pressure to form an alkyl formate, hydrolyzing the said alkyl formate to formic acid and alcohol by treating the ester in countercurrent flow with a hydrolyzing agent, and separating the alcohol and interacting it anew with carbon monoxide for the purpose of making an alkyl formate for the process.

6. A process as claimed in claim 5 in which the hydrolyzing agent is supplied to the ester stream at a plurality of points in the line of flow of the latter.

7. A process as claimed in claim 1 in which the hydrolyzing agent is water.

8. A process as claimed in claim 1 in which the hydrolyzing agent is dilute acid.

9. A process as claimed in claim 5 in which the hydrolyzing agent is water.

10. A process as claimed in claim 5 in which the hydrolyzing agent is dilute acid.

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