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PATENTED NOV. 15, 1904.

H. S. BLACKMORE.
PROCESS OF MAKING ALCOHOL AND ALDEHYDE.
APPLICATION FILED MAR. 1, 1900.

NO MODEL.

Fig. 1.

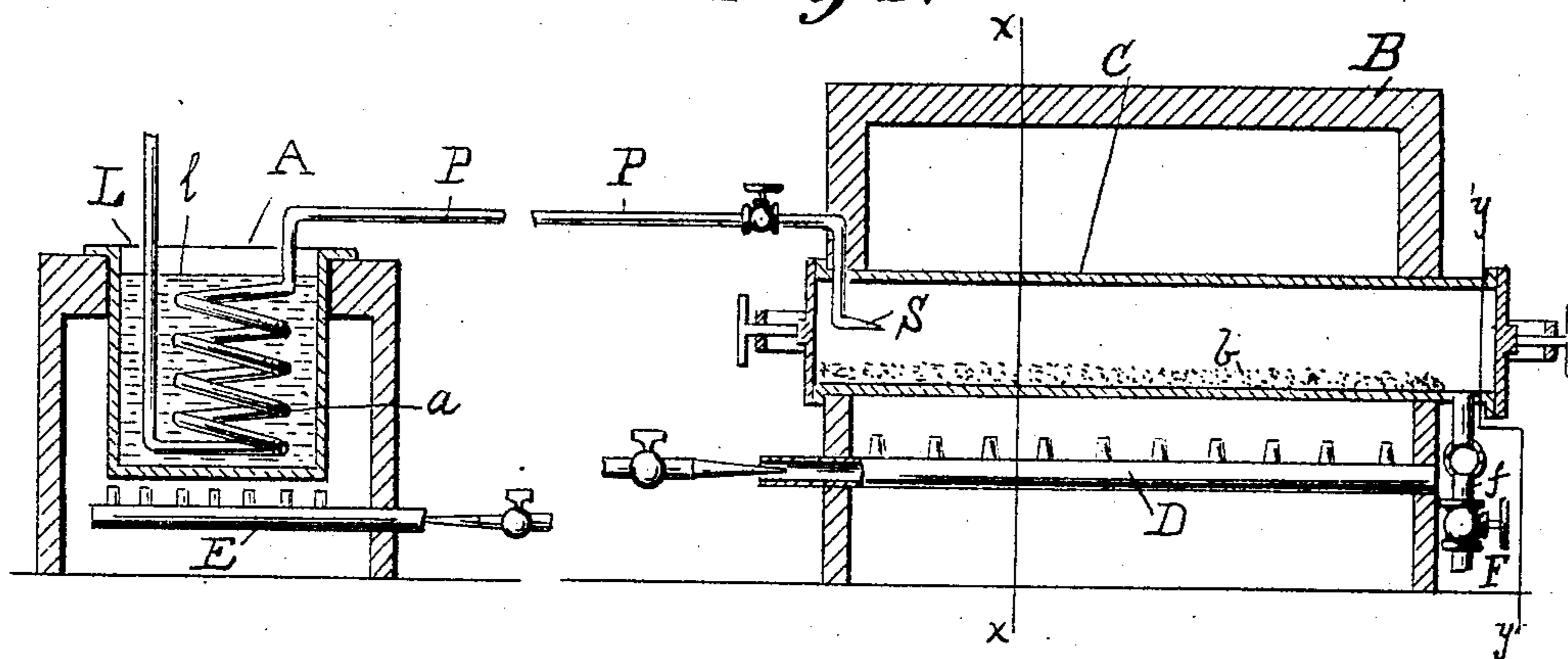


Fig. 2.

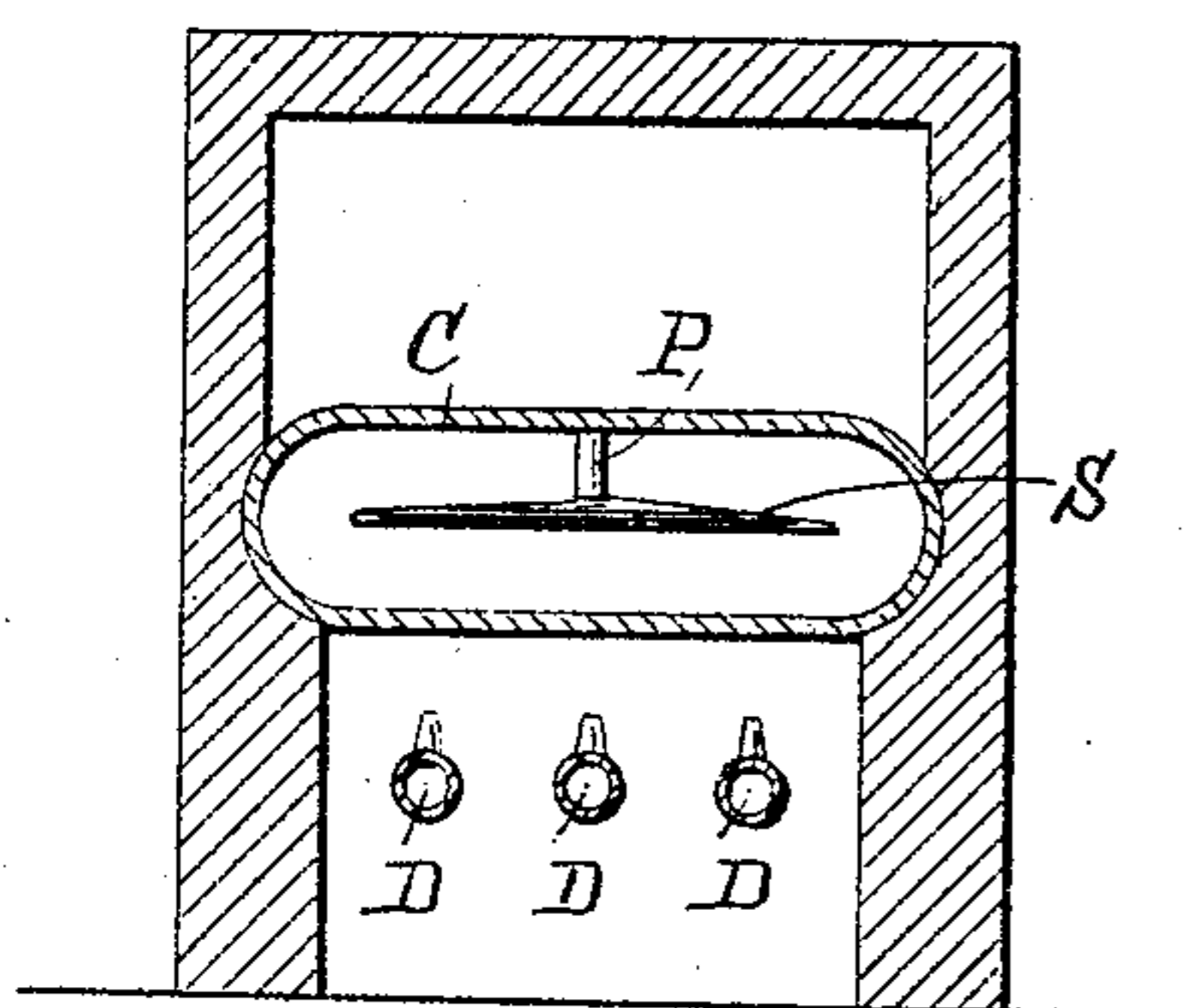
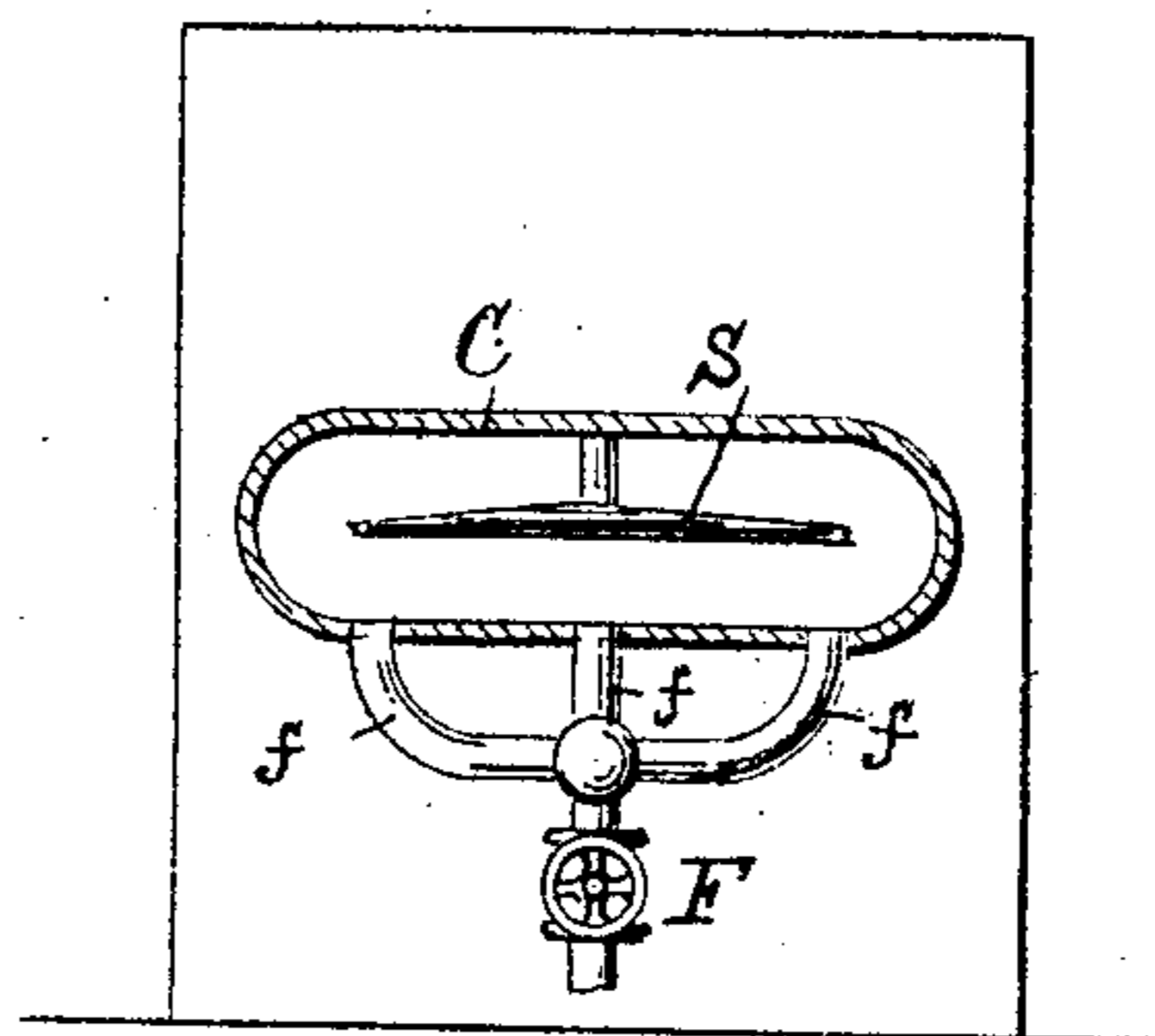


Fig. 3.



Witnesses:

D. W. G. and D. W. G.

H. K. Jenkins

Inventor:

Henry Spencer Blackmore

UNITED STATES PATENT OFFICE.

HENRY SPENCER BLACKMORE, OF MOUNT VERNON, NEW YORK, ASSIGNOR
TO ROBERT C. MITCHELL, OF MOUNT VERNON, NEW YORK.

PROCESS OF MAKING ALCOHOL AND ALDEHYDE.

SPECIFICATION forming part of Letters Patent No. 774,824, dated November 15, 1904.

Application filed March 1, 1900. Serial No. 6,954. (No specimens.)

To all whom it may concern:

Be it known that I, HENRY SPENCER BLACKMORE, a citizen of the United States, residing at Mount Vernon, in the county of Westchester and State of New York, have invented certain new and useful Improvements in Processes of Making Alcohol and Aldehyde; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

The object of my invention is to produce alcohol and aldehyde directly from hydrocarbons either in gaseous or vaporous form by subjecting them to a process of oxidation below the dissociating-point of the alcohol and aldehyde produced; and it consists in simultaneously deoxidizing a metallic compound and oxidizing the adjacent hydrocarbon, as hereinafter fully described.

My invention relates especially to the production of methyl hydroxid (wood-alcohol) and formic aldehyde, but is not confined to these compounds, as it may be applied to the production of many other alcohols or aldehydes.

In carrying out my invention on a practical basis for the production of methyl hydroxid I prefer to employ the hydrocarbon methane (CH_4) or "marsh-gas," commonly called.

The apparatus which I prefer to employ is illustrated in the accompanying drawings, of which—

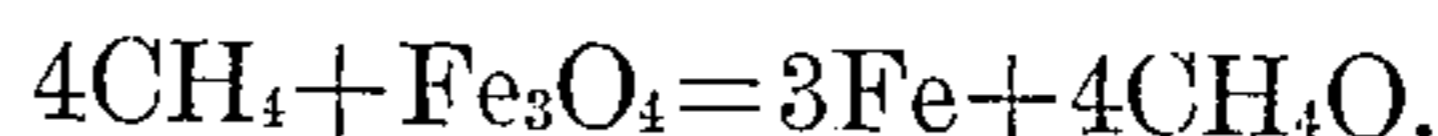
Figure 1 represents a vertical longitudinal section showing the superheater A and the transforming or oxidizing apparatus B. Fig. 2 represents a cross-section of the transforming or oxidizing apparatus B on the line xx , Fig. 1; and Fig. 3 shows an end view of same apparatus with outlet-pipes and cross-section of retort or container C on the line yy , Fig. 1.

Similar characters of reference designate corresponding parts throughout the several views.

Referring to the drawings, I place a layer of iron oxid, (red or black,) preferably ferrous-ferrie oxid, (Fe_3O_4), about two inches deep in the retort or container C, as shown at B, Fig. 1. I then close the container and

heat the same and contents thereof by means of the burners D to about 260° Fahrenheit and as far as practical maintain it continuously at this temperature. Otherwise a change in temperature might tend either to entirely stop the operation or further oxidize the hydrocarbon operated on, producing formic aldehyde. I then pass methane (CH_4) through the coil a of A, Fig. 1, which is supported in a bath of molten lead l in the pot or cauldron L, the heat being maintained by the burners E. As the methane passes through the coil a it becomes heated, and this heated gas is conveyed through the pipe P and separator or deflector S into the retort or container C and over and through the iron oxid therein. The temperature after the first heating of the oxid of iron in retort or container C is preferably maintained by the introduction of the superheated hydrocarbon, the initial heating by means of the burners D being gradually diminished. After the oxid has attained the temperature above stated methane or marsh-gas, preferably superheated, as described, to about the temperature at which lead melts or approximately 625° Fahrenheit, is rapidly passed through the retort or container C, and thereby brought in immediate contact with the oxid of iron. As it passes over and through the heated oxid the tendency is for the hydrogen of the hydrocarbon to deoxidize the same and produce metallic iron in a finely-divided state, at the same time absorbing or combining with the oxygen thereof, producing methyl hydroxid or formic aldehyde, according to the temperature to which the reagents are exposed.

The reaction which takes place in the production of methyl alcohol may be illustrated by the following chemical formula or equation:



Production of formic aldehyde at higher temperature:



or, illustrated by direct reaction,



The vapor of methyl alcohol thus produced

is conducted out of the apparatus through pipes *f f f* and *F* into and through condensers, (not shown,) and any gas remaining unacted upon is finally reconducted into the apparatus for further operation, the condensed methyl alcohol or formic-aldehyde solution being received in proper reservoirs.

The fine iron left at the end of the operation may be disposed of in the market as fer-
rum reductum, or iron by hydrogen, or it may be preferably reoxidized by passing air or oxygen over the same in a heated condition and employed in further operation, thus making the process practically continuous.

The retort or container *C*, in which the transformation takes place, may be of any convenient size or shape; but I have found a retort or container of oval shape, eight feet long, eighteen inches in diameter horizontally, and six inches deep vertically, to be a convenient and recommended size for practical purposes.

I find that fifteen hundred cubic feet of methane or marsh-gas (CH_4) will produce one hundred and twenty-five pounds of methyl hydroxid or wood-alcohol (CH_3O) from two hundred and fifty pounds of ferroso-ferric oxid (Fe_3O_4) heated to 260° Fahrenheit, the process being carried out as hereinbefore described. I also find that the same volume (fifteen hundred cubic feet) of methane (CH_4) will produce one hundred and eighteen pounds of formic aldehyde, (CH_2O), employing five hundred pounds of ferroso-ferric oxid, (Fe_3O_4), heated to 315° Fahrenheit. The methane employed in the production of formic aldehyde is supplied to the oxidizing action of the iron oxid in a heated condition more slowly than is required for the production of methyl hydroxid—*i. e.*, at about one-half the volume—in a given time to admit of more perfect oxidation.

It is obvious that other hydrocarbons may be employed and the oxid maintained at various temperatures, as found preferable for the production of other alcohols or aldehydes, as desired, and also other oxids—such as manganese, barium, copper, &c.—may be employed instead of oxid of iron without departing from the spirit of my invention, which consists simply of a process for the slow oxidation of hydrocarbons, either in gaseous or vaporous form, by means of metallic oxids in a heated condition maintained at a temperature below the dissociating-point of the alcohol or aldehyde produced, the said temperature being preferably maintained by heat occluded in the hydrocarbon introduced for oxidation by previously superheating it.

If the heat during reaction accumulates to a degree approaching the dissociating-point of the products desired, I can lower the temperature by refrigeration in any convenient manner in order to maintain the temperature below the dissociating-point.

It is preferable to have an excess of hydro-

carbon present during the operation, and care should be taken not to have the metallic oxid reach a temperature above the dissociating-point of the alcohol or aldehyde produced; otherwise the hydrocarbon will be decomposed, producing water, carbonic oxid, carbonic anhydrid, and carbid of iron. The products—alcohol and aldehyde—should also be cooled or condensed as rapidly as possible to prevent loss by volatilization.

The operation of the process may also be greatly facilitated by operating with hydrocarbon vapors or gases under superatmospheric pressure when in contact with a metallic oxid, as an excess of the same is thus always assured and the oxyhydrocarbon produced is more readily carried out of the retort or container by the current of gas or vapor unacted upon, and also the reaction progresses more rapidly, as the materials are thus brought into closer contact.

The terms "alcohol" and "alkyl hydroxid" used or employed throughout this specification and claims are intended to include glycols, aldehydes, and other hydroxyl substitution compounds of hydrocarbons and oxidation products thereof, as well as alcohol *per se*.

It is obvious that more or less aldehyde is always produced during the production of alcohol, and its production is therefore included in this application as being a peroxidized product obtained by the same process.

When the products consist of a mixture of alcohol and aldehyde, they may be afterward separated from each other by fractional distillation, or the aldehyde may be combined with bisulfites, such as sodium bisulfite, (NaHSO_3), the alcohol separated, and the aldehyde recovered from its combination with the alkali-bisulfite by any means well known to chemists.

It is well known that when a compound of hydrogen and carbon is exposed to the action of an oxidizing agent that the hydrogen thereof has an affinity for oxygen to the exclusion of the carbon so long as the temperature is maintained below $1,000^\circ$ Fahrenheit. Above that point, however, it is found that the carbon content of the hydrocarbon has a superior or selective affinity for oxygen to the exclusion of hydrogen unless the oxidizing agent is present in excess of that necessary to oxidize the whole carbon content of the hydrocarbon. In my process it will be noted that the hydrocarbon is oxidized while maintained at a temperature at which the hydrogen has an affinity for oxygen to the exclusion of carbon, and inasmuch as considerable heat is evolved during the oxidation of the hydrogen of the hydrocarbon in order to maintain the temperature below the dissociating-point of the product desired and below the point at which carbon has a selective affinity for oxygen the heat evolved is abstracted by refriger-

eration. Otherwise it would accumulate or soar up to a point at which the oxidation of hydrogen of hydrocarbon or the formation of alcohols or aldehydes would be precluded or the said alcohol or aldehyde dissociated.

Having thus fully described my invention, what I claim as new, and desire to secure by Letters Patent, is—

1. The process of making alkyl hydroxid, which consists in oxidizing hydrogen of hydrocarbon by the action of a solid containing oxygen while maintaining the temperature below the decomposing-point of the alkyl hydroxid desired by refrigeration.

2. The process of making alkyl hydroxids, which consists in exposing metallic oxid capable of deoxidation by hydrogen in heated condition to the action of hydrocarbon while maintained at a temperature below the dissociating-point of the product desired.

3. The process of making alkyl hydroxids, which consists in conveying heated hydrocarbon into the presence of metallic oxid capable of deoxidation by hydrogen, the temperature being maintained below the dissociating-point of the product desired.

4. The process of making alkyl hydroxids, which consists in oxidizing hydrocarbon by the action of metallic oxid in a heated condition, said metallic oxid being capable of deoxidation by hydrogen, and the temperature being maintained below the dissociating-point of the product desired.

5. The process of making alkyl hydroxids which consists in heating metallic oxid capable of deoxidation by hydrogen in the presence of an excess of hydrocarbon under super-atmospheric pressure, the temperature being maintained below the dissociating-point of the product desired.

6. The process of making alkyl hydroxids which consists in exposing iron oxid to the action of hydrocarbon in a heated condition, the temperature being maintained below the dissociating-point of the product desired.

7. The continuous process of making alkyl hydroxids which consists in exposing metallic oxid capable of deoxidation by hydrogen, to the action of hydrocarbon in a heated state maintained at a temperature below the dissociating-point of the product desired, collecting and condensing the product, oxidizing the metallic residue, conveying more hydrocarbon in contact with the same, and repeating the process as before.

8. The continuous process of making alkyl hydroxids which consists in passing a current of hydrocarbon through iron oxid heated to a reacting temperature at which hydrogen is oxidized in preference to carbon and maintained below the dissociating-point of the product desired, collecting the oxidized product by condensation or absorption and finally

reoxidizing the metallic residue in a heated condition by a current of air.

9. The process of producing methyl alcohol and formic aldehyde, which consists in exposing a metallic oxid capable of deoxidation by action of hydrogen, to the action of methane (CH_4) in a heated condition maintained below the dissociating-point of the product desired, and collecting and condensing the product.

10. The process of making alkyl hydroxids which consists in exposing a metallic oxid capable of deoxidation by the action of hydrogen, to the action of a hydrocarbon at a temperature at which the hydrogen has an affinity for the oxygen to the exclusion of carbon, the temperature being maintained below the dissociating-point of the product desired.

11. The process of making methyl alcohol and formic aldehyde, which consists in exposing a metallic oxid, capable of deoxidation by the action of hydrogen, to the action of methane (CH_4) heated to a temperature at which the hydrogen thereof has an affinity for the oxygen of the oxid to the exclusion of carbon and maintaining the temperature below the dissociating-point of the product desired.

12. The process of making alcohol and oxidation products thereof, which consists in oxidizing hydrogen of hydrogen carbid by exposing it to the action of oxygen of a substance containing oxygen at a temperature at which the oxygen has an affinity for hydrogen in preference to carbon, and maintaining the temperature below the decomposing-point of the product desired.

13. The process of making alcohol and oxidation products thereof, which consists in oxidizing hydrogen of hydrogen carbid by the action of metallic oxid at an elevated temperature, the said temperature being maintained below the decomposing-point of the product desired.

14. The continuous process for producing alcohols and oxidation products thereof, which consists in heating hydrogen carbid, conveying the same in contact with a metallic oxid at a temperature maintained at a point in which the oxygen thereof has an affinity for hydrogen in preference to carbon and the metal with which it is combined and below the temperature at which the product desired is decomposed, condensing and recovering the product desired, reoxidizing the metallic residue, conveying more heated hydrogen carbid in contact with the metallic oxid thus produced, and continuing the process as before.

In testimony whereof I affix my signature in presence of two witnesses.

HENRY SPENCER BLACKMORE.

Witnesses:

WARREN C. STONE,
H. N. JENKINS.