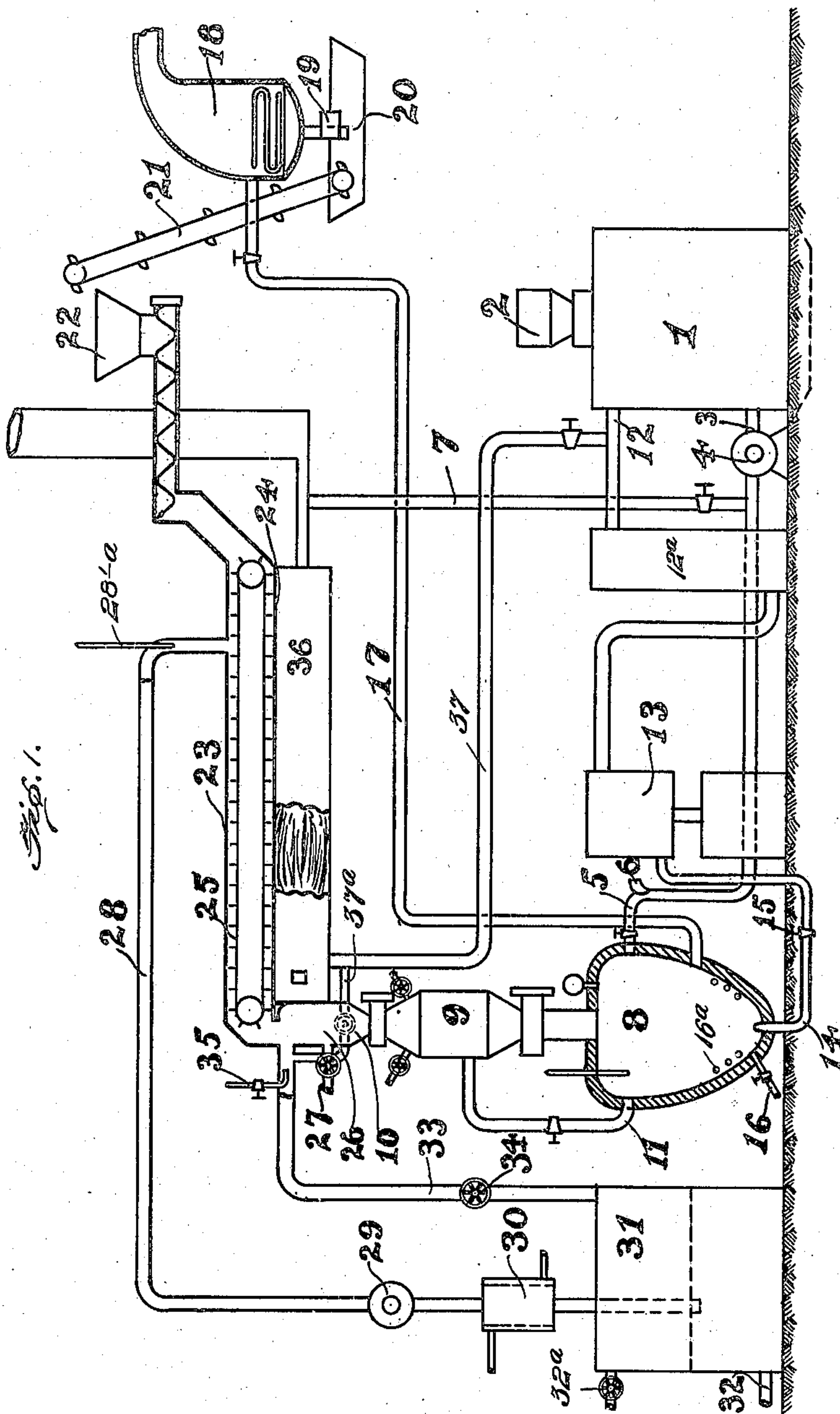


C. ELLIS & K. P. McELROY.
PROCESS OF MAKING ALDEHYDES.
APPLICATION FILED JULY 25, 1906.

915,946.

Patented Mar. 23, 1909.

3 SHEETS—SHEET 1.



WITNESSES:
Alfred M. Houghton.
Howell Battle

INVENTORS
Carlton Ellis
and
K. P. McElroy
BY
Marble & McElroy
ATTORNEYS.

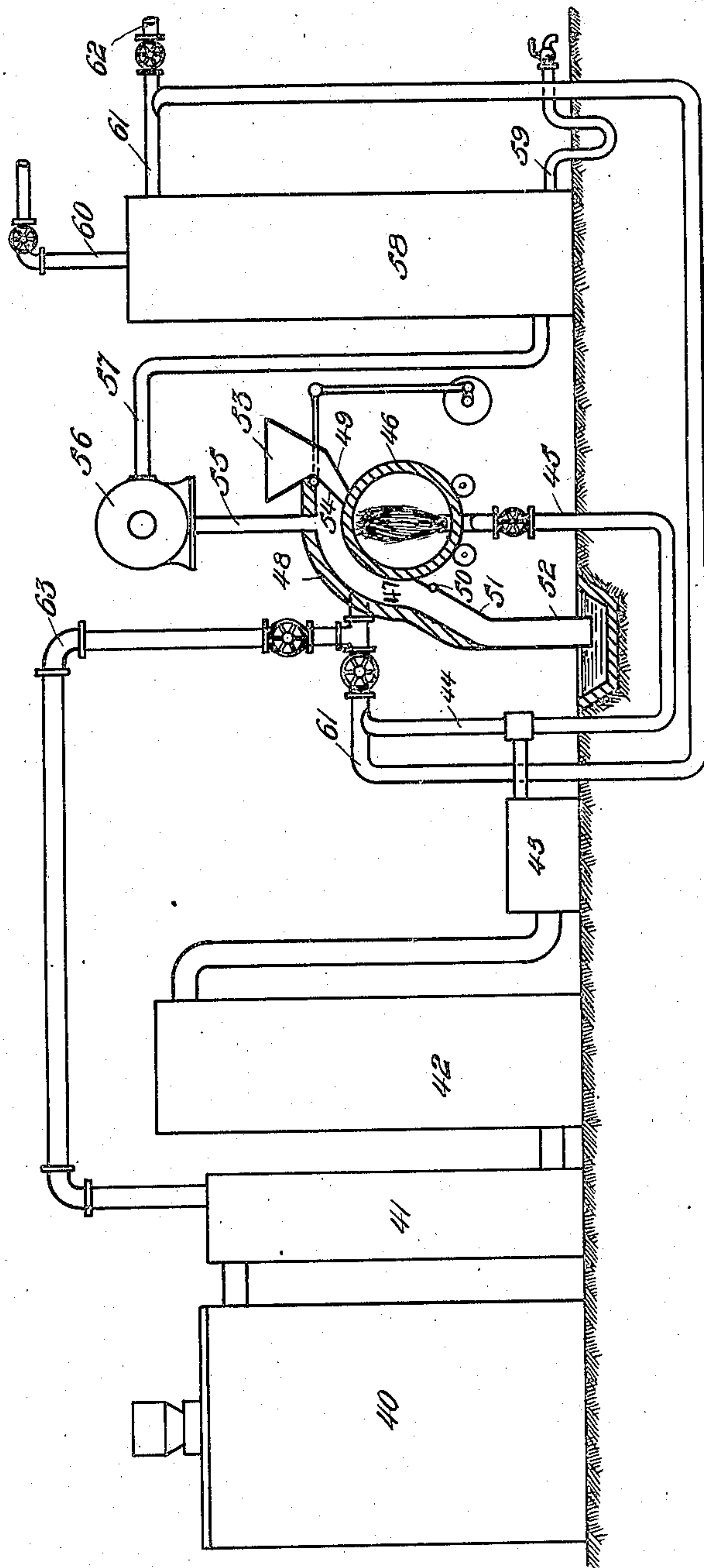
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3 SHEETS—SHEET 2.

Fig. 2.



WITNESSES:

Alfred M. Houghton.
Howell Zantle.

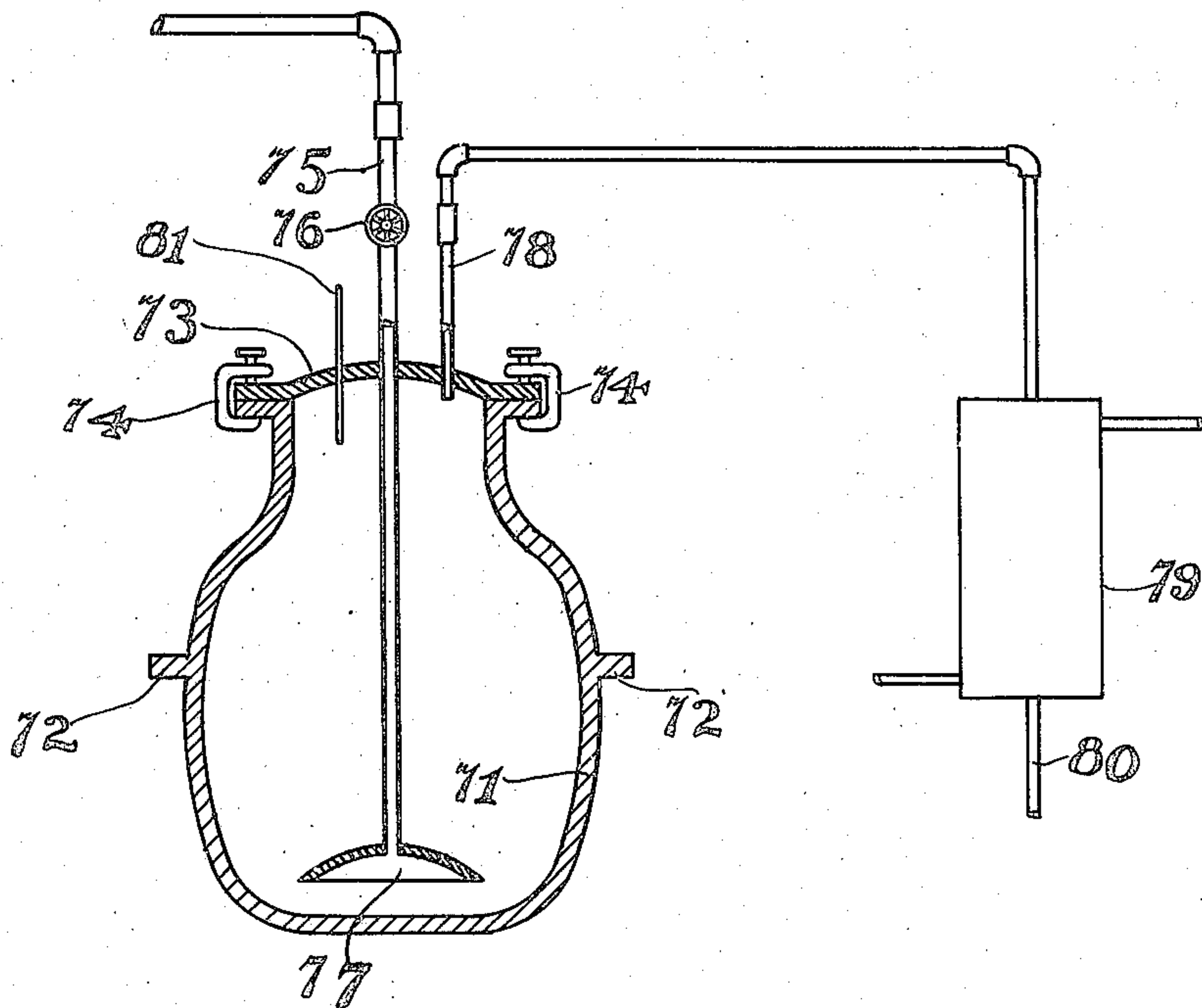
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 3 SHEETS—SHEET 3.

Fig. 3.



WITNESSES:

Alfred M. Houghton
Howell Buttle

INVENTORS

Carlton Ellis
and
K. P. McElroy
 BY

Marble & McElroy
 ATTORNEYS

UNITED STATES PATENT OFFICE.

CARLETON ELLIS, OF WHITE PLAINS, NEW YORK, AND KARL P. McELROY, OF WASHINGTON, DISTRICT OF COLUMBIA.

PROCESS OF MAKING ALDEHYDES.

No. 915,946.

Specification of Letters Patent.

Patented March 23, 1909.

Application filed July 25, 1906. Serial No. 327,647.

To all whom it may concern:

Be it known that we, CARLETON ELLIS and KARL P. McELROY, citizens of the United States, residing, respectively, in White Plains, county of Westchester, and State of New York, and in Washington, District of Columbia, have invented certain new and useful Improvements in Processes of Making Aldehydes; and we hereby declare the following to be a full, clear, and exact description of the same.

This invention relates to processes of making aldehydes and consists in a method of synthesizing aldehydes by the pyrolytic decomposition of formates; all as more fully hereinafter set forth and claimed.

It has occasionally been stated that traces of formaldehyde were sometimes, but not always, formed in heating metallic formates, but it has always been supposed that these traces were, so to speak, accidental or secondary products, the regular decomposition of the formates producing other products; some methyl alcohol at low temperatures and amounts of oxalates approaching theory at higher. It has been surmised that some formaldehyde might be formed by a secondary decomposition of one or both these decomposition products but it is not generally admitted that even these traces of formaldehyde are formed. Several methods have been proposed and are in use for utilizing the oxalate formation, but the methyl alcohol reaction is supposed to be too unproductive for practical use, the leading research in this direction, that of Lieben & Paterno (*Liebig's Annalen*, 1873, page 293), having resulted in the production of but 12 cc. of distillate from the distillation of 170 grams of calcium formate. Of this distillate, only part was methyl alcohol while formaldehyde was recorded as existing in faint traces.

While the formation of oxalates by heating formates to high temperatures has often been proposed, and has been commercially utilized to some extent, none of the numerous experimenters in this line has ever noted the formation of formaldehyde. It seems to be the accepted opinion in the art that heating formates to comparatively low temperatures produces only carbonates, CO and H₂, while sudden heating to relatively high temperatures produces oxalate, together with more or less carbonate, yields of oxalate being sometimes obtained which ap-

proach theoretical results. These impressions regarding the pyrolytic decomposition of the metallic formates are, however, incorrect. Formates, under proper conditions, break up quite regularly into formaldehyde and a carbonate of the base of the formate. But formaldehyde is quite sensitive to heat and at a temperature not much above that necessary to perform this reaction, and under some conditions even at temperatures below the same, it readily decomposes into carbon monoxid and hydrogen. With many formates, this range of temperature is about or around 360° C. This decomposition explains the usual and accepted results of formate pyrolysis, the formation of methyl alcohol and the formation of oxalates at low and high temperatures, respectively. At the lower range of temperatures, the hydrogen from a decomposing molecule of formaldehyde tends to unite with another molecule of formaldehyde to form the more stable molecule of methyl alcohol. At a higher range of temperatures, on the other hand, oxalates form a stable phase and the carbon monoxid resulting from a molecule of decomposing formaldehyde unites with a molecule of carbonate to form oxalate. In other words, the reactions are the reverse of those sometimes assumed, formaldehyde being a primary and not a secondary product.

If the temperature of the pyrolysis of formates be held at an exact point, that just high enough to form formaldehyde while below that at which a substantial decomposition takes place, the yields can be made productive. The margin between these two points is, however, under ordinary conditions rather narrow, but it may be increased by the use of several expedients. One is the use of vacuum which, under the ordinary laws of such reactions, tends to facilitate the evolution of gaseous products; i. e., causes the formate to break up at somewhat lower temperature. The use of a neutral gas current has the same effect, each gas, as the ordinary statement is, acting like a vacuum to every other gas in some respects. This gas current in properly arranged apparatus has a number of other important advantages, and it is therefore preferable to the vacuum *per se*. The two may of course be combined in a measure by using a current under reduced pressure. By sweeping a current of gases over the

decomposing formate and removing the formaldehyde as fast as formed and at the point of formation, the evolution is not only facilitated and a lower evolution temperature secured, but also the formaldehyde may be instantly removed from the place of formation and the influence of heat, and given no time to decompose. Any gas or mixture of gases and vapors will serve for this purpose as long as it is not oxidizing and does not injure the formaldehyde chemically. Steam is particularly advantageous as a component in the gas mixture since it has a specific catalytic effect in promoting the decomposition of the formate, and it is desirable to use some steam in any gas mixture which may be employed. It is perfectly suitable as a sole constituent but in such cases has the disadvantage that if the formaldehyde is removed by condensation, an unnecessary dilution results.

Preferably advantage is taken of the laws of partial pressures in producing a gas current and a gas mixture formed which has a specific retarding action upon the decomposition of formaldehyde. Since its decomposition products are carbon monoxid and hydrogen, by using a gas mixture which contains those bodies, or either of them, a "back pressure" is produced which tends to retard the formation of more hydrogen and monoxid; or, in other words, retards the decomposition of formaldehyde. Such a mixture can be made directly by mixing the required gases, or by the use of water gas or of producer gas made by a draft current containing no steam. The latter gas, being hydrogen free has some advantages. Its CO component tends to restrain the formaldehyde decomposition as well as would a mixture of CO and H, while the absence of H restrains the secondary decomposition into methyl alcohol above described. For practical reasons, it is in general preferable to operate the distillation in closed circuit, sweeping the gas mass over the decomposing formate to take up evolved formaldehyde, thence directing it through a washing apparatus or a condenser to remove formaldehyde and returning the gases to serve anew. In this manner of operation it is possible to use a directly produced mixture of carbon monoxid and hydrogen, or carbon monoxid alone, for the circulating current; the more so as some inevitable decomposition of the formaldehyde will tend to compensate for slight losses. In starting the reaction, the temperature may indeed be purposely pushed high enough to cause this decomposition and produce the requisite amount of gas for the circulating current. An atmosphere made in this manner consisting solely of hydrogen and monoxid, is very efficient for the described purpose. With the gas mass, however produced,

should ordinarily be mixed more or less water vapor prior to its contact with the formate, both for the purpose of gaining its advantageous influence upon the decomposition, and also for that of forming a solvent for the formaldehyde upon co-condensation by cooling. In the presence of a modicum of water vapor, the gases drawn off from the formate decomposition may be simply passed through an ordinary condenser, when the formaldehyde and water will condense out to form the commercial water solution. If water be not used as a component of the circulating gas mass, this latter must ordinarily be washed in water to remove the formaldehyde. Other removing means may however be adopted.

With some formates and under some circumstances, it is desirable to have a little methyl alcohol vapor in the circulating gas mass to have the advantage of its back pressure in restraining the formation of more. However, under such circumstances, the reaction itself generally furnishes the required traces; *i. e.* is automatically self-checking in this regard.

It is obvious that working upon the closed system described and returning the gas mass over and over again, the reaction is also self-checking with respect to the evolution of carbon monoxid and hydrogen, even when one or both of these gases is not, as is preferable, used for producing the circulating gas mass. The reaction can however be carried out by continuously supplied fresh masses of gas or vapor, but except in regard to the use of steam, hereinafter described, this is generally not advantageous. Special means and methods are also to be used for producing the very exact temperature conditions required. This may be done by traversing the formates in a thin layer or film over a heated surface of the required temperature. The surface may be differentially heated and the formates advanced from the cooler portions to the hotter. If the cooler portion be too cool and the hotter portion too hot, it is clear that there must be an intermediate point which the traveling layer will cross where the temperature is exactly that necessary. At this point the formaldehyde forming reaction proceeds smoothly and the vapors of the formaldehyde rising from the decomposing salt may be at once swept off and removed from the heated zone by the described gas current, preferably either crossing the traveling film transversely or flowing in an opposite direction so that the formaldehyde is instantaneously removed into a cooler region. However, the method of circulation may be arranged as desired so long as the formaldehyde is removed at the instant of formation and from the place of formation and transmitted into a cooler zone. There are however many other ways of producing the exact

temperature conditions necessary. In all cases however when using heat transmitted through the walls of a containing vessel it is desirable to treat the formate in films, layers or other divided form, each such film or layer being allowed to remain in contact with a heated surface of the correct temperature for the correct time and then removed, it being difficult to heat powders uniformly in mass, their conductivity being low. This is probably one reason for the failure of Lieben & Paterno to produce formaldehyde, their formates having been heated in U-tubes in mass. When formates are to be treated in mass, it is preferable to convey the heat to them by heating the circulating gas or vapor mass and not rely on heat conduction through the walls of a containing vessel.

Any formate not containing a readily reducible metal may be used in the foregoing process, but it is preferable to use those of the stronger bases, such as sodium, potassium, barium, calcium, strontium, zinc, lead or magnesium. Because of their fusibility and their production of less fusible carbonates in the reaction, it is difficult to handle the formates of sodium and potassium in traveling films, though they are otherwise suitable, and other means must generally be adopted. Formates of calcium, barium, strontium, magnesium and zinc are less fusible and therefore better adapted to film work. As formate of zinc breaks down into a basic in lieu of a normal carbonate it yields more or less carbon dioxide to mix with the circulating gas mass. As particularly adapted are regarded the calcium and magnesium salts because the low atomic weight of the contained metal lessens the total mass of material to be heated and because of their suitable characteristics physically. The barium and strontium salts however, though of somewhat greater molecular weight give very smooth reaction; especially the barium salt. As in the preferred form of this process the formate may be and is regenerated, the cost of the particular metal used to form the formate is not material. Hereinafter the barium formate will be generally stated as the raw material, to save repetitions, it being understood that the method is equally applicable to other formates.

The formaldehyde reaction converts the formate into a carbonate which can be readily re-converted into a formate for treatment anew, and by synthetically producing the formate, the formaldehyde manufacture may be arranged to work in a closed system, no raw materials being used but coal and water, and nothing leaving the system but formaldehyde, the base of the formate being used over and over again. Such a system will now be described.

Formates may be readily prepared by digestion of metallic carbonates with carbon

monoxid and water under high heat and pressure. A steam and gas pressure equal to that of water at 300° C. is suitable in many instances. The carbon monoxid required may be readily produced in the ordinary gas producer, but as it is desirable that the gas issuing should be rich in monoxid and as free as possible from carbon dioxide and hydrogen, both undesirable in the formate production, the producer is preferably run at a low temperature plane by the use of a balanced draft current of carbon dioxide, or products of combustion containing the same, mixed with air. Air in contact with ignited fuel of course reacts with evolution of heat while carbon dioxide reacts with absorption of heat, its reduction to monoxid by hot carbon being endothermic. By balancing the proportions of the two in the draft current the temperature plane in the producer obviously may be kept at any desired point. Since the absorption of carbon monoxid in the formate digester in treating carbonates gives rise to the production of carbon dioxide, the waste gases from such a digester form a very suitable source of the dioxide component of such a balanced draft current. It is further desirable to use this waste gas in this manner for the reason that thereby any unabsorbed monoxid may be utilized, going through the producer unchanged for subsequent use. This results in an important saving of fuel and further permits high partial pressures of carbon monoxid to be maintained in the formate digester without waste.

In the accompanying, more or less diagrammatic drawings, are shown several types of apparatus of the many adapted to perform the described process.

In this illustration: Figure 1 is a view, partly in elevation and partly in vertical section, of a complete apparatus adapted to work in closed system in the manner described; Fig. 2 is a similar view of a modified apparatus; and Fig. 3 is a view of a modified part of the system.

In Fig. 1, element 1 is a gas producer provided with the usual feed hopper 2. Draft current is supplied through twyer 3 and furnished by fan 4, provided with inlet pipe 5. On this pipe is a valved air inlet 6. Another valved pipe 7 is connected to withdraw products of combustion from the formaldehyde furnace. Pipe 5 further communicates with the formate digester 8 at a point near the top thereof. The formate digester is provided with a sealed-lock inlet 9, with a hopper 10 thereabove. A valved equalizing pipe 11 enables pressure in the inlet and the digester to be equalized in introducing material. Gas from the producer is withdrawn through gas pipe 12 and scrubber 12^a by means of an ordinary high-pressure pump 13 and introduced into the digester through pipe 14, provided with valve 15.

Near its bottom the digester is provided with a sand gate 16 for cleaning. Steam pipes 16^a furnish heat. Formate solution is withdrawn from time to time through valved pipe 17 and concentrated to crystallization in vacuum pan 18, provided with gated outlet 19. Open evaporators may of course be used. The crystallized formate is dropped into crystal well 20, whence it is withdrawn by conveyer mechanism 21 and dropped into the feed hopper 22 of the formaldehyde generator 23. This generator 23 consists essentially of a closed chamber having a heated metal bottom 24 over which travels the conveyer device 25. The sides and top of this chamber are not heated, so that the maximum temperature therein is next the heated metal bottom. This advances the formate from the hopper forward over the hot bottom, converting it into carbonate and drops the carbonate into the well 26, whence it gains access through the locked hopper to the formate apparatus for reconversion into formate. Pipe 27 furnishes water for the formate apparatus and incidentally some water vapor arising from the wetting of the hot carbonates, to the formaldehyde apparatus above. Gases are withdrawn from the formaldehyde apparatus by pipe 28, provided with thermometer 28^a and fan 29, passed through condenser 30 to seal pot 31 and the condensed formaldehyde removed through outlet 32. Valved pipe 32^a serves to adjust pressures in the system and may be attached to a suitable pump (not shown). From the seal pot, the gases, now stripped of their formaldehyde, pass by means of pipe 33, valved at 34, back into the formaldehyde apparatus to serve anew. Pipe 35 serves to add aqueous vapor. Heat for the formaldehyde apparatus is furnished by a producer gas flame burning in flue 36 below the metal bottom and supplied by valved pipe 37 communicating with the gas conduit of the producer. A valved branch 37^a serves to feed producer gas to the circulating gas mass, if it be desired.

In this apparatus it will be seen that the same quantity of base, baryta for instance, serves repeatedly, being converted into formate solution in 8, into crystallized formate in 18, into carbonate in 23, and once more converted into formate solution in 8. The producer furnishes carbon monoxid to the formate digester, and in turn receives carbon dioxid from it, together with whatever monoxid may be unused, and it further serves to heat the formaldehyde furnace, from which it may also derive such products of combustion as may be needed for the draft current. In the digester, under the high pressure and at the high temperature, carbon monoxid assimilates a molecule of water and becomes formic acid which converts the carbonate into formate, with evolution of carbon di-

oxid. In the formaldehyde apparatus, the crystallized formate, which may still be a trifle moist on entry without inconvenience, passes forward over the hot bottom in the opposite direction to the gas flame underneath and becomes increasingly hotter until it reaches a temperature at which formaldehyde is smoothly evolved, into the cooler space above such bottom. The generated formaldehyde is at once removed from the heated zone by the rapidly circulating gas mass and passes off for condensation through pipe 28, the gas mass, stripped of its formaldehyde, being returned through 33.

In the digester the producer gas entering through the nozzle of pipe 14 keeps the liquid agitated and the carbonate in suspension, much facilitating the reaction. As the liquid becomes enriched in dissolved formate and the reaction slows, the introduction of gas is stopped and the carbonate allowed to settle, whereupon the clear solution is drawn off above for evaporation and a fresh supply of carbonate and water introduced. The carbonate from the formaldehyde generator being in a state of extremely fine subdivision, when using barium, strontium and calcium salts, is eminently suitable for use in the digester, being readily attacked and converted into formate. In this form of apparatus, the use of insoluble metallic carbonates is preferable to that of such soluble carbonates as potassium and sodium for a number of reasons. The formate solution may be drawn off comparatively pure without accompanying carbonates to pass through the system and derange the working; and the formates do not fuse on the hot bottom of the formaldehyde apparatus. However, the soluble carbonates may be here used.

In the apparatus of Fig. 2, a less complete structure is shown which is however better adapted to deal with formates generally. This apparatus is not cyclical, and the formates are made elsewhere, and delivered to it ready made. In this view, 40 is a gas producer, provided with cooler 41, scrubber 42 and gas filter 43. From the filter leads a two-way pipe connection, 44 being adapted to deliver a modicum of gas to the formaldehyde apparatus, and 45 supplying a gas jet for heating the same. The formaldehyde apparatus includes a rotating cylinder 46 internally heated by the gas jet to the temperature required. The cylinder forms part of one wall of a formaldehyde chamber 47, the other walls being formed by a hood 48, a hopper wall 49, a doctor or scraper member 50 and a depending wall 51 below the same. These other walls are not heated. Downwardly from the chamber depends a leg 52 ending in a water seal, for the removal of waste carbonates. Hopper 53 serves for introduction of formates and the pivoted blade 54 serves to control the feed of the same.

The formates are introduced, spread into a thin layer on the hot rotating drum, converted into carbonate and the carbonate removed by the doctor and depending leg.

5 The formaldehyde produced, together with the circulating gas mass, are drawn off from the chamber by means of pipe 55, fan 56 and pipe 57 and sent into a scrubbing device 58. Condensates are removed by valved pipe 59.
10 A water spray may be given by pipe 60. The gas mass leaves by pipe 61, provided with valved outlet 62 for regulating pressure, and returns to the formaldehyde chamber to serve anew. A modicum of water vapor
15 may be added from the initial gas cooler by means of valved pipe 63. The rotating drum may easily be kept at exact temperature by the gas jet, and the fusibility of the alkaline formates is here immaterial, since
20 the doctor or scraper serves to keep the drum surface clean. The functions of the circulating gas mass are the same as in Fig. 1.

In Fig. 3 is shown a structure particularly
25 adapted for use with the alkaline formates. Vessel 71, built something like a converter, is provided with lugs 72, on which it may be supported and swung in emptying. Cover 73 is secured in place by clamping members
30 74. Vapor pipe 75, with valve 76, passes through this cover and ends in bell 77. Pipe 78, provided with condenser 79, removes vapors and gases and delivers its condensate through 80. Thermometer 81 serves in con-
35 trolling the temperature.

In using this apparatus, the melted formate of sodium, or of potassium, or of both admixed, is introduced into the vessel and a superheated gas mass, as, for instance, pro-
40 ducer gas and steam, or steam alone, is blown through until the formaldehyde conversion is complete. The formaldehyde is diluted by, and carried away with, the gas mass as fast as formed. Upon taking away
45 the cover, the resulting carbonates may be removed. This apparatus, it will be noted operates discontinuously in lieu of continuously like those in Figs. 1 and 2.

Other aldehydes than formaldehyde may
50 be made by mixing an appropriate salt of another organic acid with a formate; benzaldehyde for instance by mixing and pyrolytically treating molecular proportions of barium benzoate and formate; acetaldehyde
55 from acetate and formate; etc. In treating such mixtures in the closed cycle operation because of the accumulation of base, only part of the carbonate from the aldehyde apparatus should be introduced into the formate
60 digester, the remaining part being used to form the salt of the other acid.

Formation of aldehydes by pyrolysis of a mixture of a salt of another acid with a formate while not in itself new does not ordi-
65 narily give very productive yields. It may

however be performed by the present method very advantageously since the circulating gas mass and the regulated heat operate in the case of such a mixture with the same beneficial effect as with the formates
70 alone.

Of the many aldehydes which may be formed in this way are those of the fatty series from acetaldehyde up to the waxy
75 higher aldehydes, and those of the aromatic series. In all cases, molecular weights of the formate and of a salt of an acid whose aldehyde is to be formed are mixed together and submitted to pyrolysis in a gas mass of the character described. When operating in
80 closed cycle, a part of the resulting carbonate is returned to the digester to be re-converted into formate.

To recapitulate, the present method comprises forming aldehydes by the pyrolysis of
85 formates, either alone or admixed with other salts, by a regulated heat in the presence of circulating or streaming gas atmospheres carrying the aldehyde away from the point of formation as fast as formed and of such
90 character as to restrain the decomposition of formaldehyde; such gas atmosphere preferably containing carbon monoxid and some water vapor. Any formate not containing
95 a readily reducible metal is applicable, but those derived from bases forming insoluble carbonates are preferred; and with these latter formates, the production of formaldehyde is preferably combined with the re-
100 generation of the formates in a continuous cycle.

What we claim is:

1. The process of making formaldehyde which consists in decomposing a formate by regulated heat in the presence of a stream of
105 gas of regulated composition passing over said formate at the point where the formaldehyde is evolved and sweeping such formaldehyde away from such point.

2. The process of making formaldehyde
110 which consists in decomposing a formate by a low and regulated heat and removing the formaldehyde from the point of formation to a cooler point as fast as formed.

3. The process of making aldehydes which
115 consists in exposing a body of metallic salts comprising a formate to a low and regulated heat in the presence of a stream of gas of regulated composition passing over said body at the point where it is exposed to heat and
120 where aldehyde is formed and by such gas stream removing the aldehyde from the influence of the heat as fast as formed.

4. The process of making aldehydes which
125 consists in continuously moving a thin traveling layer of material comprising a metallic formate over a heated surface and recovering the aldehyde produced.

5. The process of making formaldehyde which consists in continuously moving a
130

metallic formate in a thin layer over a heated surface and recovering the formaldehyde produced.

6. The process of making formaldehyde which consists in continuously moving a metallic formate in a thin traveling layer over a heated surface of progressively increasing temperature, and removing the formaldehyde from the point of formation.

7. The process of making aldehydes which consists in continuously moving a body of metallic salts comprising a metallic formate in a thin layer through a heated zone of temperature sufficient to form such aldehyde and removing said aldehyde to a cooler zone as fast as formed.

8. The process of making formaldehyde which consists in continuously moving a metallic formate in a thin layer through a heated zone of temperature sufficient to evolve formaldehyde, and removing the formaldehyde to a cooler zone as fast as formed.

9. The process of making aldehydes which consists in decomposing a body of metallic salts comprising a metallic formate by heat in a streaming atmosphere containing substances that are formed in the pyrolytic decomposition of formaldehyde, transmitting such streaming atmosphere past the point of formation of the aldehyde and sweeping away the aldehyde from such point as fast as formed.

10. The process of making formaldehyde which consists in decomposing a metallic formate by heat in a streaming atmosphere containing substances formed in the pyrolytic decomposition of formaldehyde, transmitting such streaming atmosphere past the point of formation of the formaldehyde and sweeping away the formaldehyde from such point as fast as formed.

11. The process of making aldehydes which consists in decomposing a body of metallic salts comprising a metallic formate by heat in an atmosphere containing carbon monoxid, and withdrawing the aldehyde from the influence of the heat as fast as formed.

12. The process of making formaldehyde which consists in decomposing a metallic formate by heat in an atmosphere containing carbon monoxid and withdrawing the formaldehyde from the influence of the heat as fast as formed.

13. The process of making aldehydes which consists in decomposing a body of metallic salts comprising a metallic formate by heat, removing evolved vapors from the influence of the heat by a circulating gas mass as fast as formed, removing the aldehyde from such gas mass, and returning the gas mass for use with a fresh body of salts.

14. The process of making formaldehyde which consists in decomposing a metallic formate by heat, removing evolved formaldehyde from the influence of the heat by a cir-

culating gas mass as fast as formed, removing the formaldehyde from such gas mass, and returning the gas mass for use with a fresh body of formate.

15. The process of making aldehydes which consists in decomposing a body of metallic salts comprising a metallic formate by heat in a moistened gas mass containing carbon monoxid, removing the gas mass, removing the aldehyde therefrom, and returning the gas mass for use with a fresh body of salts.

16. The process of making formaldehyde which consists in decomposing a metallic formate by heat in a moistened gas mass containing carbon monoxid, removing the gas mass, removing the formaldehyde therefrom and returning the gas mass for use with fresh formates.

17. The process of making aldehydes which comprises decomposing a body of metallic salts comprising a metallic formate by heat in a moist atmosphere containing carbon monoxid.

18. The process of making formaldehyde which comprises decomposing a metallic formate by heat in a moist atmosphere containing carbon monoxid.

19. The process of making formaldehyde which consists in converting carbon into producer gas, causing the producer gas to act upon a metallic carbonate under heat and pressure to form a formate, pyrolytically decomposing the formate into formaldehyde and carbonate and returning the carbonate to form fresh formate.

20. The process of making formaldehyde which consists in continuously converting the same portion of a base alternately into formate and carbonate, with evolution of formaldehyde in the latter reaction.

21. The process of making formaldehyde which consists in converting a base into formate by treatment with producer gas and water under heat and pressure, conveying the formate into a heated zone of formaldehyde-evolving temperature, and re-converting the producer carbonate into formate for re-treatment in said zone, whereby the same portion of said base serves for repeated use.

22. The process of making formaldehyde which consists in converting a portion of a base into a formate by treating said base with carbon monoxid and water in a digester under heat and pressure, conveying said formate into heated zone for pyrolysis into formaldehyde and carbonate, and returning the carbonate to the digester for reconversion into formate, thereby causing said portion of base to travel continuously in closed cycle through said digester and heated zone.

23. The process of producing formaldehyde which consists in operating a gas producer with a mingled draft of air and carbon dioxid, forcing the gas produced into a heated digester containing a metallic carbonate and

water and returning the treated gases from the digester to serve as a component of the draft current, removing the formate produced in this treatment, converting it into
5 formaldehyde and a carbonate, and returning the carbonate to the digester.

24. The process of making formaldehyde which consists in forming a formate by the action of carbon monoxid and water upon a
10 basic body under heat and pressure, removing said formate, evaporating the excess of water from the formate, heating the formate to evolved formaldehyde and form a carbonate, and reusing the carbonate to form fresh
15 formate.

25. The process of making aldehydes which consists in placing a thin film or layer of a body of metallic salts comprising a formate

upon a heated surface maintained at a temperature suited for evolving an aldehyde 20 from such body, allowing the film or layer to remain in contact with such surface until the aldehyde is evolved, removing the carbonate produced and replacing it by a fresh film or layer of such body. 25

In testimony whereof we affix our signatures in the presence of witnesses.

CARLETON ELLIS.
KARL P. McELROY.

Witnesses for Ellis:

GODFREY M. S. TAIT,
HARRY B. CHALMERS.

Witnesses for McElroy:

C. W. FOWLER,
H. M. MARBLE.