RES

PATENT SPECIFICATION

682,177

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3546

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COMPLETE SPECIFICATION

Improvements in or relating to the Synthesis of Oxygenated Organic Compounds

We, STANDARD OIL DEVELOPMENT COMPANY, a corporation duly organized and existing under the laws of the State of Delaware, United States of America, having an office at Elizabeth, New Jersey, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to an improved synthesis process for the production of oxygenated organic compounds by reacting organic compounds having an olefinic double bond with gas mixtures containing carbon monoxide and hydrogen at high pressures and elevated temperatures in the presence of suitable catalysts. More particularly, the invention is concerned with an improved method for removing dissolved metal carbonyl and carbon monoxide from the oxygenated synthesis product prior to storage or further treatment such as catalytic hydrogenation.

The synthesis of oxygenated organic compounds from olefinic compounds and mixtures of CO and H_2 is well known in the art. The olefinic starting material is reacted in the liquid state with CO and H_2 in the presence of a metal catalyst, usually an iron group metal catalyst such as a suitable cobalt compound. The reaction product consists essentially of organic carbonyl compounds, mainly aldehydes, and alcohols having one carbon atom more per molecule than the olefinic feed material. The oxygenated product may be hydrogenated in a second catalytic stage to convert the aldehydes to the corresponding alcohols.

Practically all types of organic compounds having an olefinic double bond may be used as the starting material, including aliphatic olefins and diolefins, cyclo-olefins, aromatics with olefinic side-chains, oxygenated compounds having olefinic double bonds, etc. The metal catalyst may be present as a solid or in the form of an organic salt soluble in the olefinic feedstock. Suitable reaction conditions include temperatures of about 150—450° F., pressures of 100—300 atmospheres, hydrogen to carbon monoxide ratios of about 0.5—4.0:1, liquid feed rates of about 0.1—5.0 V/V/hr. and gas feed rates of about 1000—45000 standard cu. ft. of gas mixture per barrel of liquid olefinic feed.

Similar temperatures and pressures and conventional hydrogenation catalysts such as nickel, copper, tungsten, oxides or sulfides of Group VI and Group VIII metals, etc, may be employed in the second stage for the hydrogenisation of the carbonyl compounds.

The iron group metals used as catalysts in the first stage of the process react with CO to form metal carbonyls. This is particularly true for cobalt, the preferred and most active oxygenation catalyst. This cobalt carbonyl which dissolves in the liquid oxygenated product tends to decompose under low CO partial pressures even at relatively low temperatures and very rapidly at elevated temperatures, to form free CO and insoluble metallic cobalt. Metallic cobalt so separated seriously interferes with the further processing of the oxygenated reaction product because it may cause excessive pressure drop in the equipment due to deposition of cobalt in lines and vessels or it may deactivate the hydrogenation catalyst of the second stage by surface deposition of cobalt. Since cobalt carbonyl slowly decomposes under low Co pressures even on standing at atmospheric pressure it should be removed as soon upon the formation of the oxygenated product as possible.

Prior to the present invention it has been suggested to remove cobalt carbonyl from the oxygenated product by treating with hydrogen at ele-

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vated pressures and temperatures in a vessel which may be packed with an inert solid on which the separated cobalt is deposited, and from which a substantially carbonyl-free liquid product may be withdrawn, the liberated CO being removed with the hydrogen used for treating. In such treatment with hydrogen, pressures may be the same as or lower than those obtaining in the synthesis reaction zone or in the subsequent hydrogenation zone; specific pressure suggested have been 100 to 500 pounds per square inch gauge and upwards to 6000 pounds per square inch gauge. Temperatures employed may be those at which the synthesis product leaves the synthesis zone which as previously indicated may be operated at 150 to 45° F. A purging treatment with hydrogen as just described is disclosed and claimed in our prior Specification No. 629,915.

The present invention is directed to securing improvements in a metal carbonyl decomposition operation, particularly the avoidance of plugging and fouling of the system arising from carbonyl decomposition and the precipitation of free metal. In general, these improvements are secured by carrying out the carbonyl decomposition operation under closely correlated conditions of temperature and pressure and by employing particular methods of supplying heat for such operation.

Accordingly the invention provides a process for removing dissolved metal carbonyl from the liquid oxygenated product obtained from the conversion of organic compounds having an olefinic double bond with CO and H_2 in the presence of carbonyl-forming metal catalysts, which comprises subjecting said product in the liquid phase in a treating zone to a temperature high enough to maintain a metal carbonyl decomposition rate substantially higher than the rate of condensation and polymerisation of aldehyde components of said product under the treating conditions, and a pressure not substantially greater than that required to prevent substantial vaporization of liquid, maintaining said temperature by passing a highly heated fluid in heat exchange relationship with said product, and removing a liquid substantially free of dissolved metal carbonyl from said treating zone.

In accordance with our specific embodiment of the invention, plugging of the decobalting system may be substantially minimized or completely eliminated by employing, as a method of supplying the heat required for cobalt carbonyl decomposition, the mixing of the cobalt carbonyl-containing product with a preheated cobalt carbonyl-free fluid. Other methods of heat supply will appear hereinafter.

The specific conditions of temperature and pressure used in the carbonyl removal process of the invention depend to a certain extent on the boiling range of the liquid oxygenation product treated. For example it may be stated that temperatures within the approximate range of 200—400° F., preferably 250—350° F., and total pressures within the approximate range of 50—150 lbs. per sq. in. gauge are generally suitable for a conventional synthetic oxygenated, cobalt carbonyl-containing product having an average of 6 or more carbon atoms per molecule. A cobalt carbonyl-containing product having an average of 9 or more carbon atoms per molecule may be treated with good results, in which case pressures as low as 0—100 lbs. per sq. in. gauge may be used.

Having set forth its general nature, the invention will be best understood from the following more detailed description in which reference will be made to the accompanying drawing wherein:—

Figure 1 illustrates a system wherein the heat required for carbonyl removal is applied externally to a tube carrying the oxygenated product to be treated.

Fig. 2 shows an arrangement in which the cobalt carbonyl-containing liquid is heated by direct contact with a preheated fluid substantially free of cobalt carbonyl and carbon monoxide; and

Fig. 3 is an illustration of internal heat supply through immersed heat transfer surfaces.

Referring now in detail to Figure 1, the system illustrated therein essentially comprises an oxygenation reactor (10), a separator (18), a heater (30) and a soaking vessel (40) whose functions and cooperation will be forthwith explained using the removal of cobalt carbonyl from an oxygenated reaction product having an average of 7—9 carbon atoms per molecule as an example. It should be understood however that the system may be applied to the treatment of heavier or lighter oxygenated products containing the same or a different metal carbonyl.

In operation, the liquid olefinic feed stock having an average of about 6—8 carbon atoms per molecule and a gas mixture containing CO and H_2 in the approximate ratios of 1 : 1 are introduced through line (1) into the bottom of reactor (10). The catalyst, preferably in the form of a cobalt salt soluble in the feed, such as cobalt naphthenate, stearate, oleate, etc., may be added to the liquid feed in concentrations of about 0.1—3% by weight.

If desired, reactor (10) may be provided with a bed of cobalt catalyst supported on an inert carrier such as silica gel, pumice or the like.

Reactor (10) is operated at conventional oxygenation conditions including temperatures of about 300—400° F., pressures of about 2500—3500 lbs. per sq. in., a gas feed rate of about 3000—40000 standard cu. ft. per barrel of liquid feed and a liquid feed througput of about 0.2 to 2 volumes per volume of reactor space per hour. The reaction products consisting of liquid oxygenated products containing about 0.05 to 0.3% by weight of dissolved cobalt mainly as cobalt carbonyl are removed, together with unreacted gas, through line (12), cooled to about 80—120° F. in cooler (14) and passed through line (16) to a liquid-gas separator (18). Gas separated in separator (18) is withdrawn through line (20) and may be recycled to line (1) for reuse in reactor (10).

The liquid separated in separator (18), still at the pressure of reactor (10), is withdrawn downwardly through line (22) provided with pressure release valve (24). The liquid product is now under a low pressure of about 50—150 lbs. per sq. in. at which the major portion of the previously dissolved gas is released. This liquid-gas mixture is separated in low-pressure separator (25), from which the gas is withdrawn through line (27). The liquid withdrawn through line (26) is mixed, if desired, with CO-free hydrogen or inert gas supplied from line (28) in amounts of about 50 to 500 standard cu. ft. per barrel of liquid. The mixture of oxygenated liquid product and hydrogen enters heater (30) through line (29).

Heater (30) may consist of one or more pipes (32) provided with a steam jacket as indicated in the drawing. The temperature of heater (30) is so controlled that the mixture flowing through pipe (32) is heated to a temperature of about 300—400° F. by the time it leaves heater (30). The heated mixture is now under conditions of temperature, total pressure and CO partial pressure adequate to provide for the rapid decomposition of colbalt carbonyl, while appreciable boiling of the liquid produce is prevented.

Cobalt carbonyl decomposition starts in heater (30). The mixture of gas and liquid product now containing in addition to dissolved cobalt carbonyl same suspended metallic cobalt, flows through line (34) to soaking vessel (40). Both line (34) and vessel (40) may be provided with suitable insulating means or steam jackets (36) and (38), respectively, to prevent heat losses. Soaking vessel (40) is so dimensioned that sufficient residence time for the liquid product is provided at the temperature and pressure conditions specified, to permit substantially complete decomposition of the cobalt carbonyl. Residence times substantially below one hour are generally sufficient for this purpose. If desired, vessel (40) may be provided with baffles (42), preferably removable, to extend the path of the liquid. If required any cobalt metal deposited on baffles (42) may be periodically removed to prevent plugging of the system. A by-pass line (45) is provided to permit by-passing of the decobalting system during cleaning periods or for other purposes.

The gas-liquid mixture now substantially free of cobalt carbonyl, and, as a result of the low CO partial pressure, likewise substantially free of dissolved CO is passed through line (46) to a cooler (48) wherein it is cooled to about 80—120° F. the cooled mixture flows through line (50) to a gas-liquid separator (52). A gas consisting of hydrogen or inert gas and small amounts of CO is withdrawn overhead from separator (5) through line (54) to be vented or used for any suitable purpose.

The liquid product now containing less than about 0.005% by weight of cobalt carbonyl is withdrawn downwardly from separator (52) through line (56) and filter (57) which removes suspended metallic cobalt after which the liquid product is passed through line (58) provided with a pressure release valve (60) to a product accumulator (not shown) and to further conventional processing by hydrogenation, in a conventional catalytic hydrogenator (61).

Systems of the type illustrated in Figure 1, when operated at the conditions specified, permit decobalting of oxygenated product within decobalting times substantially below one hour, i.e. short enough effectively to prevent aldehyde condensation. It has been observed however that cobalt may deposit on the highly heated metal surfaces of pipe (32), which may cause plugging of pipe (32) after runs of say about 1 or 2 days' duration. This difficulty may be eliminated by employing the embodiment of the invention illustrated in Figure 2 wherein like reference numerals are used to identify elements similar to those of Figure 1.

Referring now specifically to Figure 2, the operation of the system up to the passage of the liquid product through pressure release valve (24) is identical with that described in connection with Figure 1. The depressurized cobalt carbonyl-containing liquid now passes at the temperature of separator (18) through line (26) to the top of soaking vessel (40) where it is mixed with liquid oxygenated product heated in heater (30) to a temperature of about 300—400° F. and supplied through line (33), as will appear more clearly hereinafter. The amount of heated liquid supplied through line (33) is such that the mixture in vessel (40) attains a temperature of about 250—350° F.

The thus heated liquid mixture flows down through vessel (40). By holding a liquid level in vessel (40), and allowing gas to separate from the liquid therein, it is possible to eliminate the separator (25), in which case, however, it may be advantageous to feed an inert stripping gas such as nitrogen, methane or CO—free hydrogen through line (28) in the amounts specified before. However, decomposition of cobalt carbonyl takes place so rapidly in vessel (40) at the favourable conditions specified, that the inert gas supply through line (28) may be substantially reduced and even completely eliminated, particularly at relatively low cobalt carbonyl concentrations of the liquid of say not substantially above 0.2%

A liquid product substantially free of cobalt carbonyl is withdrawn downwardly from vessel (40) through line (43). One portion of the withdrawn substantially carbonyl-free liquid, corresponding to the amount of liquid supplied through line (26) is passed on through line (46) to cooler (48) and separator (52), as described in connection with Figure 1. Suspended cobalt metal may be removed from the liquid leaving separator (52) by filtering means (57).

The remainder of the carbonyl-free liquid in line (43) is passed through line (47) provided with pump (49) to heater (30) and from there through line (33) to vessel (40) as described before. Because no dissolved cobalt carbonyl is present in heater (30) the latter may be operated at any suitable temperature which may be as high as 300—400° F., without any danger of cobalt deposition on hot heater surfaces. The actual decomposition of dissolved cobalt carbonyl takes place exclusively in vessel (40) in the absence of hot-heat-supplying surfaces In this manner, cobalt deposition on any hot heat-supplying surfaces is avoided throughout the system. Residence times in heater (30) and vessel (40) may be about 5—60 minutes, and may advantageously be maintained between about 15 and 30 minutes. If desired, separated cobalt metal may be removed from the liquid flowing line (43) by a filter (62) arranged on branch line (64), to avoid plugging of subsequent system elements.

The gases liberated in or introduced into vessel (40), containing traces of vaporised liquid, are removed overhead through line (46) and passed through cooler (66) to a gas-liquid separator (68) from which gas may be vented or recovered overhead through line (70). Any separated liquid, such as that carried by entrainment in the gas leaving vessel (40) or resulting from condensation of the minor amounts of liquid vaporized in vessel (40), is withdrawn downwardly through line (72) to be recovered or recycled to reactor (10).

As a modification of the embodiment of Figure 2, the hot liquid supplied through line 33 may be an extraneous liquid, substantially inert to the aledhyde product, for example, a hydrocarbon liquid boiling higer than the liquid product. This liquid may be introduced through line (44), in which case valve (45) is closed and no product is pumped to heater (30). The extraneous liquid may be separated from the product by distillation, extraction, or other means, and recycled to line (44) if desired.

In some instances an alternate embodiment of the invention may be used, in which the cool liquid entering vessel (40) is heated by admixture with heated gas. In this case, referring again to Figure 2, a relatively large volume of heated gas, substantially CO-free, is introduced through line (28) thus eliminating a part or all of the liquid heating otherwise accomplished in heater (30). The gas may be an inert gas such as nitrogen or methane, or it may be one of the hydrogen steams used elsewhere in the process.

A further embodiment of the invention, designed to avoid plugging difficulties is illustrated in a simplified manner by Figure 3 which shows merely the decobalting means proper, all other system elements which may be substantially the same as those described in connection with Figure 1 and/or 2 having been omitted.

The decobalting means of Figure 3 consists essentially of a single vessel (80) which takes the place of heater (30) and vessel (40) of Figures 1 and 2. Vessel (80) comprises an elongated relatively wide tube (82) which may have a diameter of say about 16" and which may be provided with a level indicator (81). Arranged within tube (82), essentially over its entire length, is a steam coil (84) which may be made of pipe having a diameter of say about ¼—¾".

In operation, liquid oxygenated product containing dissolved cobalt carbonyl is supplied to the top of vessel (80) through line (86) at a temperature of about 80—120° F. and a pressure of about 80—120 lbs. per sq. in. to substantially completely fill vessel (80) as indicated by level L_{80}. Heating steam is supplied through line (88) and withdrawn through line (90), in a manner adequate to heat the liquid within vessel (80) to about 300—400° F. If desired, CO-free hydrogen or inert gas may be supplied to the bottom of vessel (80) through line (92) in the proportions specified in connection with line (28) of Figures 1 and 2.

Carbonyl decomposition proceeds rapidly within residence times of about 5 to 60 minutes, preferably 15—30 minutes, which are not conducive to aldehyde condensation or polymerisation. Any separated cobalt metal which collects in the bottom of vessel (80) may be withdrawn through drain (94). While some cobalt metal may be deposited on heating coil (84) the free cross-sectional area of vessel (80) is so much larger than that of the pipe in heater (30) of Figure 1 that no plugging trouble will arise for an extended period of time. In addition any cobalt deposited on the outer surface of the heating coils (84) may be more readily removed than from the inside surface of the heating tube of heater (30) of Figure 1.

Liquid oxygenated product substantially free of dissolved cobalt carbonyl and CO is withdrawn through line (96) from the bottom of vessel (80) at a point above drain (94). The withdrawn liquid may be freed of any residual cobalt metal in filter (98), cooled in cooler (100) and passed to storage through line (102) provided with a level control valve (104). Separated gas containing only small amounts of vaporized liquid is withdrawn overhead from vessel (80) through line (46) to be further treated in elements (66) and (68) as outlined in connection with Figure 2.

While hydrogen is preferable whenever a gas is to be used for stripping and reduction of the CO partial pressure in all decobalting elements of the invention described above, other gases inert to the oxygenated liquid product may be employed, for example, methane, nitrogen, etc.

The invention will be further illustrated by the following specific example summarizing the results obtainable at different operating conditions for an oxygenated product containing an average of about 8 carbon atoms per molecule when using different embodiments of the invention.

EXAMPLE.

	Operation in accordance with			
	Figure 2		Figure 3	
Decobalting Vessel Conditions:				
Pressure, p.s.i.g.	100	100	100	100
Temperature, °F.	325	305	310	310
Inlet Gas	None	Hydrogen	None	Hydrogen
Inlet Gas Rate, CF/Bbl.	0	300	0	300
Oxo Aldehyde Product:				
Wt. % Soluble Cobalt				
Before Decobalting Vessel	0.18	0.085	0.033	0.107
After Decobalting Vessel	0.001	0.001	0.005	0.005

In Specification No. 672,880 there is claimed a method for the conversion of carbon monoxide-containing reactants at elevated pressure and temperature by contact with a catalyst of the iron group, which comprises passing reactants containing carbon monoxide through a reaction zone containing a catalyst of an iron group metal, maintaining said reaction zone at a temperature below 400° F. and at a pressure above 150 pounds per square inch, forming metal carbonyl during passage of reactants through said reaction zone, effecting conversion of reactants in the presence of said catalyst and said metal carbonyl, passing an effluent containing products of conversion and said metal carbonyl from said reaction zone into a secondary zone, maintaining said secondary zone at temperature approximately 50 to 100° F. above that of the reaction zone and a pressure below 100 pounds per square inch to decompose said metal carbonyl in said secondary zone, removing from said secondary zone a product stream substantially free from metal carbonyl, and periodically reversing flow of said reactants and said effluent with respect to to said reaction zone and said secondary zone.

What we claim is:—

1. A process for removing dissolved metal carbonyl from the liquid oxygenated product obtained from the conversion of organic compounds having an olefinic double bond with CO and H_2 in the presence of carbonyl-forming metal catalysts, which comprises subjecting said product in the liquid phase in a treating zone to a temperature high enough to maintain a metal carbonyl decomposition rate substantially higher than the rate of condensation and polymerization of aldehyde components of said product under the

treating conditions, and a pressure not substantially greater than that required to prevent substantial vaporization of liquid, maintaining said temperature by passing a highly heated fluid in heat exchange relationship with said product and removing a liquid substantially free of dissolved metal carbonyl from said treating zone.

2. A process according to Claim 1, wherein said temperature is maintained by mixing said product with a highly heated inert fluid free from metal carbonyl and carbon monoxide.

3. A process according to Claim 2, wherein said fluid is a liquid.

4. A process according to Claim 3, wherein said liquid is liquid oxygenated product previously freed of dissolved metal carbonyl.

5. A process according to Claim 3, wherein said liquid is an extraneous liquid.

6. A process according to Claim 2, wherein said fluid is hydrogen.

7. A process according to Claim 1, wherein said temperature is maintained by passing said highly heated fluid through a heat exchanger immersed in the liquid product in said treating zone.

8. A process according to any one of Claims 1—7 ,wherein the oxygenated product has an average of at least six carbon atoms per molecule, the metal catalyst is a cobalt catalyst and the temperature and pressure in said treating zone are in the approximate ranges of 200—400° F. and 50—150 lbs. per sq. in. gauge respectively.

9. A process according to any one of Claims 1—7, wherein the oxygenated product has an average of at least nine carbon atoms per molecule, the metal catalyst is a cobalt catalyst, and temperature and pressure in said treating zone are in the approximate range of 200—400° F. and 0—100 lbs. per sq. in. gauge respectively.

10. A process according to any one of the preceding claims, wherein the metal catalyst is soluble in the feed to the conversion operation.

Dated this 18th day of May, 1949.

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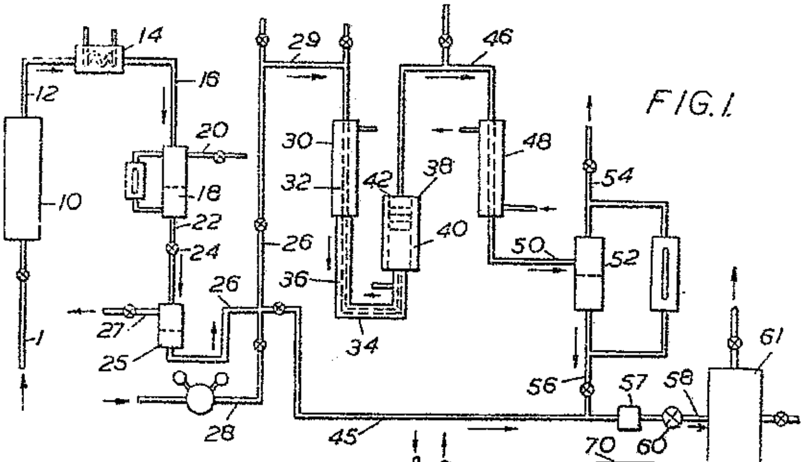
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FIG. 1.

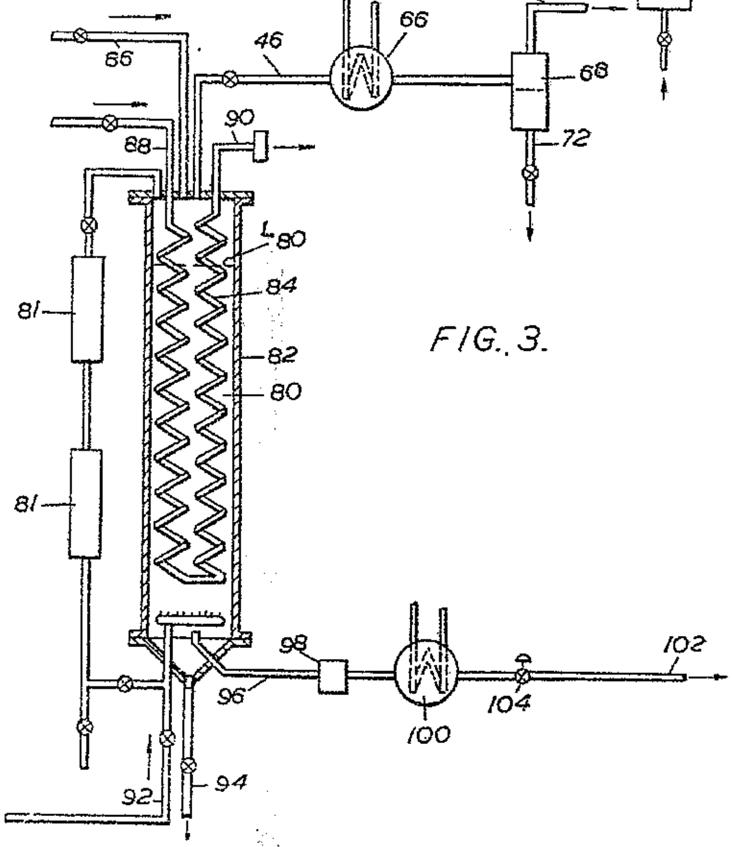
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FIG. 3.

682,177 COMPLETE SPECIFICATION

2 SHEETS *This drawing is a reproduction of the Original on a reduced scale.*

SHEETS 1 & 2

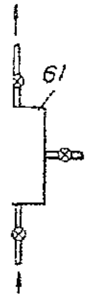
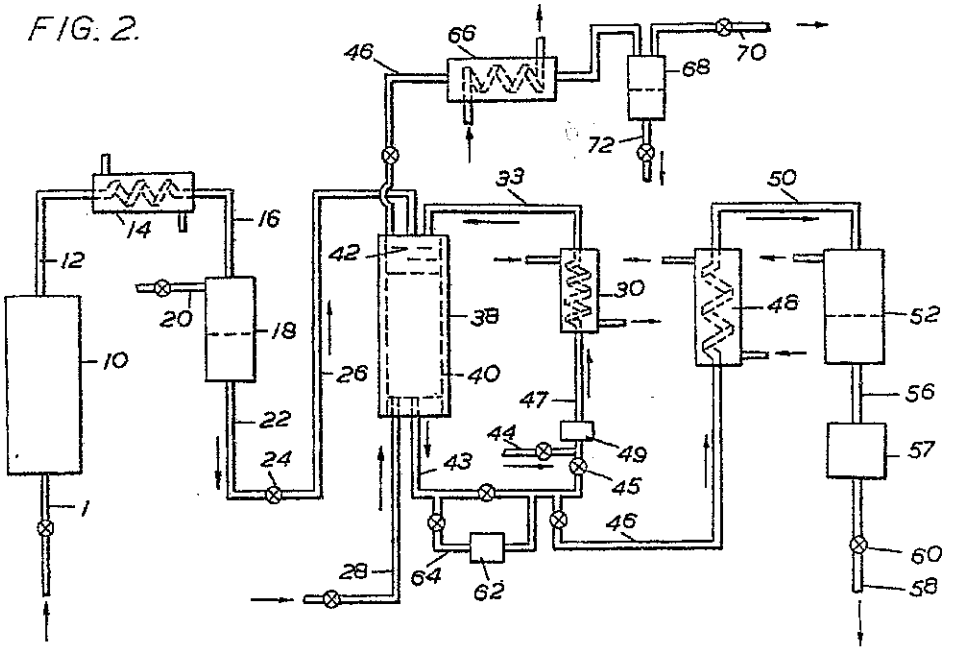
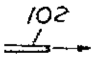


FIG. 2.





682,177 COMPLETE SPECIFICATION
2 SHEETS
This drawing is a reproduction of the Original on a reduced scale.
SHEETS 1 & 2

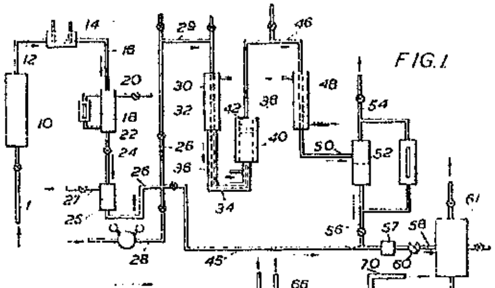


FIG. 1

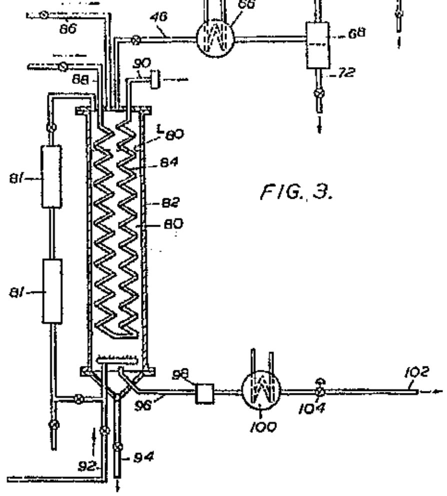


FIG. 3.

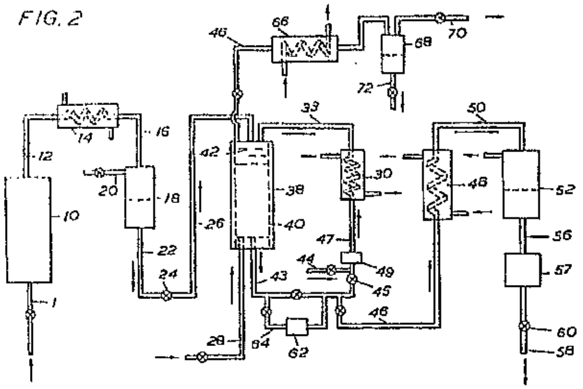


FIG. 2