PATENT SPECIFICATION

Application Date: July 23, 1938. No. 21923/38.
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PROVISIONAL SPECIFICATION
No. 21923 A.D. 1938.

Process for the Manufacture of Water Gas Enriched with Hydrogen

We, THE GAS LIGHT AND COKE COMPANY, a British Company, ALBERT EDWARD HAFFNER, a British Subject, and STUART PEXTON, a British Subject, all of 84, Horseferry Road, Westminster, London S.W.1, do hereby declare the nature of this invention to be as follows:—

This invention relates to the manufacture of blue or carburetted water gas enriched with hydrogen.

The process for the production of water gas consists essentially of the alternate passage of air and steam through burning coke, authracite or similar carbonaceous material. The period during which air is passed through the hot carbonaceous material is known as the blow period and that during which steam is passed is known as the run period. It is during the latter period that water gas consisting principally of carbon monoxide and hydrogen is produced by reaction between the steam and the hot carbonaceous material. In the known processes a substantial proportion, in some cases as much as 50%, of the steam passing into the generator during the run period is not decomposed and passes through with the water gas to be condensed at a later stage in the process.

In accordance with this invention the mixture of water gas and steam leaving the generator is brought into contact with a catalyst for promoting the reaction between carbon monoxide and steam to produce hydrogen and carbon dioxide under such conditions that this reaction takes place so that the proportion of hydrogen in the water gas is increased. Preferably the mixture of steam and water gas leaving the generator is passed into a contact chamber containing the said catalyst before the gas is passed in known manner to the superheater or carburettor. As the reaction between steam and carbon monoxide is an exothermic one, it is not necessary to supply heat to the contact chamber if this is sufficiently lagged, but any heat found to be necessary may be supplied by passing hot blow gases through the contact chamber during the blow period of the process.

Preferably the water gas plant is modified for carrying out the present invention by providing a contact chamber between the generator and superheater or carburettor, if the latter is provided, and means enabling the blow gases to be made to by-pass the contact chamber and pass direct to the superheater or carburettor or pass first through the contact chamber and thence to the superheater or carburettor.

The contact mass or catalyst may consist of spathic iron ore or a mixture of iron and chromium oxides. The latter mixture, in the proportion of 100 parts by weight of iron oxide to 7 parts by weight of chromium oxide has been found to be very effective in catalysing the reaction between steam and carbon monoxide.

The temperature at which the reaction in the contact chamber is carried out is about 450° to 600° C.

If it is found that the amount of undecomposed steam leaving the generator with the water gas is insufficient to provide the requisite amount of additional hydrogen, an additional amount of steam is added to the gas after it has left the generator and before it enters the contact chamber. It will generally be found necessary to provide such an additional amount of steam during the early part of the run period when a large proportion of the steam fed to the generator is decomposed therein.

The process of the invention is useful in the production of water gas for mixing with coal gas in the production of town's gas in view of the desirability of maintaining the specific gravity of town's gas constant within fairly narrow limits. By enriching the water gas with hydrogen by the process of this invention its specific gravity can be reduced to a figure close

[*Price* 1/-]

to that of coal gas and thus as large a proportion of it as is desired can be incorporated in town's gas in accordance with requirements.

Furthermore, the process of the invention can be used for the production of synthesis gas, i.e. a gas containing carbon monoxide and hydrogen in the proportion of 1 part by volume of carbon monoxide to 2 parts by volume of hydrogen for use in the synthetic production of hydrocarbons. In the production of synthesis gas, the gases leaving the contact chamber need not be passed through a superheater or carburettor.

In both the above applications of the invention it is necessary to remove from the enriched water gas the carbon dioxide formed in the process of the invention, and this may be done in any suitable known manner.

Dated this 23rd day of July, 1938.

N. GAVRON,
Agent for the Applicants.

PROVISIONAL SPECIFICATION
No. 34524 A.D. 1938.

Process for Varying the Composition of Water Gas

We, THE GAS LIGHT AND COKE COMPANY, a British Company, ALBERT EDWARD HAFFNER, a British Subject, and STUART PEXTON, a British Subject, all of 84, Horseferry Road, Westminster, London S.W.1, do hereby declare the nature of this invention to be as follows:—

This invention relates to a process for varying the composition of water gas and is primarily concerned with the production of a water gas enriched with hydrogen.

It has been proposed to reduce the proportion of carbon monoxide in water gas by passing the water gas with steam at a temperature of about 500° C. over a catalyst mass which promotes the reaction between carbon monoxide and steam to produce carbon dioxide and hydrogen and which absorbs the carbon dioxide present in the resulting gaseous mixture. The catalyst mass may consist of ankerite or calcium oxide or a mixture of this oxide and other compounds, such as the oxides, hydroxides or carbonates of alkaline metals. In this process the catalyst mass has to be regenerated, i.e. freed from carbon dioxide, and it has been proposed to do this by heating the catalyst mass to 800° C. to 900° C. after each run period of the water gas process with the aid of the blow gases produced during the blow period.

It has now been found that the activity of certain substances which catalyse the reaction between carbon monoxide and steam is adversely affected if heated to a temperature above 600° C., for example, an iron oxide catalyst consisting of a mixture of 100 parts by weight of iron oxide and 7 parts by weight of chromium oxide which, as is mentioned in co-pending Application No. 21923/38, has been found very effective for promoting the reaction between carbon monoxide in water gas and steam loses its activity rapidly if subjected to a regeneration treatment by heating above 600° C. It is an object of the invention to eliminate this disadvantage.

In accordance with this invention the reaction between carbon monoxide in water gas and steam is caused to take place in the presence of a catalyst mass for promoting this reaction which does not absorb carbon dioxide and the carbon dioxide is subsequently removed by bringing the gas into contact with a substance which absorbs the carbon dioxide, the latter substance being regenerated at intervals by heating. Substances which may be used for absorbing carbon dioxide are magnesium oxide or a natural source thereof or alkaline earth oxides or mixtures of magnesium oxide and alkaline earth oxides. The heat generated during the absorption of carbon dioxide may be utilised for raising steam or superheating, by direct contact, the steam required for water gas production.

In carrying out the invention the water gas produced during the run period is passed with or without additional steam through a catalyst chamber containing, for example, an iron oxide catalyst and then through an absorption chamber containing, for example, magnesium oxide. During the blow period part or all of the blow gases are passed through the absorption chamber to regenerate the absorption mass by freeing it from carbon dioxide. The blow gases are burnt and heat the absorbing material to a temperature of 600 to 800° C. The waste blow gases then pass through waste heat boilers to the stack. The absorption material is now again ready for the removal of carbon dioxide.

As the reaction between steam and

carbon monoxide is an exothermic one, it is not necessary to supply heat to the contact chamber if this is sufficiently lagged but any heat found to be necessary may be supplied by the blow gases of the process.

If it is desired to carburet the water gas, a portion of the run gases can take their normal course through the carburettor and the enrichment with hydrogen would then be confined to the uncarburetted water gas or alternatively the hydrogen-enriched gases leaving the absorption chamber may be passed back to the carburettor whereby the whole of the up-run gases are carburetted.

Where a battery of carburetted water gas plants is in operation some of the plants could be operated normally for making a gas of high calorific value while the remaining plants can be operated to produce hydrogen-enriched blue water gas.

In the back-run water gas process, two sets of catalyst chambers and absorption chambers may be provided, one set for the up-run period and the other set for the back-run period.

The process of the invention is useful for the production of water gas for mixing with coal gas in the production of town's gas in view of the desirability of maintaining the specific gravity of town's gas constant within fairly narrow limits. By enriching the water gas with hydrogen by the process of this invention its specific gravity can be reduced to a figure close to that of coal gas and thus as large a proportion of it as is desired can be incorporated in town's gas in accordance with requirements.

Furthermore, the process of the invention can be used for the production of synthesis gas, i.e. a gas containing carbon monoxide and hydrogen in the proportion of 1 part by volume of carbon monoxide to 2 parts by volume of hydrogen for use in the synthetic production of hydrocarbons.

Dated this 26th day of November, 1938.

N. GAVRON,
Agent for the Applicants.

COMPLETE SPECIFICATION

Process for the Manufacture of Water Gas Enriched with Hydrogen

We, THE GAS LIGHT AND COKE COMPANY, a British Company, ALBERT EDWARD HAFFNER, a British Subject, and STUART PEXTON, a British Subject, all of 84, Horseferry Road, Westminster, London S.W.1, 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:—

This invention relates to the manufacture of blue or carburetted water gas enriched with hydrogen.

The process for the production of water gas consists essentially of the alternate passage of air and steam through burning coke, anthracite or similar carbonaceous material. The period during which air is passed through the hot carbonaceous material is known as the blow period and that during which steam is passed is known as the run period. It is during the latter period that water gas, consisting principally of carbon monoxide and hydrogen, is produced by reaction between the steam and the hot carbonaceous material. In the known processes a substantial proportion, in some cases as much as 50%, of the steam passing into the generator during the run period is not decomposed and passes through with the water gas to be condensed at a later stage in the process.

In accordance with this invention the mixture of water gas and steam leaving the generator is brought without previous cooling or purification and with or without additional steam into contact with an iron oxide catalyst for promoting the reaction between carbon monoxide and steam to produce hydrogen and carbon dioxide, at a temperature between 450° and 600° C. so that this reaction takes place and the proportion of hydrogen in the water gas is increased, the carbon dioxide formed being subsequently removed from the gases after they have left the catalyst by bringing them into contact with a solid absorbent for the carbon dioxide.

The said catalyst preferably consists of iron oxide mixed with chromium oxide and particularly in the proportion of 100 parts by weight of iron oxide to 7 parts by weight of chromium oxide which has been found very effective for promoting the reaction between carbon monoxide and steam.

The gases leaving the catalyst are preferably not subjected to any cooling or purification before being brought into contact with the solid absorbent for the carbon dioxide. This solid absorbent may consist of magnesium oxide or a natural

source thereof or an alkaline earth oxide or a mixture of magnesium oxide and alkaline earth oxides.

If it is found that the amount of undecomposed steam leaving the generator with the water gas is insufficient to provide the requisite amount of additional hydrogen, an additional amount of steam is added to the gas after it has left the generator and before it enters the contact chamber. It will generally be found necessary to provide such an additional amount of steam during at least the early part of the run period when a large proportion of the steam fed to the generator is decomposed therein.

The regeneration of the carbon dioxide absorbent may take place during the blow period by heating it to about 800° C. by means of the blow gases.

As the reaction between steam and carbon monoxide is an exothermic one it is not necessary to supply heat to the contact chamber if this is sufficiently lagged but any heat found to be necessary may be supplied by the blow gases of the process.

In a preferred process for the production of enriched water gas in accordance with this invention wherein a generator and superheater are employed in known manner, the water gas together with steam is first brought into contact with the catalyst and then with the carbon dioxide absorbing material before being passed to the superheater. If it is desired to carburet the water gas, the gases are preferably brought into contact with the catalyst and then with the carbon dioxide absorbing material before being passed to the carburettor. Alternatively, only part of the gases which is not enriched with hydrogen may be carburetted and the other part which is enriched with hydrogen mixed with the carburetted gases at a later stage. Where a battery of carburetted water gas plants is in operation some of the plants may be operated normally for making a carburetted gas of high calorific value while the remaining plants may be operated to produce hydrogen-enriched blue water gas.

The invention will now be described by way of example as applied to the production of carburetted water gas by the down run process and by the back run process, reference being made to the accompanying drawing, in which,

Figure 1 illustrates diagrammatically apparatus for the production of carburetted water gas in accordance with the invention by the down run process, and

Figure 2 illustrates diagrammatically apparatus for the production of carburetted water gas in accordance with the invention by the back run process.

Referring to Figure 1, a down run set of the usual type consists of a generator 1, carburettor 2, superheater 3, liquid seal 4, and waste heat boiler 5. Steam inlets 7 and 8 controlled by valves 9 and 10 and air inlets 11 and 12 controlled by valves 13 and 14 are provided. Valves 15 and 16 and a stack valve 17 are also provided.

In order to adapt the set for carrying out the process of the invention there are provided a contact chamber 18 containing the catalyst consisting of 100 parts by weight of iron oxide and 7 parts by weight of chromium oxide, an absorption chamber 19 containing the carbon dioxide absorbing material, e.g. magnesium oxide, and a steam superheater 20 together with a steam inlet 21, and its valve 22 and an air inlet 23 with its valve 24. A valve 25 is provided in the pipe 26 leading to the contact chamber 18 and valves 27 and 28 are provided in the connections between the steam superheater 20 and the absorption chamber 19 and carburettor 2 respectively. Valves 29 and 30 are provided in the connections between the chamber 19 and the carburettor 2 and superheater 3 respectively.

In carrying out the process the sequence of operations is as follows:—

During the first part of the blow period valve 13 is opened admitting air to the generator 1 which contains a deep bed of burning coke and valves 14, 15, 24, 27, 29 and 17 are also opened. All the other valves are closed. The blow gases produced are burnt in steam superheater 20 and chamber 19 in order to heat up the steam superheater 20 and the material in chamber 19 to about 800° C. The material in chamber 19 is thus freed from carbon dioxide. The blow gases also serve to heat the carburettor 2 and superheater 3 in the usual manner.

During the second part of the blow period the valves 28 and 30 are opened and the valves 27 and 29 are closed, the remaining valves being left as in the first part of this period. During this second part of the blow period the vessel 19 is cooled to about 500° C. by the air entering through valve 24 to bring the material therein to a temperature suitable for the subsequent absorption of carbon dioxide in the following run period.

The run period, during which steam is passed upwardly, downwardly and then upwardly through the generator, is now commenced.

Valves 7, 15, 25, 22 and 29 are opened and the remaining valves closed. Steam enters the generator 1 through the valve

7 and passes up through the bed of red hot coke. The water gas produced and the undecomposed steam, which will generally be at a temperature of 500°—600° C. is passed into the chamber 18. The resulting gases are passed into the chamber 19 wherein the carbon dioxide is absorbed and the remaining gases then pass through carburettor 2, superheater 3 and liquid seal 4 to the purifiers. At the end of this up-run stage the down run is commenced and valves 7 and 15 are closed and valves 8 and 16 are opened. Steam now passes downwardly through the generator 1 and the water gas produced, together with the undecomposed steam as before, passes to the contact chamber 18 through the valve 16, pipe 26 and valve 25. The passage of steam upwardly through the generator is then repeated and this is followed by a blow period. During the whole of the run period the temperature within the chamber 18 and vessel 19 is kept between 450° and 600° C. Any additional steam required for the reaction in chamber 18 is admitted through the valve 22 to the heater 20 in which it is heated to 500°—600° C. and thence through connections 31 and 26 and valve 25 to the chamber 18.

Referring to Figure 2, a back-run set of normal construction consists of a generator 41, carburettor 42, superheater 43, liquid seal 44 and waste heat boiler 45. Steam inlets 46 and 47 controlled by valves 48 and 49 and air inlets 50 and 51 controlled by valves 52 and 53 are provided. Valves 54 and 55 and a stack valve 56 are also provided. For the purpose of the present invention there is provided in addition a contact chamber 57 for the catalyst, an absorption chamber 58 for the carbon dioxide absorbing material, a steam superheater 59, a steam inlet 61 and its valve 62 and an air inlet 63 and its valve 64. A valve 65 is provided in the pipe 66 between the generator and the contact chamber 57 and valves 67 and 68 are provided in the connections between the steam superheater 59 and the vessel 58 and carburettor 42 respectively. Valves 69 and 70 are provided in the connections between the vessel 58 and the carburettor 42 and the liquid seal 44 respectively. An additional steam inlet 71 and valve 72 are also provided.

In carrying out the process the sequence of operations is as follows:—

During the first part of the blow period valves 52, 64, 51, 67, 69, 54 and 56 are opened and all the other valves are closed. The blow gases from the generator 41 are burnt in the steam superheater 59 and absorption chamber 58, whence they pass through the carburettor 42, superheater 43 and finally through the waste heat boiler 45 and valve 56. During this part of the blow period the material in chamber 58 is heated to about 800° C. and thus regenerated, i.e. freed from carbon dioxide. During the second part of the blow period valves 67 and 69 are closed and valves 68 and 70 are opened, the remaining valves being left as in the first part. During this second part of the blow period the material in chamber 58 is cooled to about 500° C. by the passage of air through the chamber in order to render the material suitable for the subsequent absorption of carbon dioxide during the following run period.

At the end of the blow period the run period, during which steam is passed upwardly, downwardly and then upwardly through the generator, is commenced.

Valves 48, 65, 62, 69 and 54 are opened and all other valves closed. Steam is now admitted to the generator 41 through the valve 48 and passes upwardly through the bed of red hot coke. The water gas produced together with undecomposed steam is passed at a temperature of 500°—600° C. through valve 65 into the contact chamber 57 wherein the reaction between carbon monoxide and steam takes place, thence to the absorption chamber 58 wherein carbon dioxide is absorbed and then through the carburettor 42 and superheater 43 in the usual manner. Any additional steam required for the carbon monoxide-steam reaction in chamber 57 is admitted through the valve 62 to the heater 59 in which it is heated to 500°—600° C. and thence through 73 to the top of the generator where it mixes with the water gas and undecomposed steam passing to the chamber 57.

At the end of this up-run the back-run, in which steam is passed downwardly through the generator, is commenced.

Valves 49, 68, 55, 72 and 70 are opened and all the other valves closed. Steam is admitted through valve 49, passes through superheater 43, carburettor 42, heater 59 and then downwardly through the generator 41. The water gas produced, together with undecomposed steam passes from the bottom of the generator through valve 55 into the chamber 57, the gases from which pass through the absorption chamber 58 and thence via valve 70 and the liquid seal 44 to the purifiers. Any additional steam required for the carbon monoxide and steam reaction in chamber 57 is supplied at a temperature of 500°—600° C. through the inlet 71 and valve 72. At the end of this stage a further up-run follows and this in turn is followed by a blow period.

The production of blue water gas in

accordance with the invention may be carried out by a process similar to either of those described above for the production of carburetted water gas except that the carburettor is omitted.

The process of the invention is useful in the production of water gas for mixing with coal-gas in the production of town's gas in view of the desirability of maintaining the specific gravity of town's gas constant within fairly narrow limits. By enriching the water gas with hydrogen by the process of this invention its specific gravity can be reduced to a figure close to that of coal gas and thus as large a proportion of it as is desired can be incorporated in town's gas in accordance with requirements.

Furthermore, the process of the invention can be used for the production of synthesis gas, i.e. a gas containing carbon monoxide and hydrogen in the proportion of 1 part by volume of carbon monoxide to 2 parts by volume of hydrogen for use in the synthetic production of hydrocarbons. In the production of synthesis gas, the gases leaving the contact chamber need not be passed through a superheater or carburettor.

In Patent Specification No. 195,798 there is described a process for the production of hydrogen or gases rich in hydrogen which consists in effecting the complete gasification of coal by means of an intermittent mixed gas generator, taking off from the generator the hot mixture of gases resulting from the complete gasification, which consists largely of hydrogen and carbon monoxide with some carbon dioxide, and subjecting the said mixture of gases whilst still in the heated condition and without any intermediate cooling to treatment with steam in the presence of a catalyst in a carbon monoxide converter so as to effect replacement of the carbon monoxide in the gases by carbon dioxide and hydrogen. No particular catalyst is referred to in this prior specification and the method described for the removal of carbon dioxide consists in washing the gas in an absorption tower or towers with water, preferably under pressure, and with or without the addition of lime water, ammonia or the like.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the production of water gas enriched with hydrogen in which the mixture of water gas and steam leaving the generator is brought without previous cooling or purification and with or without additional steam into contact with an iron oxide catalyst for promoting the reaction between carbon monoxide and steam to produce hydrogen and carbon dioxide, at a temperature between 450° and 600° C. so that this reaction takes place and the proportion of hydrogen in the water gas is increased, the carbon dioxide formed being subsequently removed from the gases after they have left the catalyst by bringing them into contact with a solid absorbent for the carbon dioxide.

2. A process as claimed in Claim 1 wherein the said catalyst comprises a mixture of iron and chromium oxides.

3. A process as claimed in Claim 2 wherein the said catalyst comprises iron oxide and chromium oxide in the proportion of 100 parts by weight of iron oxide to 7 parts by weight of chromium oxide.

4. A process as claimed in any of the preceding claims wherein the gases are not subjected to any cooling or purification during their passage from the iron oxide catalyst to the solid absorbent for the carbon dioxide.

5. A process as claimed in Claim 4 wherein the said solid absorbent consists of magnesium oxide.

6. A process for the production of blue water gas as claimed in any of the preceding claims in which a generator and superheater are employed in known manner and in which the water gas, together with steam, is first brought into contact with the said catalyst and then with the said carbon dioxide absorbing material before being passed to the superheater.

7. A process for the production of carburetted water gas in accordance with any of Claims 1 to 5 in which a generator, carburettor and superheater are employed in known manner and in which the water gas, together with steam, leaving the generator is first brought into contact with the said catalyst and then with the said carbon dioxide absorbing material before being passed to the carburettor.

8. A process as claimed in any of the preceding claims wherein additional steam is added to the mixture of water gas and steam from the generator before it comes into contact with the catalyst and this additional steam is superheated to a temperature between 450° and 600° C. by being passed through a superheater which is heated during the blow period by burning the blow gases therein.

9. A process as claimed in any of the preceding claims wherein the regeneration of the carbon dioxide absorbing material is carried out by heating it to about 800° C. by means of burning blow gases during

the blow period of the water gas process.

10. A process as claimed in Claim 9 wherein the regeneration of the carbon dioxide absorbing material takes place during the first part of the said blow period and the said material is cooled to about 500° C. by the passage of air therethrough during the second part of the blow period.

11. A process for the production of water gas enriched with hydrogen substantially as hereinbefore described.

12. Apparatus for carrying out the process claimed in any of the preceding claims comprising a generator, a superheater, a contact chamber for the said catalyst and an absorption chamber for the said solid absorbent, the contact chamber and absorption chamber being connected between the generator and superheater in such a manner that gases leaving the generator may be passed first through the contact chamber, then through the absorption chamber and thence to the superheater.

13. Apparatus for carrying out the process claimed in any of the preceding claims comprising a generator, a carburettor, a contact chamber for the said catalyst and an absorption chamber for the said solid absorbent, the contact chamber and absorption chamber being connected between the generator and carburettor in such a manner that gases leaving the generator may be passed first through the contact chamber, then through the absorption chamber and thence to the carburettor.

14. Apparatus for the production of water gas enriched with hydrogen arranged and adapted to operate substantially as hereinbefore described with reference to Figure 1 or Figure 2 of the accompanying drawing.

Dated this 11th day of August, 1939.
N. GAVRON,
Agent for the Applicants.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1940.

[This Drawing is a reproduction of the Original on a reduced scale.]

Fig. 1.

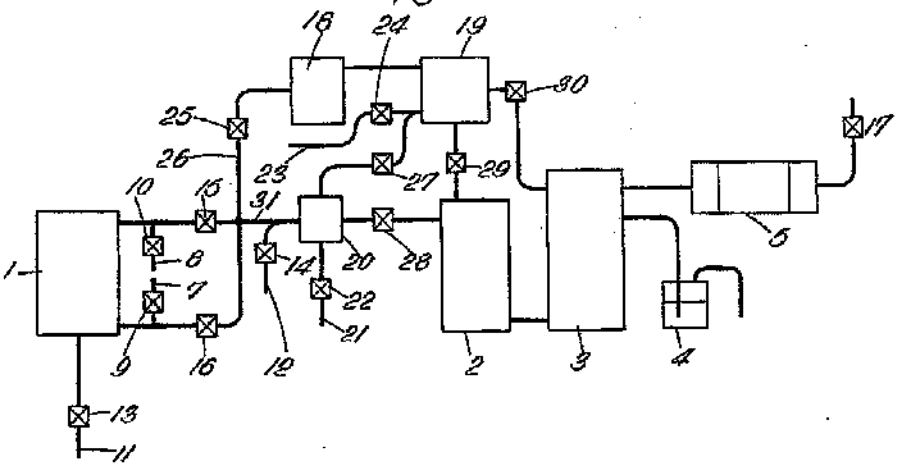
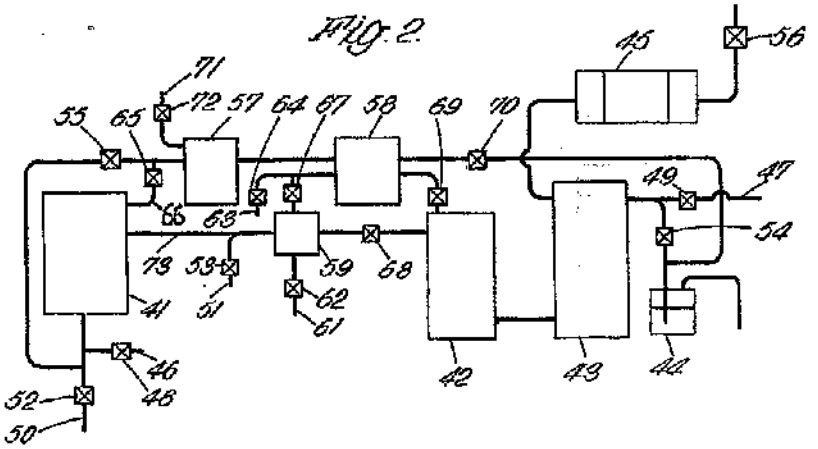


Fig. 2.



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