G. CLAUDE.

PROCESS OF LIQUEFYING GASES.

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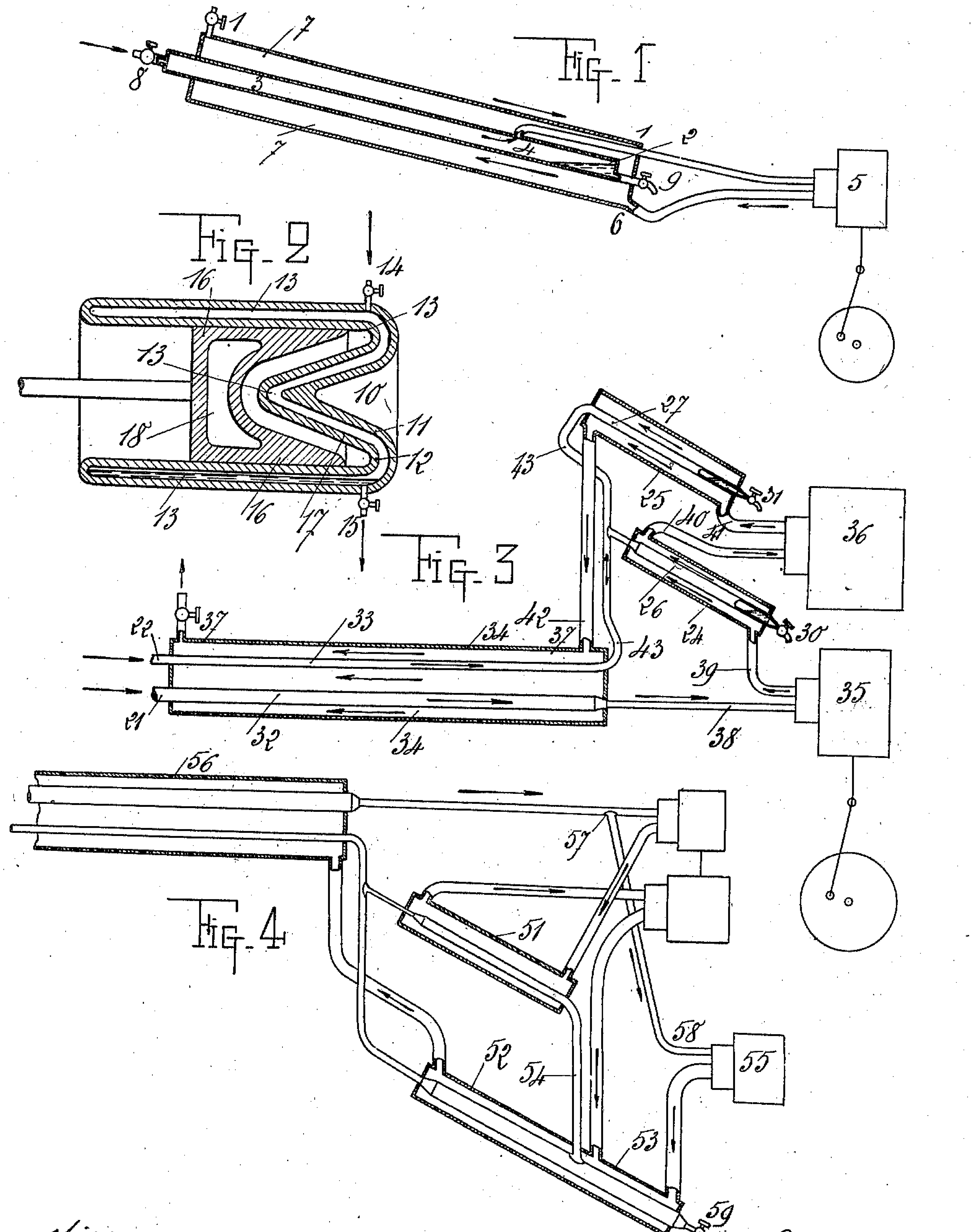
967,104. Patented Aug. 9, 1910.



Witnesses
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UNITED STATES PATENT OFFICE.

GEORGES CLAUDE, OF PARIS, FRANCE, ASSIGNOR TO SOCIETE L'AIR LIQUIDE (SOCIETE ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE), OF PARIS, FRANCE.

PROCESS OF LIQUEFYING GASES.

967,104. Specification of Letters Patent. Patented Aug. 9, 1910.

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To all whom it may concern:

Be it known that I, Georges Claude, a citizen of the French Republic, residing at Paris, France, have invented certain new and useful Improvements in Processes of Liquefying Gases, of which the following is a full, clear, and exact description.

The present invention relates to the liquefaction of gases by expansion accompanied by the production of external work, and it has for its object improvements whereby I am enabled to increase the yields of liquefied gas and of recovered work.

The apparatus for carrying out the present invention is shown in the accompanying drawings, and wherein;

Figure 1 is a sectional elevation of the apparatus constructed according to my invention. Fig. 2 is a detail sectional view. Fig. 3 is a sectional elevation of a modified form of apparatus, and Fig. 4 is a similar view of a still further modified form.

To well understand my improved process and apparatus it is necessary to observe that in apparatus hitherto used for the liquefaction of gases by means of the cold produced by the expansion of gases while doing external work and of the accumulation of the cold produced in a counter-current apparatus on the Siemens principle, the liquefaction is generally performed in two separate parts; a portion is liquefied in the expanded gas itself as a consequence of the fall of temperature accompanying the expansion; the other portion is liquefied in the compressed gas cooled by the gaseous residue of the expansion, under the influence of the pressure of this compressed gas. The first liquefaction taking place at a low pressure and consequently at a very low temperature, it requires the various parts of the expansion motor to come down to this low temperature. The second liquefaction taking place in the compressed gas could be effected at a higher temperature than the very low temperature necessary in the expansion motor. If this second liquefaction alone were used, the temperature reached in the expansion and utilized to effect the liquefaction could also be higher than the temperature necessary when liquefaction takes place in the motor.

As it is known that the less low the temperature at which the expansion with external work takes place, the better is the mechanical and frigorific yield it follows that it would be advantageous to perform the whole of the liquefaction in the compressed gas. I have realized this advantage according to my invention in the apparatus shown by way of example by Fig. 1.

In the following description the letters P P′ and O O_1 O_2 O_3 signify certain pressures and temperatures respectively, the precise values of which will appear later.

The gas enters at 8 under pressure P and at temperature O into the pipe 3 of the exchanger 7. The portion of the gas to be expanded is taken at some distance from the cold end of the exchanger, at 4, for instance, it is led to the expansion motor 5 and is returned in 6, cooled by the expansion; it travels in the second compartment 7 of the exchanger of temperature, in opposite direction to the compressed gas. The portion of the gas under pressure, not taken out at 4, and already cooled by its passage in the exchanger, is then submitted in the part 2—4, (a kind of blind end in which there is no circulation), to the cold expanded gas coming directly from the expansion cylinder at 6. In this compartment under its high initial pressure, it becomes liquefied. This liquefaction causes a progressive reheating of the expanded gas along the space 2—4. If the liquefier is long enough and if the exchanging surfaces are sufficient the escaping gas arriving at the part 4 will have reached the temperature of liquefaction which I will call O_2 corresponding to the pressure P. Under these conditions all the cold produced has been utilized and the whole of the liquefaction has taken place under a high pressure and consequently, as I have explained, in the best condition for a high yield, as it is no more necessary to go to so low a temperature as when the liquefaction takes place at the low pressure existing after the expansion. At the same time by this process there has been no liquefaction in the motor, and inconvenience resulting from the presence of liquid in the motor is avoided. The liquefied gas is extracted through cock 9. But it follows moreover from this method of working that in practice there is an essential difference in the method in which liquefaction takes place in the expansion motor. Whereas in the last case the lubrication is automatically assured by the presence of the liquefied gas itself formed in the expansion apparatus, on the contrary in the other case it is necessary to provide a constant lubrication. For this purpose suitable lubricating substances had to be found that could be used at these low temperatures. I use for this purpose the light ethers of Russian or American petroleums, called also gasolenes, etc., and the use of the petroleum oils themselves and of analogous hydrocarbons; the more volatile products being used for the lowest temperatures. My trials have proved that these substances are perfectly suitable to be used as lubricants at very low temperatures and their use as such was not known until my researches. The light hydrocarbons, mixed if necessary and in suitable ratios, especially when starting with petroleum or vaselines less difficult to solidify, are introduced inside the expansion motors by the well known means in use for introducing lubricating agents in the cylinders of steam or compressed air engines.

In the particular case, when the gas treated is air and when its liquefaction has for its object to economically extract its oxygen, this method has the further advantage of yielding a liquid richer in oxygen than air. If the degree of pressure P to which the air is compressed before entering the expansion motor is near the critical pressure of the air, the temperature O_2 to which it must be reduced by the cooling action of the exhaust air from the expansion motor must be near the critical temperature in order to effect the liquefaction of the said compressed air. Hence to effect this liquefaction, the exhaust air from the expansion motor must be below the critical temperature of the air, since otherwise the exchange of temperatures between the compressed air and the expanded air would not result in a reducing of the temperature of the compressed air to the requisite degree. Since the exhaust air is under a far less pressure than the critical pressure, it is of course possible to operate the expansion motor so as to expand the air to an extent sufficient to lower its temperature below the critical temperature without involving any liquefaction of the air in the motor itself; in other words according to this invention the air must be expanded sufficiently to reduce its temperature below the critical temperature but not to the temperature at which it will in its expanded condition liquefy.

It is advantageous to carry out the process with the compressed air compressed near to its critical pressure, because the heat of liquefaction of a gas under a pressure near to its critical pressure is very small, practically *nil*, and hence a comparatively small extraction of heat from such compressed gas will result in the production of a considerable quantity of liquefied gas. The carrying out of the process with the compressed air compressed to a degree near to its critical pressure involves of course the expanded air employed to cool it being reduced to a temperature below the critical temperature. In order, however, to avoid the formation of any liquid in the expansion motor, the degree of expansion resorted to, although it must be sufficient to bring the temperature of the expanded air below the critical temperature, must not, as above stated, be sufficient to bring it to the temperature at which the expanded air would liquefy. When the liquefied air is withdrawn from the apparatus and brought from approximately its critical pressure to atmospheric pressure, a great amount of it will be vaporized and the remaining liquid will be rich in oxygen. The gaseous mixtures rich in nitrogen will be collected and sent to the exchangers of temperatures and reheated to utilize their cold. But the process I have just described for liquefying gases under a high pressure is not sufficient to obtain a very good result, if, as it is advantageous to do in practice, a considerable degree of expansion is resorted to. Also since according to this invention no liquefaction occurs in the expansion motor, all the cold produced in this motor results in a fall of temperature of the expanded gas which brings down the final temperature of this gas to a temperature say O_1 much inferior, if the expansion is great, to the liquefaction temperature O_2 of the compressed gas under the pressure P. It is naturally necessary that it should be so, since the quantity of gas liquefied by this method will be produced by the reheating of the expanded gas from the temperature O_1 up to the temperature O_2 and consequently will be so much the greater, the greater is the difference between the temperatures O_1 and O_2. But since the higher the temperature at which the expansion takes place, the better is the frigorific yield, and since the liquefaction of the gas under pressure can take place as soon as the temperature of the expanded gas is slightly below the temperature O_2, it would be advantageous to make use of this circumstance by effecting the whole of the expansion at a temperature near O_2. To obtain this result the conditions of the expansion must be modified, since we have seen that in performing the expansion in a single stage the temperature of the expanded gas is reduced notably lower than the temperature O_2.

To obtain the necessary conditions, according to my invention instead of producing by the expansion a great fall of temperature from the temperature O to the temperature O_1 and utilizing afterward in a single operation this fall of temperature to liquefy the gas under the pressure P, I effect by means of a series of successive expansions, slight falls of temperature from the temperature O to a temperature O_3 only slightly lower than the temperature O_2; each of these expansions is utilized to produce the liquefaction of a portion of the compressed gas at the pressure P. Each expansion will thus correspond to a slight fall of temperature from the temperature O to the temperature O_3 followed by a reheating up to the temperature O_2 with a simultaneous liquefaction of some of the compressed gas under the pressure P. Under these conditions the work of the motor or motors will take place at temperatures whose lowest limit of temperature is O_3, which is nearer to the temperature O_2 than the temperature O_1 is, and is therefore much less low than in the case of a single expansion followed by a single reheating, the result being that the mechanical and frigorific yield of the machine is notably increased. A practical way to realize this principle is to use, for instance, a series of expansion motors in which the gas will be submitted successively, by its expansion, to progressive falls of pressure. The gas will be obliged in its passage from one motor to the next to go through one of the two compartments of a liquefier. This liquefier will be, for instance, similar to a surface condenser, one of its compartments being occupied by the gas to be liquefied, this gas being as I have explained under the highest possible pressure and without circulation, but only renewed by the influence of this pressure. In its passage through the liquefier, the expanded gas will be reheated up to about the temperature O_2 of liquefaction of the gas under the pressure P and consequently it will go to the following motor less cool and capable of undergoing expansion under better conditions.

It may be advantageous in practice to use as successive expansion organs, the cylinders of increasing dimensions of a machine which will present much analogy with the compound engines or turbines commonly used as steam engines, each of the cylinders or expansion chambers being connected to the next by means of a temperature exchanger or liquefier, in which the gas will circulate as I have explained above. After its passage in the last expansion organ and in the last liquefier, the gas completely expanded, brought back to the temperature O_2 will be led to the temperatures-exchanger after having liquefied all the gas under pressure that could be liquefied. It will travel in this exchanger in an opposite direction to the compressed gas so as to yield to the latter the totality of its cold and come out of the exchanger at a temperature as near as possible to the temperature of the compressed gas coming to the exchanger. In every case the compressed gas to be liquefied may be sent directly to the liquefier. But generally, it will be preferable to also pass this gas in the exchanger of temperature and in opposite direction to the expanded gas. It will thus enter the liquefier or liquefiers, as cold as possible. If the pressure used in the liquefier is only equal to the pressure of admission of the gas to be expanded, this result can be easily obtained in taking the supply for the liquefier or liquefiers from the pipe of the compressed and cooled gas before its entrance into the first expansion organ. If on the contrary it is advisable to raise the pressure of liquefaction over the pressure of admission of the gas to be expanded, a special compartment can be kept in the exchanger for the highly compressed gas. This arrangement is illustrated by way of example in Fig. 3. In this figure, 32 and 33 represent two inner compartments of an exchanger 37; 32 is kept for the gas to be expanded, which entering at 21, under pressure and dry, passes directly, after being cooled, to the first expansion cylinder 35 of a machine, which I have supposed, by way of example, to have two expansion cylinders. The compartment 33 receives in 22 the highly compressed gas to be liquefied, and which after being cooled passes by 43 into the compartments 26 and 27 of the liquefiers 24 and 25 in which it is liquefied. It is drawn off in the liquid state by the cocks 30 and 31. The vapor formed during the drawing off of the liquefied gas and its exposure to atmospheric pressure may be collected and added to the exhaust gas from the last expansion cylinder to give up its cold in the liquefier 25 and in the exchanger 37. The compressed gas comes as I have said, by 38 to the first expansion cylinder 35 in which it is partially expanded, becoming colder. It then passes by 41 to the second liquefier 25 and flows by 42 into the compartment 34 of the exchanger 37. I have also found means to realize the advantages of the expansion at a less low temperature, in the case of a single expansion of the compressed gas. This means consists in utilizing the cold as it is produced, during the expansion itself, to liquefy the gas under pressure. This last method is theoretically the best as the expansion is then isothermic, taking place at the theoretical temperature of liquefaction O_2. To realize this in practice, the surfaces of contact between the gas under pressure and the gas to be liquefied must be developed as much as possible, the gas under pressure surrounding the expansion chamber or being surrounded by it. Fig. 2 gives an illustration of this method. In this figure the horizontal expansion cylinder 10 has a double wall 11—12 forming a chamber 13. The surfaces of contact between the compressed gas and the gas being expanded is further increased as much as possible by ending the piston face 18 over which the expansion takes place, for instance, by a hollow cone and in giving to the wall of the expansion chamber a corresponding shape.

It is understood, that in all apparatus herein described, all the cold parts are carefully surrounded with non-conducting material, to reduce the reheating by the surrounding air. It is also understood that all the expansion organs, are lubricated, when necessary, in a constant manner, by means of petroleum ether, or analogous substances. When the gas liquefied under pressure, more or less near to its critical pressure, is brought under a lower pressure, there is naturally an abundant boiling, the main cause of cooling the liquid to its normal temperature under this lower pressure, being in this case the small amount of work done by the vaporized gas against the pressure in the receptacle where it is received. I have found a process to diminish this vaporization, when it is objectionable. It consists in cooling the liquefied gas before drawing it off, down to a temperature near to the normal temperature of the liquefied gas, under the pressure at which it is drawn off. This supercooling can be realized to a certain extent, simply by increasing the length of the liquefiers. This will allow the liquid formed in the front part of the liquefiers to remain in contact with the exhaust gas supplied to the liquefier, for a certain time, until it reaches the extractor and before any reheating of the exhaust gas. In this way advantage is taken for the cooling of the liquid of a portion of the necessary difference of temperature between the liquefaction temperature O_2 and the temperature O_3 of each partial expansion. But in this particular case, as the very principle of my process consists in diminishing as much as possible this difference, it is preferable to make use of another supply of cold and to use for cooling the liquid the exhaust gas of a special expansion motor. This motor will be supplied by a portion of the compressed gas to be expanded, but the expansion in it will be complete instead of only partial. A great fall of temperature will thus be produced; therefore, a final temperature much lower than O_3. After having cooled the liquid, which can then be drawn off without any great vaporization, the exhaust gas coming from this machine will finish its course together with the gas coming from the other machines. Fig. 4 shows by way of example the application of this method to the cooling of the liquid air formed in the liquefiers 51 and 52, according to the present description; the air liquefied in the liquefier 51 passes by the pipe 54 into the inner compartment of the liquefier 52 and together with the air liquefied in this compartment passes to the lower end thereof where it is further cooled by the exhaust air from the motor 55. This air after having played its part in cooling the liquid passes in 52 along with the exhaust air from the last expansion cylinder of the compound expansion engine already described, and after being utilized in this last liquefier 52 it passes to the main exchanger 56. As regards the motor 55, it is supplied by a branch 57—58, of the compressed and cool air to be expanded, but this air undergoes in 55 a complete and not a partial expansion. The liquid air, very cold, is extracted by a cock 59.

What I claim is:

1. The process of liquefying gas which consists in cooling and compressing the gas near to its critical pressure, expanding some of said compressed and cooled gas with production of external recoverable work sufficiently to reduce its temperature below its critical temperature but not down to its liquefaction temperature, causing this expanded gas to be partially reheated by liquefying some of the gas cooled and compressed near to its critical pressure, and finally causing this expanded and partially reheated gas to cool the compressed gas to be expanded and to be liquefied by circulating in the opposite direction to it.

2. The process of liquefying gas which consists in cooling and compressing the gas near to its critical pressure, partially expanding some of said compressed and cooled gas with production of external recoverable work sufficiently to reduce its temperature below its critical temperature but not down to its liquefaction temperature, causing this partially expanded gas to be partially reheated by liquefying some of its gas, cooled and compressed near to its critical pressure submitting this partially reheated gas to a further and complete expansion with production of external recoverable work which again reduces its temperature below its critical temperature but not down to its liquefaction temperature, reheating this completely expanded gas firstly by liquefying a further quantity of the gas cooled and compressed near to its critical pressure and finally by cooling the gas to be compressed and the gas to be expanded by circulating in the opposite direction to the latter.

3. The process of liquefying air which consists in cooling and compressing the air near to its critical pressure, partially expanding some of said compressed and cooled air in a motor doing external work sufficiently to reduce its temperature below its critical temperature but not down to its liquefaction temperature, causing this partially expanded air to be partially reheated by liquefying some of the air, cooled and compressed near to its critical pressure submitting this

partially reheated air to a further and complete expansion in a motor doing external work which again reduces its temperature below its critical temperature but not down to its liquefaction temperature, reheating this completely expanded air firstly by liquefying a further quantity of air cooled and compressed near to its critical pressure and finally by cooling the air to be compressed and the air to be expanded by circulating in the opposite direction to the latter.

4. The process of liquefying a gas which consists in cooling and compressing the gas near to its critical pressure compressing another gas, cooling it, expanding said compressed and cooled gas with production of external recoverable work sufficiently to reduce its temperature below the critical temperature of the gas intended to be liquefied but not down to its own liquefaction temperature, causing this expanded gas to be partially reheated by liquefying the gas intended to be liquefied and previously compressed and cooled, and finally causing the expanded and partially reheated gas to cool the gas to be expanded and the gas to be liquefied by circulating in the opposite direction to them.

5. The process of liquefying a gas which consists in cooling and compressing the gas near to its critical pressure compressing another gas, cooling it, partially expanding said compressed and cooled gas with production of external recoverable work sufficiently to reduce its temperature below the critical temperature of the gas intended to be liquefied but not down to its own liquefaction temperature, causing this partially expanded gas to be partially reheated by liquefying a portion of the gas intended to be liquefied and previously compressed and cooled, submitting the partially reheated gas to a further and complete expansion with production of external recoverable work which again reduces its temperature below the critical temperature of the gas intended to be liquefied but not down to its own liquefaction temperature, reheating this completely expanded gas firstly by liquefying another portion of the gas intended to be liquefied and previously compressed and cooled, and finally by cooling the gas to be expanded and the gas to be liquefied by circulating in the opposite direction to them.

6. The process of liquefying a gas which consists in compressing another gas, cooling it, expanding said compressed and cooled gas with production of external recoverable work at a temperature as near as possible to the temperature of the liquefaction of the gas intended to be liquefied and previously compressed and cooled, liquefying the latter by keeping it in as long and as extensive indirect contact as possible with the expanding gas in order to absorb the cold as it is produced by the expansion, and causing the expanded gas to cool the gas to be liquefied and the gas to be expanded.

7. In a process of liquefying gas cooled and compressed near to its critical pressure, by expanding some of it with production of external recoverable work sufficiently to reduce its temperature below the critical temperature but not down to its liquefaction temperature, causing this expanded gas to be partially reheated by liquefying some of the gas cooled and compressed near to its critical pressure, and afterward causing this expanded and partially reheated gas to cool the compressed gas to be liquefied, cooling the liquid under pressure so obtained, so as to avoid its excessive evaporation when drawing it off under a lower pressure, by causing it to flow for some distance in indirect contact with gas at a lower temperature than that of the liquid under pressure.

8. In a process of liquefying gas cooled and compressed near to its critical pressure, by expanding some of it with the production of external recoverable work sufficiently to reduce its temperature below its critical temperature, but not down to its liquefaction temperature, causing this expanded gas to be partially reheated by liquefying some of the gas cooled and compressed near to its critical pressure, and afterward causing this expanded and partially reheated gas to cool the compressed gas to be liquefied, cooling the liquid under pressure so obtained, so as to avoid its excessive evaporation when drawing it off under a lower pressure, by subjecting a portion of the compressed and cooled gas to a complete expansion with the production of external work, and bringing this expanded gas into indirect contact with the aforesaid liquid before its withdrawal.

In testimony that I claim the foregoing I have hereunto set my hand this eighth day of January 1903.

GEORGES CLAUDE.

Witnesses:
EMILE COMHOUD,
AUGUSTUS E. INGRAM.