Aug. 31, 1965 A. FUDERER 3,203,194

COMPRESSION PROCESS FOR REFRIGERATION

Filed Nov. 26, 1963 3 Sheets-Sheet 1

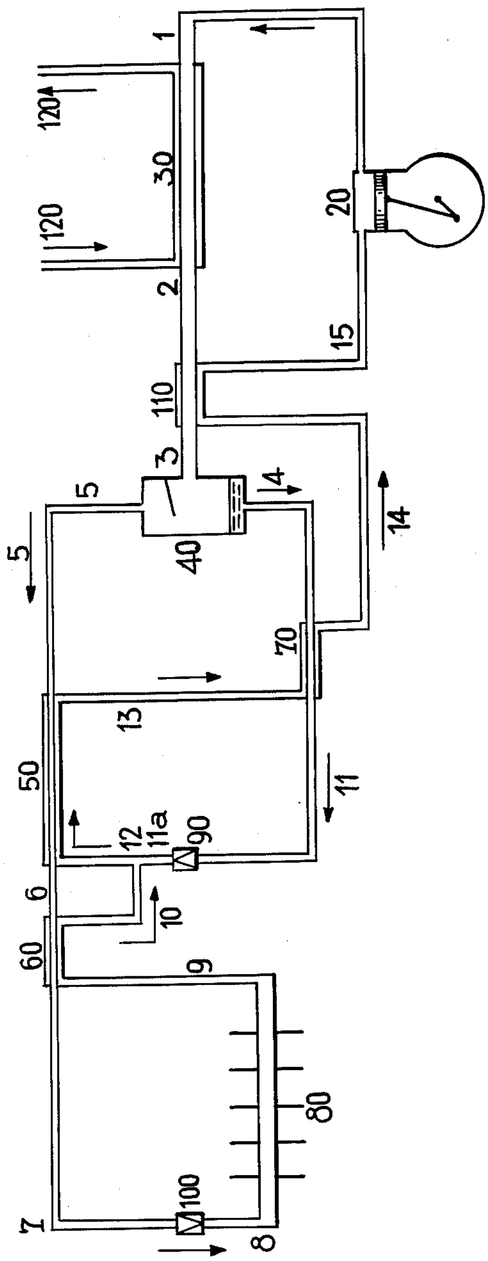

FIG. 1.

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FIG. 3. i-ξ Diagram for $CF_2Cl_2+CF_4$ (R12+R14) p = 2 atm. absolute

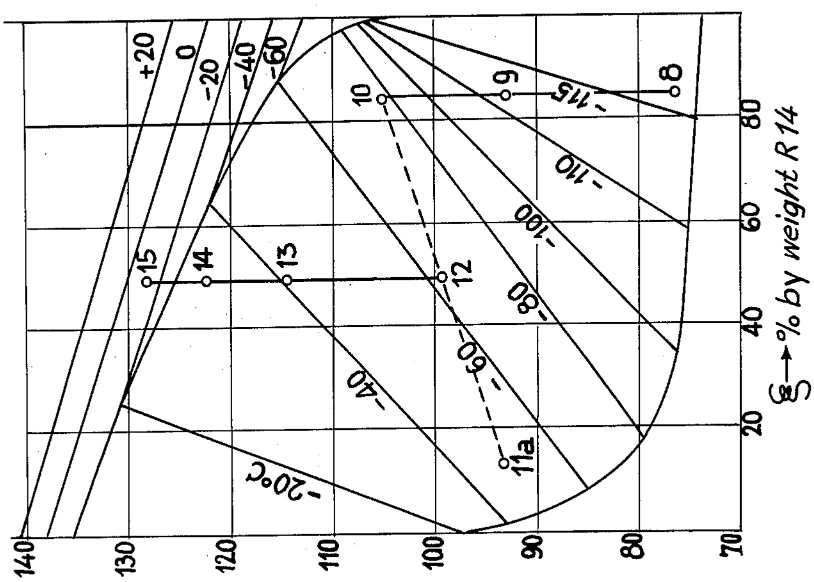
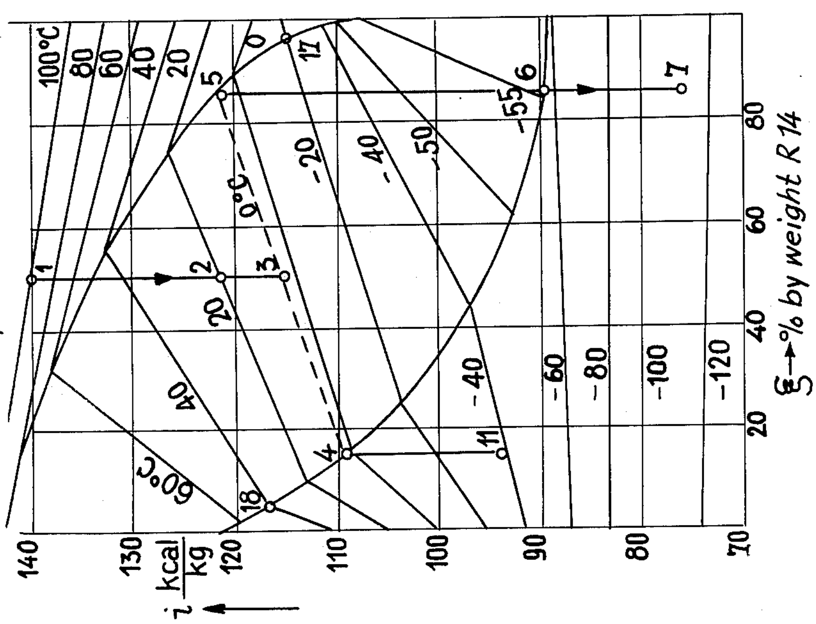


FIG. 2. i-ξ Diagram for $CF_2Cl_2+CF_4$ p = 25 atm. absolute



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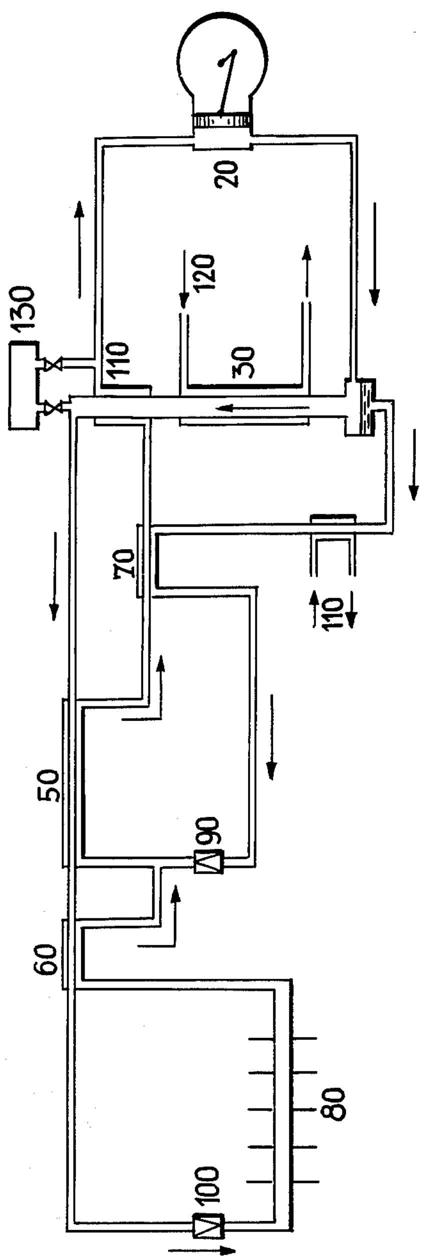

FIG. 4.

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7 Claims. (Cl. 62—114)

The present invention relates to a compression process for refrigeration with the use of a mixture of refrigerants.

For refrigeration according to the compression process a readily vaporizable liquid refrigerant is evaporated, the vapors obtained are aspirated by a compressor, compressed, condensed in a condenser under high pressure, and again evaporated in an evaporator. Most of the known refrigeration units are operated with a uniform product as refrigerant. It is likewise known, however, how to use as refrigerant a mixture of substances of different boiling points. This measure serves to improve, in the first place, the volumetric refrigeration capacity of the compressor. In the known processes the refrigerant or mixture of refrigerants is completely condensed in the condenser. For obtaining still lower temperatures it has been proposed to connect two or more compression cycles in cascade connection. In this case two refrigeration units, each consisting of a compressor, a condenser, and an evaporator, are combined in such a manner that the evaporator of the higher stage forms a heat exchanger with the condenser of the lower stage. The low temperature required for condensing the lower boiling refrigerant is obtained by evaporating the previously condensed higher boiling refrigerant.

The present invention provides a compression process for refrigeration with the use of a mixture of refrigerants which comprises condensing the compressed vaporous mixture of refrigerants in a first condensation stage by partially condensing substantially the higher boiling component, separating the liquid phase from the vaporous phase, transferring the vaporous, lower boiling component to a second condensation stage where it is condensed, producing the required temperature of condensation by expanding and evaporating the higher boiling component of the mixture of refrigerants condensed in the first condensation stage, producing the required final temperature by expanding and evaporating the condensed lower boiling component of the mixture of refrigerants, mixing the components of the mixture with one another and conducting them to the compressor for closing the cycle.

In comparison with the aforesaid known process using a two-stage cooling system with cascade connection and two compressors, in the process of the invention only one compressor is necessary for obtaining the same low temperature, this representing considerable technical progress.

The refrigeration process according to the invention can be used as lower or upper stage of a cascade connection, whereby one stage is saved. It is suitable for producing temperatures in the range of from −20° C. to −180° C., and preferably −50° C. to −160° C., for example for the liquefaction of methane and air.

The process of the invention presents advantages not only in smaller units with piston-type compressors but also in larger units with turbocompressors.

Suitable components of the refrigerant mixture are substances having low solidification temperatures, preferably hydrocarbons, especially alkanes and alkenes with 1 to 4 carbon atoms and the halogenated derivatives thereof, more especially partially or completely fluorinated and/or chlorinated methanes and ethanes. Nitrogen can likewise be used. In general, the higher as well as the lower boiling refrigerants constitute uniform chemical compounds. But this is not absolutely necessary. The higher as well as the lower boiling component may be a mixture, namely a mixture forming an azeotrope on boiling or a mixture of components the boiling points of which are not too far from one another, for example air or a mixture of fluorinated chlorohydrocarbons which does not form an azeotrope.

The boiling points of the combined refrigerants shall be sufficiently remote from one another, since otherwise the difference in the composition of the two phases is not great enough, i.e. the separation of the refrigerants is very incomplete.

The difference in the boiling points of the higher boiling and the lower boiling refrigerants shall preferably range from 40° C. to 140° C. and more preferably from 60° C. to 100° C. If one or both refrigerants constitute mixtures the differences in temperature as defined above shall be between the upper boiling limit of the lower boiling refrigerant and the lower boiling limit of the higher boiling refrigerant.

It is, therefore, possible to combine refrigerants in various ways. Suitable pairs of refrigerants are, for example,

monofluorotrichloromethane/trifluoromonobromomethane;
trifluorotrichloroethane/difluorodichloromethane;
monofluorotrichloromethane/trifluoromonochloromethane;
monofluorotrichloromethane/ethane;
monofluorodichloromethane/trifluoromonochloromethane;
difluorodichloromethane/ethylene;
difluoromonochloromethane/tetrafluoromethane;
propane/tetrafluoromethane;
propane/methane;
trifluoromonochloromethane/methane;
trifluoromonochloromethane/nitrogen;
ethane/nitrogen;
tetrafluoromethane/air;
the azeotropic mixture of difluorodichloromethane and difluoromonochloromethane/tetrafluoromethane.

Suitable pairs of refrigerants for turbocompressors are, for example, monofluorotrichloromethane/difluoromonochloromethane and tetrafluorodichloroethane/trifluoromonochloromethane.

With the first combination of refrigerants a temperature of −25° C. can be obtained on the average with a pressure ratio of about 1:3 only, while with the second combination of refrigerants a temperature of −63° C. can be reached on the average with a pressure ratio of about 1:5. In either case a medium temperature of condensation above +30° C. is taken as a basis.

The process of the invention is illustrated with reference to the accompanying drawings. FIGURES 1 and 4 represent by way of example suitable flow sheets of the process of the invention and FIGURES 2 and 3 are phase diagrams. In the drawings the numerals have the following meaning:

20—compressor
30—condenser
40—flash chamber
50—evaporator condenser
60—supercooling device for condensate of lower boiling refrigerant
70—supercooling device for condensate of higher boiling refrigerant
80—evaporator
90—first expansion valve
100—second expansion valve
110—auxiliary condenser (heat exchanger)
120—pipes for cooling water

FIGURES 2 and 3 represent phase diagrams according to Merkel Bošnjakovič (cf. Plank, "Handbuch der Kältetechnik," Springer Verlag, Berlin, vol. II, pp. 285, 291 et seq.). There are plotted on the ordinates the enthalpy i[kilocalories $kg.^{-1}$] and on the abscissas the percent by weight ξ of the lower boiling refrigerant.

Numerals 1–15 designate the thermal states occurring in the refrigerating process.

The following example serves to illustrate the invention but it is not intended to limit it thereto.

Example

As higher boiling refrigerant difluorodichloromethane (CF_2Cl_2, boiling point −30° C.) and as lower boiling refrigerant tetrafluoromethane (CF_4, boiling point −128° C.) are used. The diagram of FIGURE 2 shows the system at a (constant) pressure of liquefaction of 25 atmospheres. The diagram of FIGURE 3 shows the system at a (constant) evaporation pressure of 2 atmospheres. With the expansion of the system (in the valves) is connected an isenthalpic transition of FIGURE 2 to FIGURE 3, with the compression is connected a transition with enthalpy increase of FIGURE 3 to FIGURE 2.

A mixture of 50% of CF_2Cl_2 and 50% of CF_4 corresponding to the initial state **15** (2 atm., −10° C.) is aspirated by compressor **20** and compressed to state **1** (25 atm., 100° C.). In condenser **30**, cooled by water cooling **120**, part of the mixture is condensed (state **1**→**2**). If necessary the condensation can be continued in auxiliary condenser **110** (state **2**→**3**). About one half of the vapor is condensed. In state 3 the liquid phase **4** and the vaporous phase **5** exist which separate in liquid separator **40**. The liquid phase **4** contains 15% of CF_4 and the vaporous phase **5** contains 85% of CF_4. The liquid **4** is cooled in supercooling device **70** to about −40° C. (state **4**→**1**) and expanded in the first expansion valve **90** with constant enthalpy to 2 atmospheres (state **11**→**11***a*). The vaporous phase **5** is condensed in evaporator-condenser **50** (state **5**→**6**). It is further cooled in supercooling device **60** to −**110**° C. (state **6**→**7**). Expansion to 2 atmospheres takes place then through the second expansion valve **100** with constant enthalpy *i* (state **7**→**8**). Part of the liquid evaporates in evaporator **80** whereby the temperature rises from about −116° C. to −112° C. (state **8**→**9**). A further part evaporates in undercooling device **60** (state **9**→**10**). The two phases are here combined (**11***a* and **10**) and a mixture of the original composition of 50% of CF_4 and 50% of CF_2Cl_2 (state **12**) is formed again. In condenser-evaporator **50** the major part of the liquid still present evaporates at gradually rising temperature (state **12**→**13**). The increase in temperature and evaporation continue in supercooling device **70** until state **14** is reached. The remainder of the liquid evaporates in auxiliary condenser **110** in which the vapor is slightly superheated (state **15**). In this state the mixture is aspirated by the compressor.

In the i/ξ diagrams of FIGURES 2 and 3 the temperature conditions as well as the enthalpy amounts are well visible. It must be considered that from 1 kilogram mixture in state 3 about 500 grams of phases 4 and 5 respectively are formed. Therefore, the enthalpy differences in these phases must be multiplied by 0.5.

Instead of the expansion valves any other expansion device may be used. In many cases auxiliary condenser **110** can be dispensed with.

It is often sufficient to use a one-stage compressor **20**. If necessary, however, a multi-stage compressor may be used. The thermodynamics of the process can be improved by applying a two-stage compression. The two-stage compression is of special advantage when the boiling points of the refrigerant used are more than 100° C. remote from one another, for example when a mixture of about 80% by weight of difluorodichloromethane and 20% by weight of methane is used. In this case with a temperature of liquefaction of 32° C. on the average an evaporation temperature of −156° C. can be reached.

An essential feature of the process of the invention is the variable temperature. In the present example the evaporation starts at −116° C. When one half of the liquid has evaporated the temperature has increased to about −112° C. (state **8**→**9**). A further part of the liquid evaporates in the supercooling device. The temperature further increases from −112° C. to about −76° C. (state **9**→**10**) whereby the condensate can be supercooled in countercurrent from about −55° C. to −110° C. (state **6**→**7**). In analogous manner the condensate of the higher boiling refrigerant can be supercooled. It is remarkable that the cooling is accomplished by the evaporation of the phase taking place at rising temperature.

Owing to the variable temperatures a countercurrent heat exchange is favorable in the process of the invention and even necessary if—as in the present example—the temperatures vary within wide limits, i.e. with a combination of two refrigerants of very different boiling points. This substantial supercooling of the condensate at such favorable temperature conditions considerably reduces the loss of energy which mostly occurs when the liquid is expanded.

Besides the aforesaid advantage of saving one compressor, the process of the invention offers the further advantage that a thermodynamic efficiency is obtained which in many cases, especially with a suitable selection of the intermediate states and appropriate dimensions of the heat exchangers, may be more favorable than the efficiency of a known two-stage refrigeration process operating under the same conditions.

It is of importance in which zone of the device or in which states the two phases are again mixed with one another. The addition of the substantially or completely evaporated lower boiling refrigerating component to the higher boiling component shall preferably take place directly after the place of the cycle of refrigerants where the higher boiling component is expanded. Thereby, the partial pressure of the higher boiling refrigerant suddenly decreases and the evaporation takes place at a lower temperature.

In the device diagrammatically illustrated in FIGURE 4 the condenser **30** consists of vertically arranged tubes. The compressed mixture of refrigerants is introduced into the condenser from below. The condensate essentially consisting of the higher boiling refrigerant streams downward owing to the force of gravity in contercurrent with the mixture of refrigerant and vapor, whereby an action of rectification is produced. In this case the condenser also acts as liquid separator and oil separator for the lower boiling phase, so that the liquid separator **40** shown in FIGURE 1 can be dispensed with. Auxiliary condenser **110** now serves as a kind of dephlegmator. This condenser rectifier need not be heated since the vapors of refrigerent stream in at the bottom with a sufficiently elevated temperature. The temperature in the upper part of the condenser is considerably lower than in the lower part and state 3 plotted in FIGURE 2 does not consist of phases 4 and 5 but approximately of phases **17** (vapor −20° C.) and **18** (liquid +40° C.). Liquid

18 may be cooled with water to about +25° C. whereby a lower temperature is reached in evaporator **80**.

FIGURE 4 additionally contains a gas tank **130** which is connected by means of valves with the high pressure side (directly towards the condenser) and with the low pressure side. At least one valve in the connection pipes to the container **130** must be closed, otherwise a "short circuit" occurs in the refrigeration process. When the valve on the high pressure side is open, a greater amount of gaseous refrigerant, mainly the low boiling component, is in container **130**, owing to the elevated pressure. When the valve on the high pressure side is closed, defined amounts of the lower boiling refrigerant can be introduced into the cycle through the other valve whereby a regulation becomes possible. With a greater amount of lower boiling refrigerant in the cycle the pressures everywhere in the refrigeration unit and, consequently, the volumetric refrigerating capacity and the expenditure of work of the compressor are a little higher.

Alternatively, the refrigeration process can be realized in a manner such that the cold produced by evaporating the higher boiling component is not used up totally for condensing the lower boiling component and supercooling the own condensate. Part of the cold can be utilized for other purposes. Therefore it is a further advantage of the present process that simultaneously two different low temperaures can be produced, using a sole compressor. Thus, the process of the invention may simultaneously serve two purposes, for example to manufacture Dry Ice and liquefy methane.

I claim:

1. In a compression process for refrigeration using a mixture of refrigerants, which process comprises compressing said mixture of refrigerants, partially condensing substantially the higher boiling component from compressed vapors of said mixture of refrigerants in a first condensation stage, separating the resultant condensed and vapor phases, condensing the separated vapors of the lower boiling component of said mixture of refrigerants in a second condensation stage, expanding and evaporating the condensed components to produce refrigerating temperatures, mixing the resultant vapors, and then recycling the vapors to the compression stage, the improvement wherein the expansion and evaporation of

the separated condensed higher boiling component are used to cool and condense vapors of the lower boiling component in said second condensation stage.

2. The process of claim **1**, which comprises using a mixture of two individual refrigerating components, the boiling temperatures of which differ by 40 to 140° C.

3. The process of claim **1**, which comprises using a mixture of refrigerants of more than two individual components.

4. The process of claim **1**, which comprises supercooling the condensates of the higher boiling component and of the lower boiling component by countercurrent heat exchangers, the cooling being brought about by the evaporation at rising temperatures of the corresponding component.

5. The process of claim **1**, which comprises mixing the higher boiling component and the lower boiling component directly after the place of the cycle of the mixture of refrigerants where the higher boiling component is expanded.

6. The process of claim **1**, which comprises varying the proportion of the lower boiling component of the mixture of refrigerants in the cycle by means of a container for the said component which is connected with the high pressure side and with the low pressure side of the cycle.

7. The process of claim **1**, which comprises utilizing the cold produced by evaporating the higher boiling component only partially for condensing the lower boiling component and supercooling the condensate.

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