

Refrigerant

5 The invention relates to a refrigerant for a cooling device and to a
test chamber with the refrigerant and to a use of a refrigerant, the
refrigerant for a cooling device which comprises a cooling circuit
with at least one heat exchanger in which the refrigerant undergoes a
phase transition consisting of a refrigerant mixture composed of a
10 mass fraction of carbon dioxide, a mass fraction of pentafluoro-
ethane, and a mass fraction of at least one other component.

Refrigerants of this kind typically circulate within a closed cooling
circuit of cooling devices and undergo a sequence of different changes
in state of matter. Refrigerants should be of such a nature that
15 they can be used in a cooling circuit within a predefined temperature
difference. Single-component refrigerants and refrigerant mixtures of
at least two components are known from the state of the art. The
refrigerants are classified according to the latest version of German
industry standard DIN 8960 Section 6 as at the priority date.

20 As per statutory regulations, a refrigerant must not significantly
contribute to the depletion of ozone in the atmosphere or to global
warming. This means that essentially no fluorinated or chlorinated
substances should be used as refrigerants, which is why natural
refrigerants or gasses are an option. Moreover, a refrigerant should
25 be nonflammable in order to not complicate filling, shipping and
operation of a cooling circuit because of any safety regulations that
may have to be observed. Also, production of a cooling circuit
becomes more expensive if a flammable refrigerant is used because of
the constructional measures required in that case. Flammability refers

to the refrigerant's property of reacting to ambient oxygen by releasing heat. A refrigerant is flammable in particular if it is classified in fire class C of European standard EN2 and DIN 378 classes A2, A2L and A3 in their latest versions as at the priority date.

5 Moreover, a refrigerant should have a relatively low CO₂ equivalent; i.e., a relative global warming potential (GWP) should be as low as possible in order to avoid indirect damage to the environment in case the refrigerant is released. The GWP indicates how much a defined mass of a greenhouse gas contributes to global warming, carbon
10 dioxide serving as the reference value. The value describes the mean warming effect over a specific period, 100 years being set here for the sake of comparability. For a definition of the relative CO₂ equivalent or GWP, reference is made to Intergovernmental Panel on Climate Change (IPCC), Assessment Report, Appendix 8.A, Table
15 8.A.1 in the latest version as at the priority date.

Refrigerants with a low GWP, such as < 2500 , have the disadvantage that these refrigerants tend to have a significantly lower cold capacity in the temperature ranges relevant for a cooling circuit than refrigerants with a comparatively higher GWP. A lower GWP can be
20 achieved with refrigerant mixtures that have a comparatively high mass fraction of carbon dioxide; however, these refrigerant mixtures may have zeotropic properties due to the different substances mixed, which is undesirable in many cooling circuits.

In a zeotropic refrigerant mixture, a phase transition happens across
25 a temperature range which is known as the temperature glide. The temperature glide refers to a difference between the boiling temperature and the dew point temperature at constant pressure. Zeotropic refrigerant mixtures typically contain a high mass fraction of a non-

flammable component, which is characterized by a comparatively high GWP, however. At first glance, carbon dioxide appears to be a suitable component for a refrigerant mixture because it is nonflammable and has a low GWP. In a mixture of carbon dioxide with
5 another component, however, it is essential that a mass fraction of a carbon dioxide has to be comparatively large if the other component is flammable. This is disadvantageous, however, because carbon dioxide has a freezing temperature or freezing point of $-56.6\text{ }^{\circ}\text{C}$, which hardly allows temperatures of up to $-60\text{ }^{\circ}\text{C}$ to be achieved at
10 a high carbon dioxide concentration.

Also, the use of refrigerants should be as simple as possible, i.e., not require extensive technical restructuring of a cooling device. With refrigerants having a temperature glide of $> 3\text{ K}$ in particular, an expansion element and a heat exchanger or evaporator of the cooling
15 circuit in question have to be adjusted to the evaporation temperature of the refrigerant and corresponding control has to be provided. Furthermore, a distinction must be drawn between refrigerants that are designed for static operation of a cooling device, i.e., a cooling device having a temperature at the heat exchanger or evaporator that
20 is substantially constant over a longer period of time, and refrigerants that are designed for a dynamic cooling device, which exhibits comparatively quick temperature changes at the heat exchanger. Dynamic cooling devices of this kind are integrated in test chambers, for example, which means that a refrigerant used has to be usable
25 within a large temperature range.

Test chambers are typically used to test physical and/or chemical properties of objects, in particular devices. For instance, temperature test chambers or climate test chambers in which temperatures in a range of $-60\text{ }^{\circ}\text{C}$ to $+180\text{ }^{\circ}\text{C}$ can be set are known. In climate test

chambers, desired climatic conditions can additionally be set, to which the device or the test material is then exposed for a defined period of time. Test chambers of this kind are often or sometimes realized as mobile devices which are merely connected to a building
5 via required supply lines and comprise all modules needed to control the temperature and climate. The temperature of a test space holding the material to be tested is typically controlled in a circulating air duct within the test space. The circulating air duct forms an air treatment space in the test space, in which heat exchangers for
10 heating or cooling the air flowing through the circulating air duct and the test space are disposed. A fan or ventilator aspirates the air located in the test space and directs it to the respective heat exchangers in the circulating air duct. In this way, the test material can be temperature-controlled or exposed to a defined temperature
15 change. During a test interval, a temperature can repeatedly change between a maximum temperature and a minimum temperature of the test chamber. A test chamber of this kind is known from EP 0 344 397 A2, for example.

The refrigerant circulating in a cooling circuit must be of such a
20 nature that it can be used in the cooling circuit within the aforementioned temperature difference. In particular, a dew point temperature of the refrigerant cannot be higher than a minimum temperature of the temperature range of the cooling circuit that is to be achieved because the minimum temperature would not be achievable otherwise
25 when the refrigerant is evaporated in the heat exchanger serving to cool the test space. The dew point temperature of azeotropic refrigerants is reached immediately behind the expansion element in the heat exchanger. Straight cooling circuits for test spaces require a very high spatial temperature stability to precisely control the tem-

perature of the test chamber, which cannot be achieved at all or only to a limited degree using zeotropic refrigerants. High temperature stability cannot be achieved in this case because the dew point temperature or a dew point of the zeotropic refrigerant may locally shift as a function of a temperature in the test space in the area of the heat exchanger in the test space because of temperature differences. Hence, a use of zeotropic refrigerants, i.e., of refrigerants having a temperature glide, in cooling circuits of test chambers is avoided.

Furthermore, cooling devices in which a zeotropic refrigerant mixture is successively evaporated are known. This means that components of the refrigerants are evaporated one after the other by means of an expansion element. Cooling devices of this kind are also referred to as mixed fluid cascade systems and are suitable for realizing a substantially static cryogenic temperature.

WO 2017/157864 A1 discloses a refrigerant which contains carbon dioxide and pentafluoroethane among other components. Ranges of 30 to 70 wt% for carbon dioxide and 20 to 80 wt% for pentafluoroethane are indicated for the refrigerant, for example. Difluoromethane as a mixing partner is also disclosed.

Hence, the object of the present invention is to propose a refrigerant for a cooling device, a test chamber with a refrigerant, and a use of a refrigerant by means of which temperatures up to at least $-60\text{ }^{\circ}\text{C}$ can be achieved in an environmentally friendly and safe manner.

This object is attained by a refrigerant having the features of claim 1, a test chamber having the features of claim 12 and a use of a refrigerant having the features of claim 18.

In the refrigerant according to the invention for a cooling device comprising a cooling circuit with at least one heat exchanger, the refrigerant undergoes a phase transition in the heat exchanger, the refrigerant being a refrigerant mixture composed of a mass fraction
5 of carbon dioxide, a mass fraction of pentafluoroethane, and a mass fraction of at least one other component, wherein the mass fraction of carbon dioxide in the refrigerant mixture is 20 to 74 mass percent, the mass fraction of pentafluoroethane being 8 to 65 mass percent, the other component being fluoromethane.

10 Carbon dioxide (CO_2) is also known as a refrigerant or component under the designation R744, fluoromethane (CH_3F) is known under the designation R41, pentafluoroethane (C_2HF_5) is known under the designation R125 and difluoromethane (CH_2F_2) is known under the designation R32 according to the latest version of German industry
15 standard DIN 8960 as at the priority date of the application.

The invention provides a refrigerant mixture of carbon dioxide and one or more fluorinated refrigerants which have a low GWP and are nonflammable or flammable to a limited degree only. A fraction of carbon dioxide has to be as low as possible because otherwise a
20 freezing point of the refrigerant mixture would rise with an increasing mass fraction of carbon dioxide. However, a lower mass fraction of carbon dioxide reduces a GWP-reducing effect of the carbon dioxide. This is why partly fluorinated refrigerants have a significantly higher GWP than carbon dioxide, while also having an improved flame-
25 retardant effect. Pentafluoroethane and fluoromethane in particular contain significant amounts of fluorine atoms, which leads to an undesirably high GWP. As was surprisingly found, however, a sufficiently low GWP, i.e., < 2500 , for example, can be achieved with a refrigerant mixture containing a mass fraction of carbon dioxide of

20 to 74 mass percent with pentafluoroethane and fluoromethane. As was also found, a flame-retardant effect of pentafluoroethane is comparatively greater than that of carbon dioxide. Moreover, the negative properties of pentafluoroethane and of carbon dioxide can be reduced by adding fluoromethane as a third component of the refrigerant mixture. Thus, a refrigerant mixture containing pentafluoroethane and fluoromethane can be classified as nonflammable. At the same time, fluoromethane has a lower freezing temperature with carbon dioxide than with pentafluoroethane. Consequently, a mixture of pentafluoroethane, fluoromethane and carbon dioxide can achieve a lower freezing temperature than pentafluoroethane and carbon dioxide alone. Fluoromethane thus lowers the freezing point of the refrigerant mixture significantly, a certain mass fraction of carbon dioxide being required in order for the refrigerant mixture to be nonflammable. At the same time, however, fluoromethane leads to a high final compression temperature and is flammable, which is why fluoromethane is suitable only within limits as a sole mixing partner for carbon dioxide. Pentafluoroethane cannot lower a freezing point of the refrigerant mixture as far as fluoromethane, but has a greater flame-retardant effect than carbon dioxide, which is advantageous.

Consequently, the refrigerant mixture may be a ternary mixture.

A mass fraction of fluoromethane in the refrigerant mixture may be 7 to 25 mass percent. A freezing point of the refrigerant mixture can be significantly reduced by adding the fluoromethane in the mentioned range. This reduction can be set in such a manner that the freezing point of the refrigerant mixture is lower than the intended evaporation temperature and, at the same time, the vapor pressure associated with the evaporation temperature may be higher or only slightly lower than the ambient pressure.

Advantageously, the mass fraction of fluoromethane may be 13 to 21 mass percent.

Particularly advantageously, the mass fraction of fluoromethane is 15 to 19 mass percent.

5 The mass fraction of carbon dioxide may be 26 to 34 mass percent. Pentafluoroethane is nonflammable, which means that a mixture of carbon dioxide, pentafluoroethane and fluoromethane in the mass fractions indicated above is nonflammable, as well. The GWP of pentafluoroethane of 3150 is significantly higher than that of other
10 possible components. Hence, it may also be partly replaced with other substances in the refrigerant mixture in order to reduce the GWP of the refrigerant mixture. Furthermore, the flame-retardant effect of pentafluoroethane is greater than that of carbon dioxide, which means that a mass fraction of carbon dioxide in the refrigerant
15 mixture can be reduced, which lowers the freezing point further and still ensures non-flammability but increases the GWP.

Advantageously, the mass fraction of carbon dioxide may be 28 to 51 mass percent.

The mass fraction of pentafluoroethane may be 49 to 57 mass
20 percent. As described above, a mixture of carbon dioxide with pentafluoroethane and fluoromethane has proven particularly advantageous. Accordingly, this refrigerant mixture may consist solely of the three components indicated. This refrigerant mixture may have a temperature glide of 4.1 K to 15.6 K at evaporation pressures
25 around 1 bar. Furthermore, this refrigerant mixture leads to a concentration-dependent reduction of the freezing point. Hence, flammable and nonflammable refrigerant mixtures for different tempera-

ture applications may arise when mass fractions deviate from the indicated mass fractions.

Advantageously, the mass fraction of pentafluoroethane may be 51 to 55 mass percent.

- 5 In the following Table, examples of refrigerants according to the embodiments described above are indicated.

Refrigerant	R744 [mass%]	R125 [mass%]	R41 [mass%]	GWP [-]	Glide [°C]	Boiling point [°C]
1	20–74	8–65	7–25	303–2282	15.6–4.1	–86.1 to –76
2	26–34	49–57	13–21	1734– 2007	14.8– 12.7	–80.8 to –78.1
3	28–32	51–55	15–19	1800– 1939	13.8– 13.1	–80.4 to –79.3

Table

Furthermore, the refrigerant may have a temperature glide of 4 K to
 10 16 K. A temperature glide of the refrigerant should not be > 16 K
 so that a cooling device can be operated in a reasonable way.

The refrigerant may have a relative CO₂ equivalent of < 2300,
 preferably < 2000, particularly preferably < 1000, over 100
 years. Consequently, the refrigerant may be of little harm to the
 15 environment.

The refrigerant may be nonflammable. If the refrigerant is nonflam-
 mable, the cooling circuit and a test chamber in particular can be
 designed more cost-effectively because no special safety measures in

terms of flammability of the refrigerant will have to be observed. In this case, the refrigerant may at least not be classified in fire class C and/or refrigerant safety group A1. Moreover, shipping and transport of the cooling circuit is easier because the cooling circuit can be filled with the refrigerant before being transported, irrespective of the mode of transport. If a flammable refrigerant is used, filling may not be possible until start-up at the installation site. Furthermore, use of the nonflammable refrigerant in the presence of ignition sources is possible.

10 The test chamber according to the invention for conditioning air comprises a test space which serves to receive test material and which can be sealed against an environment and is temperature-insulated, and a temperature control device for controlling the temperature of the test space, a temperature in a temperature range
15 of $-70\text{ }^{\circ}\text{C}$ to $+180\text{ }^{\circ}\text{C}$ being establishable within the test space by means of the temperature control device, the temperature control device having a cooling device comprising a cooling circuit with a refrigerant according to the invention, a heat exchanger, a compressor, a condenser and an expansion element. Regarding the advantages
20 of the test chamber according to the invention, reference is made to the description of advantages of the refrigerant according to the invention.

By means of the temperature control device, a temperature in a temperature range of $-80\text{ }^{\circ}\text{C}$ to $+180\text{ }^{\circ}\text{C}$, preferably $-90\text{ }^{\circ}\text{C}$ to
25 $+180\text{ }^{\circ}\text{C}$, particularly preferably $-100\text{ }^{\circ}\text{C}$ to $+180\text{ }^{\circ}\text{C}$, may be established within the test space. Unlike in a mixed fluid cascade system, the refrigerant with all components contained in the refrigerant can be evaporated at once by means of the expansion element. Since a freezing point of the carbon dioxide is $-56.6\text{ }^{\circ}\text{C}$, refrigerant

mixtures that contain a large mass fraction of carbon dioxide are no longer suitable for achieving temperatures below $-56.6\text{ }^{\circ}\text{C}$, on principle. The use of the refrigerant according to the invention, however, allows a dew point temperature of the refrigerant of less
5 than $-70\text{ }^{\circ}\text{C}$ to be achieved.

The cooling circuit may have an internal heat exchanger, and the internal heat exchanger may be connected to a high-pressure side of the cooling circuit upstream of the expansion element and downstream of the condenser and to a low-pressure side of the cooling
10 circuit upstream of the compressor and downstream of the heat exchanger. By use of the internal heat exchanger and cooling of the liquefied refrigerant of the high-pressure side by means of the internal heat exchanger, temperatures below $-56\text{ }^{\circ}\text{C}$ can be reached easily. The evaporation temperature of the refrigerant cooled by
15 means of the internal heat exchanger can be reduced at the expansion element relative to an evaporation temperature of an uncooled refrigerant. The cold capacity transferred from the low-pressure side to the high-pressure side via the internal heat exchanger can thus be used at least in part, preferably exclusively, to reduce the evapora-
20 tion temperature of the refrigerant at the expansion element. Furthermore, use of a zeotropic refrigerant having a temperature glide is made possible in the first place because the location of the dew point temperature of the refrigerant or the dew point of the refrigerant can be shifted into the internal heat exchanger in this case. As a
25 consequence of the temperature glide of the zeotropic refrigerant, the achieved dew point temperature of the refrigerant may be comparatively high and thus prevent the heat exchanger from cooling further.

Hence, only part of the refrigerant may be evaporated in the heat exchanger and the unusable part of the wet vapor portion of the refrigerant can be shifted into the internal heat exchanger. On the whole, this allows refrigerants which contain a mass fraction of carbon dioxide and which, while being environmentally friendly, have zeotropic properties to be used to establish low temperatures in a test space. Moreover, if part of the temperature glide or part of the wet vapor of the refrigerant is shifted from the heat exchanger in the test space into the internal heat exchanger, a comparatively improved temperature stability can be achieved with the zeotropic refrigerant. In this case, a cold capacity output via the heat exchanger can be generated in a section of the temperature glide only, which means that a shift of the dew point of the refrigerant in the cooling circuit has hardly any impact on a temperature stability of the heat exchanger. Furthermore, a single heat exchanger may be used to cool a fluid, i.e., the air in the test space, in this case.

The heat exchanger may be dimensioned in such a manner that only part of the refrigerant can evaporate in the heat exchanger. This results in the advantage that the dew point or the location of the dew point temperature of the refrigerant can be shifted out of the heat exchanger into the internal heat exchanger. Because of a temperature glide of the zeotropic refrigerant, partial evaporation of the refrigerant in the heat exchanger achieves a lower temperature in the heat exchanger than the following remaining evaporation of the refrigerant in the internal heat exchanger.

In one embodiment of the test chamber, the heat exchanger may be disposed in the test space. In this case, the heat exchanger may also be disposed in an air treatment space of the test space so that air circulated by a fan can come into contact with a heat exchanger. In

this way, a circulated amount of air of the test space can be cooled directly in the test space by means the cooling device via the heat exchanger. The test chamber may have the cooling circuit as a sole, single cooling circuit. In this case, the cooling circuit is connected
5 directly to the test space.

In another embodiment of the test chamber, the condenser may be realized as a cascade heat exchanger of another cooling circuit of the cooling device. Accordingly, the test chamber may have at least two cooling circuits, in which case the cooling circuit may form a second
10 stage of the cooling device and another cooling circuit, which is disposed upstream of the cooling circuit, may form a first stage of the cooling device. In this case, the condenser serves as a cascade heat exchanger or a heat exchanger for the cooling circuit. This embodiment of a test chamber allows particularly low temperatures
15 to be established in the test space.

The temperature control device may have a heating device comprising a heater and a heating heat exchanger in the test space. The heating device may be an electric resistance heater which heats the heating heat exchanger in such a manner that the temperature in the
20 test space can be raised by means of the heating heat exchanger. If the heat exchanger and the heating heat exchanger can be specifically controlled by means of a control device to cool or heat the air circulated in the test space, a temperature in the temperature range indicated above can be established within the test space by means of
25 the temperature control device. A temperature stability over time of ± 1 K, preferably ± 0.3 K to ± 0.5 K or less than ± 0.3 K, may be established in the test space during a test interval irrespective of the test material or of an operating state of the test material. A test interval is a segment of a full test period in which the test material is

exposed to a substantially constant temperature or climatic condition. The heating heat exchanger may be combined with the heat exchanger of the cooling circuit in such a manner that a shared heat exchanger body through which the refrigerant can flow and which has heating elements of an electric resistance heater can be realized. The condenser may be cooled with air, water or another coolant. In principle, the condenser can be cooled using any suitable fluid. The essential aspect is that the thermal load generated at the condenser is discharged via the cooling air or the cooling water in such a manner that the refrigerant can condense until it is completely liquefied.

A first bypass having at least one controllable second expansion element may be realized in the cooling circuit, in which case the first bypass may be connected to the cooling circuit upstream of the internal heat exchanger and downstream of the condenser and the first bypass may be realized as a controllable additional internal cooling system. The first bypass may thus form a re-injection device for refrigerant. Accordingly, refrigerant can be recycled from the controllable second expansion element in the internal heat exchanger on the low-pressure side. In this case, the first bypass may be connected to the low-pressure side of the cooling circuit upstream of the internal heat exchanger and downstream of the heat exchanger. The refrigerant cooled or having its temperature level lowered by the second expansion element may be led through the internal heat exchanger and intensify cooling of the refrigerant on the high-pressure side of the internal heat exchanger. Also, a cooling capacity of the internal heat exchanger can be controlled even more precisely in this way.

A second bypass comprising at least one third expansion element may be formed in the cooling circuit, in which case the second bypass

bypasses the expansion element downstream of the condenser and upstream of the internal heat exchanger and the refrigerant can be metered by means of the third expansion element in such a manner that a suction gas temperature and/or a suction gas pressure of the refrigerant can be controlled upstream of the compressor on the low-pressure side of the cooling circuit. In this way, potential overheating and damage of the compressor, which may be a compressor device, for example, can be prevented among other things. Consequently, gaseous refrigerant located upstream of the compressor can be cooled via the second bypass by actuation of the third expansion element by adding still-liquid refrigerant. The third expansion element can be actuated by means of a control device which itself is coupled to a pressure and/or temperature sensor in a cooling circuit upstream of the compressor. Particularly advantageously, a suction gas temperature of $\leq 30\text{ }^{\circ}\text{C}$ can be set via the second bypass. Also, the refrigerant can be metered in such a manner that an operating time of the compressor can be controlled. On principle, it is disadvantageous for the compressor or compressor device to be switched on and off repeatedly. A service life of a compressor can be prolonged if the compressor operates for longer periods of time. A refrigerant can be led past the expansion element or the condenser via the second bypass in order to delay an automated deactivation of the compressor and to prolong an operating time of the compressor, for example.

Another bypass comprising at least one other expansion element may be formed in the cooling circuit, the other bypass bypassing the compressor downstream of the compressor and upstream of the condenser in such a manner that a suction gas temperature and/or a suction gas pressure of the refrigerant can be controlled upstream of

the compressor on the low-pressure side of the cooling circuit and/or that a pressure difference between the high-pressure side and a low-pressure side of the cooling circuit can be equalized. The second bypass may additionally be equipped with a settable or controllable valve, such as a magnetic valve. Connecting the high-pressure side and the low-pressure side via the other expansion element ensures that the gaseous refrigerant thus compressed gradually flows from the high-pressure side to the low-pressure side of the cooling circuit in the event of a system standstill. This also ensures gradual pressure equalization between the high-pressure side and the low-pressure side even when the expansion element is closed. A cross-section of the other expansion element may be dimensioned in such a manner that the refrigerant flowing from the high-pressure side to the low-pressure side has only a marginal impact on the normal operation of the cooling device. At the same time, a gaseous refrigerant located upstream of the compressor may be cooled by adding the liquid refrigerant via the other bypass.

Furthermore, the internal heat exchanger may be realized as a sub-cooling section or a heat exchanger, in particular a plate heat exchanger. The sub-cooling section may simply be realized by two line sections of the cooling circuit that are in contact with each other.

The expansion element may have a throttle and a magnetic valve, in which case refrigerant can be metered via the throttle and the magnetic valve. The throttle may be a settable valve or a capillary via which refrigerant is routed by means of the magnetic valve. The magnetic valve itself may be actuated by means of a control device.

Also, the temperature control device may comprise a control device comprising at least one pressure sensor and/or at least one tempera-

ture sensor in the cooling circuit, in which case a magnetic valve can be actuated by means of the control device as a function of a measured temperature and/or pressure. The control device may comprise means for data processing which process sets of data from sensors and control the magnetic valves. In this case, a function of the cooling device may also be adjusted to the refrigerant used via an appropriate computer program, for example. Furthermore, the control device may signal a malfunction and initiate a shut-down of the test chamber, if necessary, in order to protect the test chamber and the test material from damage due to critical or undesirable operating states of the test chamber.

When used according to the invention, a refrigerant consisting of a refrigerant mixture composed of a mass fraction of carbon dioxide of 20 to 74 mass percent, a mass fraction of pentafluoroethane of 8 to 65 mass percent, and a mass fraction of at least one other component, the other component being fluoromethane, the refrigerant is used to condition air in a test space of a test chamber, the test space serving to receive test material and being sealable against an environment and temperature-insulated, a cooling device of a temperature control device of the test chamber comprising a cooling circuit with the refrigerant, a heat exchanger, a compressor, a condenser and an expansion element is used to establish a temperature in a temperature range of $-60\text{ }^{\circ}\text{C}$ to $+180\text{ }^{\circ}\text{C}$, preferably $-70\text{ }^{\circ}\text{C}$ to $+180\text{ }^{\circ}\text{C}$, particularly preferably $-80\text{ }^{\circ}\text{C}$ to $+180\text{ }^{\circ}\text{C}$, within the test space.

The refrigerant can be cooled by means of an internal heat exchanger of the cooling circuit, which is connected to a high-pressure side of the cooling circuit upstream of the expansion element and downstream of the condenser and to a low-pressure side of the cooling

circuit upstream of the compressor and downstream of the heat exchanger, of the high-pressure side, the cooling of the refrigerant of the high-pressure side by means of the internal heat exchanger being usable to lower an evaporation temperature at the expansion element. During lowering of the evaporation temperature of the refrigerant of the high-pressure side, a suction pressure of the refrigerant of the low-pressure side can be kept constant. A greater system complexity, such as in the form of additional control of the suction pressure and control of the expansion element as a function of the suction pressure, is not necessarily required in that case. In particular, the compressor may also be operated at constant output irrespective of an operating state of the cooling circuit. When piston pumps are used as compressors in particular, it is essential for them to be in operation for long periods of time and at a constant speed in order to achieve a long service life.

The refrigerant of the high-pressure side may be cooled by the refrigerant of the low-pressure side at a constant suction pressure on the low-pressure side by means of the internal heat exchanger. Consequently, the refrigerant can evaporate at constant suction pressure on an evaporation section of the cooling circuit from the expansion element up to and including the internal heat exchanger. If the suction pressure or evaporation pressure of the refrigerant is constant, the refrigerant can evaporate from the expansion element at a low evaporation temperature to the internal heat exchanger at a high evaporation temperature according to the temperature glide of the refrigerant. The dew point temperature resulting from the temperature glide may be higher than the temperature of the fluid to be cooled or of the air in the test space. Once an evaporation temperature of the refrigerant is equal to the temperature of the air to be

cooled in the test space at the same suction pressure, the air cannot be cooled any further. However, the dew point temperature reached in the other heat exchanger is lower than the liquid temperature of the refrigerant on the high-pressure side of the internal heat exchanger, which means that a liquid temperature of the refrigerant can be reduced further. Accordingly, an evaporation temperature downstream of the expansion element can be lowered without changing the suction pressure, allowing further cooling of the air in the test space to be achieved.

Thus, a first portion of the refrigerant routed via the expansion element can be evaporated in the heat exchanger and a second portion of the refrigerant can be evaporated in the internal heat exchanger. An evaporation section of the cooling circuit within which the refrigerant evaporates may extend from the expansion element as far as to the internal heat exchanger. The evaporation section may run through the internal heat exchanger, in which case a dew point of the refrigerant may be located at an exit of the internal heat exchanger upstream of the compressor. A first portion/second portion ratio may change during operation of the cooling circuit as a function of a temperature in the test space or at the heat exchanger. For example, a comparatively large temperature difference between the temperature of the heat exchanger and a temperature in the test space may lead to accelerated heating of the refrigerant in the heat exchanger, which results in a shift of the dew point of the refrigerant toward an entry of the internal heat exchanger or an exit of the heat exchanger upstream of the compressor. This kind of shift of the dew point can be tolerated as long as no comparatively low temperature or target temperature has been established in the test space yet. When the temperature of the heat exchanger approaches the temper-

ature in the test space, the dew point shifts and the second portion thus grows relative to the first portion of the refrigerant.

The evaporation temperature of the refrigerant of the high-pressure side can be lowered in a self-controlled manner. Depending on the
5 temperature at the heat exchanger, refrigerant no longer evaporating can be discharged from the heat exchanger in the flow direction because the temperature at the heat exchanger is no longer sufficient to cause a phase transition of the refrigerant in this case. Thus, wet vapor or liquid refrigerant is re-evaporated in the internal heat
10 exchanger because here a temperature difference between the high-pressure side and the low-pressure side can always be greater than at the heat exchanger. If a temperature of the liquid refrigerant upstream of the expansion element is reduced by means of the internal heat exchanger by the heat exchange at the internal heat exchanger,
15 the energy density of the refrigerant upstream of the expansion element and the temperature difference thus achievable at the heat exchanger increase. The interaction of the expansion element, the heat exchanger and the internal heat exchanger does not have to be controlled, in principle.

20 Particularly advantageously, the cooling device is operated exclusively below the critical point of the refrigerant. If the cooling device is operated below the triple point of the refrigerant, reaching of a supercritical state of the refrigerant can be precluded. Thus, the cooling device does not have to be configured for operation in the
25 supercritical state, which saves costs for production of the cooling device.

In particular, the constant suction pressure may also be maintained during lowering of the evaporation temperature of the refrigerant of

the high-pressure side by means of the internal heat exchanger. Accordingly, the cooling of the refrigerant of the high-pressure side via the internal heat exchanger can also be exploited in part or exclusively to lower an evaporation temperature of the refrigerant at
5 the expansion element.

A dew point temperature of the refrigerant may be higher than a minimum temperature of the temperature range. In the test chambers known from the state of the art, the minimum temperature of the temperature range can no longer be established with a refrigerant of
10 this kind in that case, but a comparatively higher minimum temperature, which substantially corresponds to the dew point temperature of the refrigerant. In the test chamber according to the invention, however, a refrigerant whose dew point temperature is higher than an achievable minimum temperature of the temperature range can be
15 used because the liquefied refrigerant on the high-pressure side can be cooled by means of the internal heat exchanger, which means that an evaporation temperature of the refrigerant at the expansion element can be comparatively lower.

The refrigerant can be evaporated absolutely at a suction pressure or
20 evaporation pressure in a pressure range of 0.3 to 5 bar. Use of the refrigerant within that pressure range allows cost-effective production of the cooling circuit because no special pressure-resistant modules and components have to be used to construct the low-pressure side of the cooling circuit.

25 Also, the refrigerant can be condensed absolutely at a condensation pressure in a pressure range of 5 to 35 bar. Here, too, the high-pressure side can be constructed using modules and components that do not have to be adapted to comparatively higher pressures.

Other embodiments of a use are apparent from the description of features of the claims depending on device claim 1.

Hereinafter, preferred embodiments of the invention will be explained in more detail with reference to the accompanying drawings.

- 5 **Fig. 1** is a pressure-enthalpy diagram for a refrigerant;
- Fig. 2** is a schematic illustration of a first embodiment of a cooling device;
- Fig. 3** is a schematic illustration of a second embodiment of a cooling device;
- 10 **Fig. 4** is a schematic illustration of a third embodiment of a cooling device;
- Fig. 5** is a schematic illustration of a fourth embodiment of a cooling device;
- Fig. 6** is a schematic illustration of a fifth embodiment of a cooling device.
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Fig. 2 shows a first embodiment of a cooling device 10 of a test chamber (not shown). Cooling device 10 comprises a cooling circuit 11 with a refrigerant, a heat exchanger 12, a compressor 13, a condenser 14 and an expansion element 15. Condenser 14 is cooled by another cooling circuit 16 in the case at hand. Heat exchanger 12 is disposed in a test space (not shown) of the test chamber. Furthermore, cooling circuit 11 has a high-pressure side 17 and a low-pressure side 18, to which an internal heat exchanger 19 is connected.

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Fig. 1 shows a pressure-enthalpy diagram (log p/h diagram) for the refrigerant circulating in cooling circuit 11, the refrigerant being a zeotropic refrigerant. According to a combined view of **Figs. 1** and **2**, starting from position A, the refrigerant upstream of compressor 13 is aspirated and compressed, whereby a pressure is achieved downstream of compressor 13 according to position B. The refrigerant is compressed by means of compressor 13 and is subsequently liquefied in condenser 14 according to position C. The refrigerant passes through internal heat exchanger 19 on high-pressure side 17, where it is cooled further, position C' upstream of expansion element 15 thus being reached. By means of internal heat exchanger 19, the portion of the wet vapor area (positions E to E') not usable in heat exchanger 12 can be used to further reduce a temperature of the refrigerant (positions C' to C). At expansion element 15, the refrigerant is relaxed (positions C' to D') and partially liquefied in heat exchanger 12 (positions D' to E). Then, the wet vapor of the refrigerant enters internal heat exchanger 19 on low-pressure side 18, where the refrigerant is re-evaporated until the dew-point temperature or the dew point of the refrigerant is reached at position E'. Hence, a first subsection 20 of an evaporation section 22 of the refrigerant runs through heat exchanger 12, a second subsection 21 of evaporation section 22 running through internal heat exchanger 19. The essential aspect is that a suction pressure of compressor 13 on low-pressure side 18 is kept constant on evaporation section 22 even if the evaporation temperature at expansion element 15 changes.

The refrigerant is a refrigerant mixture composed of a mass fraction of carbon dioxide of 20 to 74 mass percent, a mass fraction of pentafluoroethane of 8 to 65 mass percent, and a mass fraction of at

least one other component, the other component being fluoro-methane. In principle, it is possible for the refrigerants listed in the Table above to be used in cooling circuit 11 and the cooling circuits described below.

5 **Fig. 3** shows a schematic illustration of a simplest embodiment of a cooling device 23, cooling device 23 being self-controlling. Cooling device 23 comprises a cooling circuit 24 with a heat exchanger 25, a compressor 26, a condenser 27, an expansion element 28 and an internal heat exchanger 29. Depending on a temperature at heat
10 exchanger 25, refrigerant not fully evaporated escapes from heat exchanger 25 because the temperature at heat exchanger 25 or in a test space (not shown) is no longer high enough to cause a phase transition. In this case, refrigerant still liquid is re-evaporated in internal heat exchanger 29 because a temperature difference there
15 has to be greater than at heat exchanger 25 at all times. Once the temperature of the liquid refrigerant upstream of expansion element 28 has been reduced by heat exchange in internal heat exchanger 29, the energy density and the temperature difference achievable with it at heat exchanger 25 increase. Cooling device 23 does not
20 require elaborate control by way of sensors etc.

Fig. 4 shows a cooling device 30 which differs from the cooling device of **Fig. 3** in that it has a first bypass 31 and a second bypass 32. A controllable second expansion element 33 is disposed in first bypass 31, first bypass 31 being configured as an additional internal
25 cooling system 34. First bypass 31 is connected to cooling circuit 24 immediately downstream of condenser 27 upstream of internal heat exchanger 29 and downstream of heat exchanger 25 and upstream of internal heat exchanger 29. First bypass 31 thus bypasses expansion element 28 with heat exchanger 25, internal heat exchanger 29

being suppliable with evaporating refrigerant via second expansion element 33. A suction gas mass flow introduced into internal heat exchanger 29 can be cooled additionally by means of first bypass 31 in case of high suction gas temperatures, which may be caused by heat exchanger 25. In this way, evaporation of refrigerant upstream of the expansion element can be precluded. Hence, first bypass 31 can be used to react to changing load cases of cooling device 30. Second bypass 32 has a third expansion element 35 and is connected to cooling circuit 24 downstream of condenser 27 and upstream of internal heat exchanger 29 and downstream of internal heat exchanger 29 and upstream of compressor 26. This allows a suction gas mass flow upstream of compressor 26 to be reduced far enough via second bypass 32 to avoid inadmissibly high final compression temperatures.

Fig. 5 shows a cooling device 36 which differs from the cooling device of **Fig. 4** in that it has another cooling circuit 37. Other cooling circuit 37 serves to cool a condenser 38 of a cooling circuit 39. Condenser 38 is realized as a cascade heat exchanger 40 in the case at hand. Furthermore, cooling circuit 39 has another bypass 41 having another expansion element 42. Other bypass 41 is connected to cooling circuit 39 downstream of compressor 26 and upstream of condenser 38 and downstream of internal heat exchanger 29 and upstream of compressor 26. Thus, refrigerant not yet liquefied but compressed can flow back to upstream of compressor 26 via other bypass 41, whereby a suction gas temperature and/or a suction gas pressure of the refrigerant can be controlled.

Fig. 6 shows a cooling device 30 having a cooling circuit 44 and another cooling circuit 45 and, in particular, an internal heat exchanger 46 in cooling circuit 44. In the case at hand, a heat ex-

changer 47 is disposed in a temperature-insulated test space of a test chamber (not shown).

Claims

1. A refrigerant for a cooling device (10, 23, 30, 36, 43) having a cooling circuit (11, 24, 39, 44) comprising at least one heat exchanger (12, 25, 47) in which the refrigerant undergoes a phase transition, the refrigerant being a refrigerant mixture composed of a mass fraction of carbon dioxide (CO_2), a mass fraction of pentafluoroethane (C_2HF_5), and a mass fraction of at least one other component,
10 characterized in that
the mass fraction of carbon dioxide in the refrigerant mixture is 20 to 74 mass percent, the mass fraction of pentafluoroethane being 8 to 65 mass percent, the other component being fluoromethane (CH_3F).
- 15 2. The refrigerant according to claim 1,
characterized in that
a mass fraction of fluoromethane in the refrigerant mixture is 7 to 25 mass percent.
3. The refrigerant according to claim 2,
20 characterized in that
the mass fraction of fluoromethane is 13 to 21 mass percent.
4. The refrigerant according to claim 3,
characterized in that
the mass fraction of fluoromethane is 15 to 19 mass percent.

5. The refrigerant according to any one of the preceding claims,
characterized in that
the mass fraction of carbon dioxide is 26 to 34 mass percent.
6. The refrigerant according to claim 5,
5 characterized in that
the mass fraction of carbon dioxide is 28 to 51 mass percent.
7. The refrigerant according to any one of the preceding claims,
characterized in that
the mass fraction of pentafluoroethane is 49 to 57 mass percent.
- 10 8. The refrigerant according to claim 7,
characterized in that
the mass fraction of pentafluoroethane is 51 to 55 mass percent.
9. The refrigerant according to any one of the preceding claims,
characterized in that
15 the refrigerant has a temperature glide in a range of 4 K to 16 K.
10. The refrigerant according to any one of the preceding claims,
characterized in that
the refrigerant has a relative CO₂ equivalent of < 2300 over
100 years.
- 20 11. The refrigerant according to any one of the preceding claims,
characterized in that
the refrigerant is nonflammable.

12. A test chamber for conditioning air, the test chamber comprising
a test space which serves to receive test material and which can
be sealed against an environment and is temperature-insulated,
and a temperature control device for controlling the temperature
5 of the test space, a temperature in a temperature range of
−70 °C to + 180 °C being establishable within the test space by
means of the temperature control device, the temperature control
device having a cooling device (10, 23, 30, 36, 43) comprising
a cooling circuit (11, 24, 39, 44) with a refrigerant according to
10 any one of the preceding claims, a heat exchanger (12, 25, 47),
a compressor (13, 26), a condenser (14, 27, 38) and an expansion
element (15, 28).
13. The test chamber according to claim 12,
characterized in that
15 the cooling circuit (11, 24, 39, 44) has an internal heat exchanger
(19, 29, 46), the internal heat exchanger being connected to a high-pressure side (17) of the cooling circuit upstream
of the expansion element (15, 28) and downstream of the
condenser (14, 27, 38) and to a low-pressure side (18) of the
20 cooling circuit upstream of the compressor (13, 26) and downstream
of the heat exchanger (12, 25, 47).
14. The test chamber according to claim 12 or 13,
characterized in that
the heat exchanger (12, 25, 47) is dimensioned in such a manner
25 that only part of the refrigerant can evaporate in the heat exchanger.

15. The test chamber according to any one of claims 12 to 14,
characterized in that
the condenser (14, 27, 38) is realized as a cascade heat ex-
changer (40) of another cooling circuit (36, 43) of the cooling
5 device.
16. The test chamber according to any one of claims 12 to 15,
characterized in that
the temperature control device has a heating device comprising a
heater and a heating heat exchanger in the test space.
- 10 17. The test chamber according to any one of claims 12 to 16,
characterized in that
a first bypass (31) having at least one controllable second expan-
sion element (33) is realized in the cooling circuit (24, 39, 44),
the first bypass being connected to the cooling circuit upstream
15 of the internal heat exchanger (29, 46) and downstream of the
condenser (27, 38), the first bypass being realized as a control-
lable additional internal cooling system (34).
18. A use of a refrigerant consisting of a refrigerant mixture com-
posed of a mass fraction of carbon dioxide (CO_2) of 20 to
20 74 mass percent, a mass fraction of pentafluoroethane (C_2HF_5) of
8 to 65 mass percent and a mass fraction of at least one other
component, the other component being fluoromethane (CH_3F),
for conditioning air in a test space of a test chamber, the test
space serving to receive test material and being sealed against an
25 environment and temperature-insulated, a cooling device (10,
23, 30, 36, 43) of a temperature control device of the test
chamber, which comprises a cooling circuit (11, 24, 39, 44)

with the refrigerant, a heat exchanger (12, 25, 47), a compressor (13, 26), a condenser (14, 27, 38) and an expansion element (15, 25, 28), being used to establish a temperature in a temperature of -60°C to $+180^{\circ}\text{C}$, preferably -70°C to $+180^{\circ}\text{C}$, particularly preferably -80°C to $+180^{\circ}\text{C}$, within the test space.

19. The use according to claim 18, characterized in that an internal heat exchanger (19, 29, 46) of the cooling circuit (11, 24, 39, 44) connected to a high-pressure side (17) of the cooling circuit upstream of the expansion element (15, 25, 28) and downstream of the condenser (14, 27, 38) and to a low-pressure side (18) of the cooling circuit upstream of the compressor (13, 26) and downstream of the heat exchanger (12, 25, 47) is used to cool the refrigerant of the high-pressure side, the cooling of the refrigerant of the high-pressure side by means of the internal heat exchanger being exploited to lower an evaporation temperature at the expansion element.

20. The use according to claim 18 or 19, characterized in that the refrigerant of the high-pressure side (17) is cooled by the refrigerant of the low-pressure side (18) at constant suction pressure on the low-pressure side by means of the internal heat exchanger (19, 29, 46).