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REFRIGERATION PROCESS

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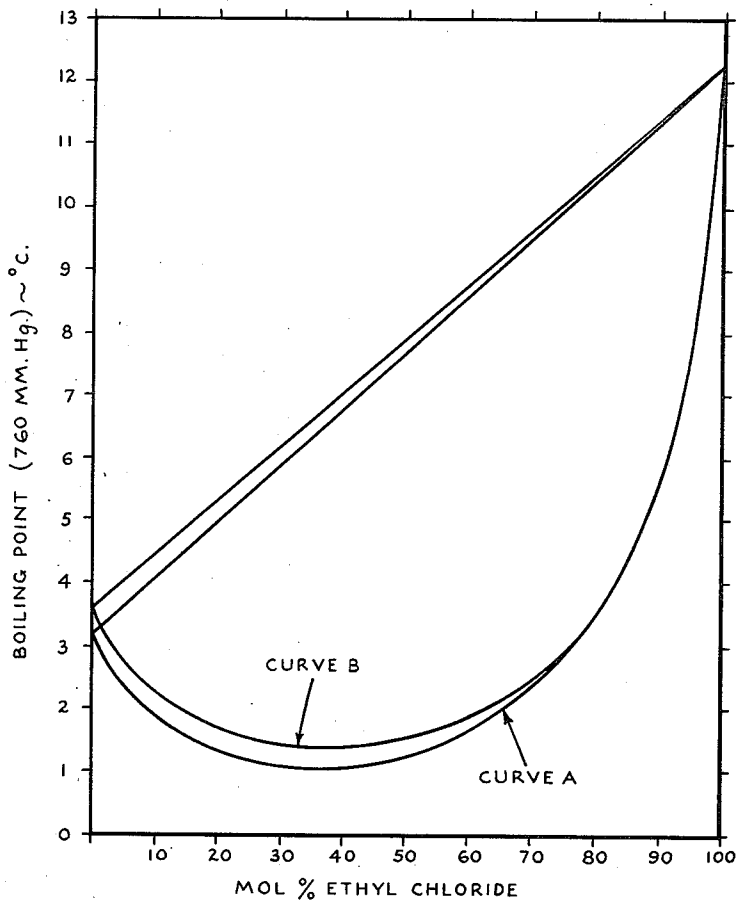

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REFRIGERATION PROCESS

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This invention relates to azeotropic compositions containing dichlorotetrafluoroethane. These fluorine compounds are useful as refrigerants and as aerosol propellants.

Dichlorotetrafluoroethanes are commercially produced as mixtures of the two isomers, one representative mixture containing mainly the symmetrical isomer $CClF_2CClF_2$ with a few percent of the unsymmetrical isomer CCl_2FCF_3, and another typical mixture containing mainly the unsymmetrical isomer with a few percent of the symmetrical isomer. The boiling points of the pure isomers are 3.64° C. and 3.14° C. for the symmetrical and unsymmetrical isomers respectively; the boiling points of commercial products being intermediate these limits. Since the difference in boiling points of the two isomers is so small, minor composition variations are of no practical importance, and accordingly unless otherwise indicated the term "dichlorotetrafluoroethane" as used herein is intended to embrace substantially pure CCl_2FCF_3 or substantially pure $CClF_2CClF_2$ or mixtures thereof in any proportions.

Objects of the invention include provision of dichlorotetrafluoroethane-ethyl chloride mixtures which boil at substantially constant temperature and function as a single substance. These mixtures are useful as refrigerants and as aerosol propellants. As refrigerants, such mixtures at lower cost afford increased pressure and greater refrigerating capacity with respect to refrigerating apparatus designed for use of dichlorotetrafluoroethane alone, and as aerosols such mixtures at lower cost provide increased pressure, and improved solubility for common aerosol ingredients.

Commercial dichlorotetrafluoroethanes boil in the range of 3.2 to 3.6° C. at normal atmospheric pressure, 760 mm. of Hg. In accordance with the invention it has been found that mixtures consisting of about 63–64 mol percent of commercial dichlorotetrafluoroethanes and 36–37 mol percent of ethyl chloride form azeotropes boiling in the range of about 1.1 and 1.4° C. Further, it has been found that the boiling point composition curve is very flat and that mixtures containing ethyl chloride in the range of about 22–50 mol percent all boil between about 1.1 and 1.6° C., and that with regard to particular specific mixtures within the indicated 22–50 mol percent range, boiling points of such mixtures may vary only to the extent of about 0.2° C.

The boiling points of mixtures under consideration were determined with the following results:

Table I

Mol percent ethyl chloride in solution:	Boiling point (760 mm. Hg at 0° C.), ° C.
0.0	3.2
12.0	1.8
21.4	1.3
39.3	1.1
51.1	1.3
73.4	2.7
88.1	5.1
100.0	12.2

In the foregoing tests, the specific material employed was a mixture of ethyl chloride and dichlorotetrafluoroethane which, as indicated by the 3.2° C. boiling point, was mostly CCl_2FCF_3 plus a few percent of $CClF_2CClF_2$. The data of Table I are shown graphically by curve A of the attached drawing.

Table II

Mol percent ethyl chloride in solution:	Boiling point (760 mm. Hg at 0° C.), ° C.
0.0	3.6
6.0	2.7
31.6	1.4
34.9	1.4
46.0	1.5
51.1	1.6
79.7	3.4
92.2	6.4
100.0	12.2

In the tests of Table II, the specific material employed was a mixture of ethyl chloride and dichlorotetrafluoroethane which, as indicated by the 3.6° C. boiling point, was nearly pure $CClF_2CClF_2$ containing very little CCl_2FCF_3. The data of Table II are shown graphically by curve B of the drawing.

The above data and curves show that minimum-boiling azeotropes are formed each with approximately 36–37 mol percent of ethyl chloride. The ethyl chloride-commercial dichlorotetrafluoroethane mixtures indicated afford the further advantage that there are only minor differences in boiling point when the composition is varied over a considerable range on either side of the 36–37 mol percent ethyl chloride compositions. Mixtures containing between about 22 to about 50 mol percent of ethyl chloride all boil between about 1.1° C. and about 1.6° C. It is noted that in both tests, each dealing with a mixture containing a specific dichlorotetrafluoroethane, boiling points of the approximately 36–37 mol percent ethyl chloride compositions fall in the range of about 1.1–1.4° C., and temperature variation over the approximately 22–50 mol percent ethyl chloride range is only about 0.2° C. Hence, essentially no fractionation occurs on distillation over the approximate 22–50 ethyl chloride mol percent range. Moreover, in the case of other mixtures containing other specific dichlorotetrafluoroethanes, e.g. a mixture of ethyl chloride and a dichlorotetrafluoroethane consisting of say equal weight or mol percent parts of the isomers, the just mentioned boiling point range of 1.1–1.4° C. and temperature variation range of only about 0.2° C. hold likewise.

For most advantageous refrigerant use, it is preferred to employ compositions at or close to the 36–37 mol percent ethyl chloride content in order to avoid even minor differences in liquid and vapor composition. However, in aerosol propellant use, differences in liquid and vapor composition are of lesser consequence, hence the whole range of 22–50 mol percent ethyl chloride composition may be employed to advantage. To insure non-flammability, compositions containing at least about 50 mol percent of dichlorotetrafluoroethane are preferred.

Apart from use of the indicated amounts of dichlorotetrafluoroethane and ethyl chloride, make-up of the compositions of the invention requires no special procedures. The dichlorotetrafluoroethane and the ethyl chloride employed should be substantially pure, and contain no substances deleteriously affecting use either as refrigerants or aerosol propellants. The compositions of the invention are chemically non-reactive, non-inflammable and substantially non-toxic.

It is known in the refrigerating art, with respect to equipment designed to utilize a particular refrigerant e.g. dichlorotetrafluoroethane, that it is often desirable to increase refrigerating capacities, and that, in general, capacity is proportional to the pressure of the gas at the

suction side of the compressor. However, for a given item of equipment it is not possible to use a referigerant having a boiling point too far below that for which the equipment was designed because pressures would be too high and power input required would overload the compressor motor. A moderate increase in pressure is permissible, and use of a slightly lower boiling refrigerant affords increased capacity, other operating factors remaining constant. Substitution of the compositions of the invention for dichlorotetrafluoroethane in apparatus designed for use of dichlorotetrafluoroethane alone as the refrigerant effects an increased refrigerating capacity of about 15%. Similarly, if a given refrigerating unit is equipped with motor designed to operate compressor at a given speed with normal 60 cycle current, use of such motor with 50 cycle current will lead to decreased motor speed and subsequent decrease in refrigerating capacity. The substitution of the compositions of the invention will substantially compensate for the decreased efficiency and restore a unit designed for dichlorotetrafluoroethane alone to near normal 60 cycle efficiency. The compositions of the invention may be used as refrigerants in any cooling systems in which cooling is effected by evaporation and expansion of liquid refrigerants such as domestic and commercial refrigerators, and domestic or commercial cooling or air-conditioning systems. As is well known in the refrigerating art, in these systems the expanded gas is compressed and condensed to a liquid and is recycled to the expansion stage.

For aerosol use the products of the invention supply distinct advantages. Whereas commercial dichlorotetrafluoroethanes boil in the range of 3.2–3.6° C. and have vapor pressures in the range of 27.6–28.1 p.s.i.g. at 70° F., such pressures are not sufficient to propel the aerosol product to give the desired fine particle size in the spray. Consequently it is usually necessary to mix dichlorotetrafluoroethane with another higher pressure propellant to obtain the desired pressure. The propellants customarily used are dichlorodifluoromethane (CCl_2F_2) and monochlorodifluoroethane (CH_3CClF_2) each of which is more expensive than ethyl chloride. The compositions of the invention, therefore, supply increased pressure at reduced cost. A further advantage of the invention compositions is that in the event of a vapor phase leak in the aerosol container, the composition of the remaining liquefied gas propellant remains unchanged. When mixed propellants are used which are not of azeotropic composition the more volatile component is more readily lost .

Further advantage afforded by the invention is increased miscibility of common organic aerosol ingredients in the 36–37 mol percent ethyl chloride compositions over miscibility in dichlorotetrafluoroethanes alone. For example, whereas only about 21% by weight of a dichlorotetrafluoroethane alone will dissolve in 75.6% strength ethanol, about 28% of such compositions will dissolve in 75.6% strength ethanol. Similarly, whereas only about 12% by weight of a dichlorotetrafluoroethane alone will dissolve in 68.5% strength ethanol, about 17.5% by weight of such compositions will dissolve in the same

strength alcohol. This feature permits lower strength alcohols to be used without sacrificing miscibility with the propellant; for example lower strength alcohols are desired to reduce astringency of cosmetic aerosol preparations. To express the advantage in a different way, assuming 20% of propellant in an aerosol formulation is required to produce the desired pressure, 75% strength alcohol is required to be miscible with a dichlorotetrafluoroethane alone, whereas only 70% strength alcohol is required to be miscible with the compositions under consideration. This advantage increases within limits as the percent propellant required in the formulation is decreased. Other more striking differences in solubility of the 36–37 mol percent ethyl chloride compositions are as follows:

Table III

	Solubility percent in 36–37 mol percent C_2H_5Cl compositions	Solubility percent in commercial dichlorotetrafluoroethane dominantly $CClF_2CF_3$
Oleyl alcohol	completely miscible	6.5
Cottonseed oil	do	2.1
Tricresylphosphate	do	5.0

As compared with use of dichlorotetrafluoroethane alone, for either refrigerant or aerosol propellant purposes, the costwise advantages afforded by the invention are marked. Thus, by use of the compositions of the invention, not only are there obtained substantially improved pressure conditions, but in many instances as much as fifty mol percent of the relatively expensive chlorofluorocarbon may be replaced by the relatively inexpensive ethyl chloride.

I claim:

1. The process of producing refrigeration which comprises evaporating, in the vicinity of a body to be cooled, a mixture consisting of dichlorotetrafluoroethane and ethyl chloride which mixture boils at a substantially constant temperature and functions as a substantially single substance, and in which mixture the mol percent of ethyl chloride is in the range of 22–50, and subsequently condensing the said mixture.

2. The process of producing refrigeration which comprises evaporating, in the vicinity of a body to be cooled, a mixture consisting of dichlorotetrafluoroethane and approximately 36–37 mol percent of ethyl chloride which mixture boils at substantially constant temperature and functions as a substantially single substance, and subsequently condensing the said mixture.

References Cited in the file of this patent

UNITED STATES PATENTS

2,101,993	Fleischer	Dec. 14, 1937
2,255,584	Hubacker	Sept. 9, 1941
2,449,114	Gebauer	Sept. 14, 1948
2,524,590	Boe	Oct. 3, 1950
2,630,686	Reed et al.	Mar. 10, 1953