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REFRIGERATOR EMBODYING STABILIZED MIXTURES OF OIL AND ALIPHATIC HALIDES

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1

This invention relates to mechanical refrigerators embodying an aliphatic halide refrigerant medium and a petroleum oil lubricant in combination with a stabilizing additive.

It has been found that a mixture of halogenated aliphatic compound and petroleum oil, particularly as used in a mechanical refrigerator, is subject to a deteriorative reaction, particularly pronounced when subjected to heating during compression. Even though the system has been dried exhaustively to remove any possible traces of moisture, it has been found that the mixture will react to produce sludge, gums, and the so-called "copper-plating" wherein copper from the copper tubing, copper conductors and other copper members of the refrigerator are deposited on steel or other metallic parts. As the mixture of petroleum lubricant and the refrigerant is subjected to still higher temperatures, a charring of the oil will occur. Other undesirable reactions take place as will be set forth hereinafter. Tests with previously suggested additives for refrigerants have shown that they are not particularly effective since most of such additives simply absorb excessive moisture and react with free acids. However, at high temperatures, the mixture is reactive in the refrigerator systems to produce the undesirable results recited.

The object of this invention is to provide a stabilized mixture of petroleum oil, and a halogenated aliphatic refrigerant.

A further object of the invention is to provide for introducing into a sealed refrigerator system containing the halogenated aliphatic refrigerant and petroleum oil a small amount of boric anhydride.

Another object of the invention is to provide a refrigerator comprising a sealed system wherein a mixture of halogenated aliphatic refrigerant and a lubricating oil is in contact with boric anhydride as a stabilizer.

Other objects of the invention will in part be obvious and will in part appear hereinafter. For a better understanding of the nature and objects of the invention, reference should be had to the following detailed description.

It has been discovered that boric anhydride produces an unexpected stabilizing effect when it is placed in contact with a mixture of halogenated aliphatic refrigerant and petroleum oil lubricant, all enclosed within a sealed refrigerator system. Mechanical refrigerators are commonly constructed with a sealed system including a compressor composed of an electric motor having copper wire windings, steel shafts and compressor parts, tubing or the equivalent comprising a condenser where the compressed vapors or

2

refrigerant liquefy, a capillary tube or an expansion valve or the like controlling the flow of liquid refrigerant, and an evaporator in which the liquid refrigerant vaporizes and thereby produces cooling. The vapor of the refrigerant passes over the motor and its copper windings thereby cooling them. In the compressor, the refrigerant vapors are compressed thereby becoming highly heated. The refrigerant possesses no substantial lubricating characteristics and it is necessary to have present a small amount of oil which is entrapped or carried by the vapors of refrigerant to the moving parts of the compressor and motor to provide for lubricating the bearing surfaces. The coppering effect has been found to occur within such a system because of some reaction whose mechanism is not completely known. It causes copper to be carried over from some of the windings of the motor and plated on the steel parts. In some cases, coppering can extend to the metallic bearing parts of the compressor so as to cause bearing failures and may reach the capillary tube wherein the expansion of the fluid refrigerant is controlled. A sludge or gum may be produced by reaction between the petroleum oil and the aliphatic halide refrigerant particularly at elevated temperatures of above 100° C. Sludge can clog the capillary tube and thereby cause improper functioning of the refrigerator.

Heretofore, the sealed systems were charged with petroleum oil and aliphatic halide refrigerants dried to predetermined extent to prevent the freezing of small amounts of water at critical points of the system. However, investigation indicates that minute amounts of water probably cause only slight corrosion. More highly improved and exhaustive dehydration processes have been put into operation so that normal household refrigerators for instance very rarely suffer deterioration from corrosion or copper plating, but it appears that the highly dried mixture of oil and refrigerant will char more rapidly at elevated temperatures. More recently, it has been discovered that higher compressor temperatures which are necessitated under some conditions cause a reaction to occur between the aliphatic halide and petroleum oil, even within a highly water freed system, whereby a deteriorative reaction occurs resulting in sludging and eventual charring of the oil as well as including the coppering effect.

In accordance with this invention, an amount of boric anhydride or boron oxide (B_2O_3) is disposed within the sealed system in contact with the mixture of petroleum oil and aliphatic halide refrigerant. The boric anhydride may be in the

form of a fused lump or other shape fastened to the walls of the system or it may comprise pellets or other particles disposed within a porous casing or cartridge permeable to the liquid. As little boric anhydride as 0.01% of the weight of the mixture of refrigerant and petroleum oil has some benefit. However, it is recommended that larger amounts of the order of 1% and higher of boric anhydride be employed to insure the most efficient results. Thus acids produced by decomposition of the aliphatic halide may react with the boric anhydride and deplete it. Consequently, a substantial amount of the boric anhydride should be disposed in the system even though only minute amounts of decomposition products may be expected to be produced. The boric anhydride may be disposed in several positions or places in the system. Thus a small amount may be placed in the line preceding the compressor, or in the path of the compressed refrigerant carrying small amounts of the oil or in the liquefied refrigerant coming from the condenser. There is no upper limit on the amount of the boric anhydride or the number of places at which it may be located.

Orthoboric acid (H_3BO_3) has been tried in the same manner as the boric anhydride with some benefit, but boric acid is not as effective as boric anhydride.

The following examples illustrate the benefits of the present invention. A mixture of approximately 50% by volume of a refrigerator petroleum lubricating oil and 50% by volume of dichlorodifluoromethane was prepared. The mineral oil was a highly refined naphthene oil having a viscosity of 150 seconds Saybolt at 100° F. The mixture was dried to remove all traces of moisture and other undesirable impurities. The mixture may be put in contact with steel and copper wire at room temperature up to about 100° C. without exhibiting any undesirable deterioration. However, when heated to a temperature of 175° C., the mixture became progressively darker, turning yellow in two days and eventually turning black and opaque within 60 days with considerable sludge formed. The copper wire was etched and a copper colored deposit appeared on the steel. At the end of the period, charring of the oil was observed.

Another sealed system was prepared duplicating the former but containing 1% by weight, based on the weight of the refrigerant oil mixture, of fused boric anhydride in the form of small pellets. The latter system was heated at a temperature of 175° C. for 450 days. At the end of this period, the color of the mixture had darkened very slightly, comparable to the condition of the first system at the end of the second day. There was no observable sludge, no etching of the copper and no coppery deposit on the steel in the second system.

The refrigerant medium may comprise one or more aliphatic halides or mixtures embodying the aliphatic halides as the major component. There may be disposed dehydrating agents or other additives in the refrigerant as is well known. Chlorofluoromethanes are the preferred refrigerant. The petroleum oil may comprise paraffin base or naphthene base oils or other known hydrocarbon lubricants.

The boric anhydride is ordinarily secured by fusing boric acid at an elevated temperature. However, it may be secured by other processes and is well known as such. For the purpose of this invention, it is desirable that the boric anhydride

be in pellets or other large particles that may be retained in place to prevent their being caught and transported to the capillaries where they may cause damage.

Since certain obvious changes may be made in the above procedure and different embodiments of the invention could be made without departing from the scope thereof, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

I claim as my invention:

1. In a refrigerator comprising a sealed system including a compressor, in combination, a supply of refrigerant medium disposed in the sealed system whereby vapors of the refrigerant medium are compressed in the compressor and condensed to a liquid, the refrigerant medium comprising a halogenated aliphatic compound, a petroleum oil for lubricating the compressor in admixture with the refrigerant medium, the mixture of petroleum oil and halogenated aliphatic compound being subject to deteriorative reaction in the system when heated by compression, and boric anhydride disposed in the system in contact with the mixture of petroleum oil and refrigerant medium to reduce deteriorative reaction.

2. The refrigerator of claim 1, wherein the refrigerant comprises a chlorofluoromethane.

3. In a refrigerator comprising a sealed system including a compressor, in combination, a supply of refrigerant medium disposed in the sealed system whereby vapors of the refrigerant medium are compressed in the compressor and condensed to a liquid, the refrigerant medium comprising a halogenated aliphatic compound, a petroleum oil for lubricating the compressor in admixture with the refrigerant medium, the mixture of petroleum oil and halogenated aliphatic compound being subject to deteriorative reaction in the system when heated by compression, and a porous casing permeable to the mixture containing a small amount of boric anhydride disposed in the system in contact with the mixture of petroleum oil and refrigerant medium to reduce deteriorative reaction.

4. In a refrigerator comprising a sealed system including a compressor, in combination, a supply of refrigerant medium disposed in the sealed system whereby vapors of the refrigerant medium are compressed in the compressor and condensed to a liquid, the refrigerant medium comprising a halogenated aliphatic compound, a petroleum oil for lubricating the compressor in admixture with the refrigerant medium, the mixture of petroleum oil and halogenated aliphatic compound being subject to deteriorative reaction in the system when heated by compression, and at least 0.01% of the weight of the mixture of a boron compound selected from the group consisting of boric anhydride and boric acid disposed in the system in contact with the mixture of petroleum oil and refrigerant medium to reduce deteriorative reaction.

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