June 28, 1960 B. J. EISEMAN, JR 2,943,057

INHIBITING COPPER PLATING IN CLOSED REFRIGERATION SYSTEMS

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Fig. 1

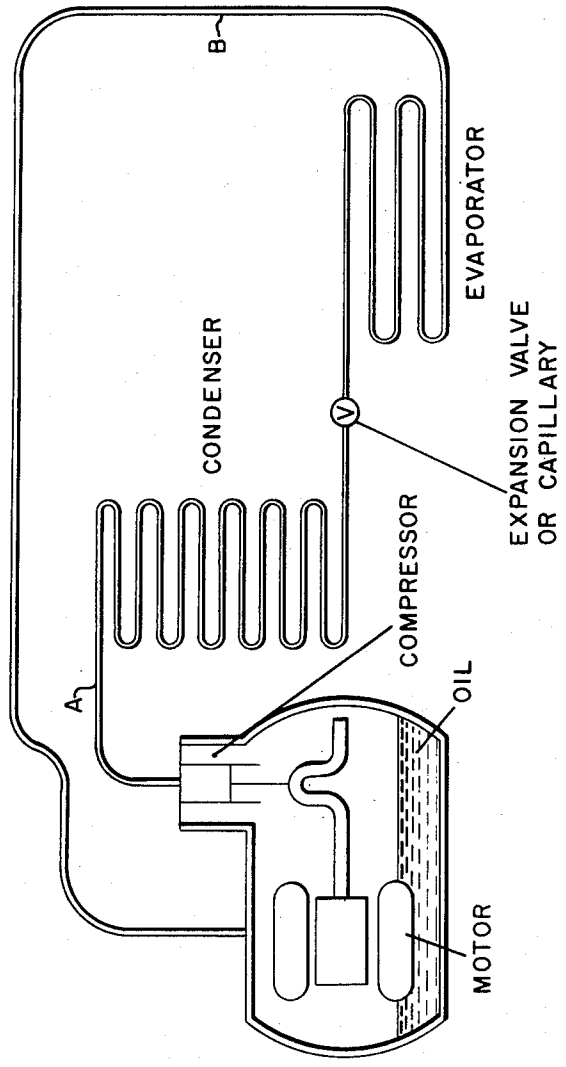

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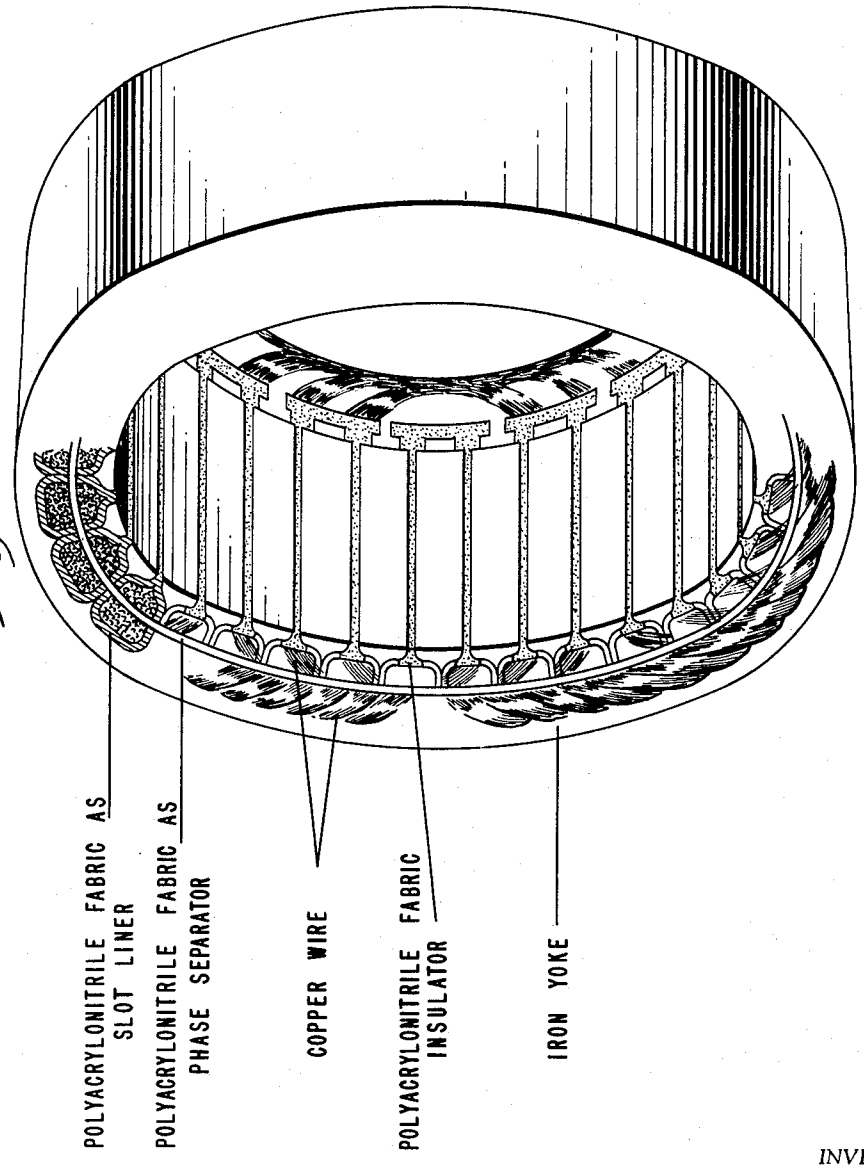
Fig. 2



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INHIBITING COPPER PLATING IN CLOSED REFRIGERATION SYSTEMS

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This invention relates to a refrigeration process and, particularly, to a process for operating a refrigeration system with a halogenated aliphatic hydrocarbon refrigerant and inhibiting copper plating in such system.

In the operation of refrigeration systems employing a halogenated aliphatic hydrocarbon containing chlorine, bromine, and/or fluorine as the refrigerant, corrosion and copper plating often develop. It is believed that the corrosion is due to breakdown of the refrigerant and the lubricant, resulting in part in the formation of reactive corrosion products. Such products and mixtures contact the mechanical elements and result in copper plating. Copper plating is the removal of copper from copper-containing mechanical elements (such as copper tubing, copper conductors and the like), and the deposition of such copper or of compounds having the appearance of copper, and of decomposition products on mechanical elements made of other metals (such as steel valves and pistons, bearings, and the like), causing failure of such mechanical elements and of the refrigeration system.

It is obvious that, if such corrosion and, particularly, such copper plating can be prevented or materially inhibited, the useful life of the mechanical elements and of the refrigeration system can be considerably prolonged. This problem has existed for many years, and those skilled in the art have proposed the addition of various substances to the refrigerants and to the lubricants to stabilize them or to otherwise eliminate the corrosion and the copper plating, with varying degrees of success. Such substances have various defects, some being insufficiently effective and some being unstable or reactive and forming undesirable solid or semi-solid products resulting in sludges or gummy materials which can clog the capillary tubes and like elements.

It is an object of my invention to provide a new and improved process for operating refrigeration systems employing halogenated aliphatic hydrocarbon refrigerants. Another object is to provide such a process wherein copper plating is materially inhibited. A further object is to provide such a process which involves contacting the refrigerant and the lubricant with a solid material which is effective to inhibit copper plating and which does not have the objectionable features of other materials proposed for the purpose. Other objects are to provide a novel process and to advance the art. Still other objects will appear hereinafter.

The above and other objects are accomplished by my invention which comprises operating a refrigeration system with a hydrocarbon lubricating oil and a refrigerant of the class consisting of chloroalkanes, chlorofluoroalkanes and bromofluoroalkanes, and contacting the oil and the refrigerant with at least 0.3% by weight, based on the refrigerant, of a polymeric material which is solid at 300° F. and has a viscosity average molecular weight of at least about 20,000 and which is a member of the class consisting of polyacrylonitriles, copolymers and

terpolymers of acrylonitrile in which copolymers and terpolymers the acrylonitrile predominates.

There is tendency for copper plating to occur in some refrigeration systems when there is used therein refrigerants of the class above set forth. However, I have found that polymeric materials, of the class set forth above, are very effective to materially inhibit or delay such copper plating if the refrigerant and the oil are brought into contact therewith continuously or intermittently at frequent intervals during such operation. The precise mechanism through which such polymeric materials so function is not known. Such polymeric materials are known to the art, are solids, are insoluble in the refrigerants and in hydrocarbon lubricating oils, and do not react with the refrigerants or the oils. The polymeric materials appear to be stable under the conditions encountered in the refrigeration systems and do not react to form objectionable products, such as sludges and gummy materials. They are resistant to the acids which may be generated in the refrigeration system, and remain effective over long periods of time.

Polymeric materials useful in my process include the polymers of acrylonitrile itself (polyacrylonitriles), copolymers of acrylonitrile and a vinyl pyridine in which the acrylonitrile predominates, and terpolymers of acrylonitrile, a vinyl pyridine, and a methylacrylate and interpolymers of acrylonitrile, a butylacrylate and methacrylic acid, said interpolymer being present as a binder with polyacrylonitrile fibers and as a component of an acrylic enamel containing a phenol-formaldehyde resin, the acrylonitrile predominating. Preferably, the acrylonitrile forms about 85% or more of the polymeric material. The vinyl pyridines consist of vinyl pyridine itself and its homologues, represented by 2-methyl-vinyl pyridine. The methylacrylates are the methyl esters of acrylic acid and its homologues, such as methacrylic acid.

Also, the effective polymeric materials are those which are solid at temperatures up to 300° F. Usually, the polymeric materials will have a viscosity average molecular weight of at least about 20,000, preferably from about 20,000 to about 500,000. The "viscosity average molecular weight" is the molecular weight that is determined by measuring the viscosity of fractions of the polymeric material in solutions, determining the osmotic pressure of each fraction from a chart on which viscosities are plotted against osmotic pressures and determining the average molecular weight of each fraction from a second chart on which osmotic pressures are plotted against molecular weights; all in accordance with the principles and methods described and discussed in the chapter by Bagley and Mark appearing on pages 75 through 109 in "High Molecular Weight Organic Compounds" edited by Burk and Grummitt and published in 1949 by Interscience Publishers, Inc. of New York.

The polymeric materials may be in the form of coarse granules or pellets, preferably porous, but more usually will be in the form of coatings, sheets, fibers or fabric which, preferably, are attached to the refrigeration apparatus in positions where they will be contacted by the refrigerant and the lubricant. For example, the polymeric material may be used to replace, at least in part, the insulation on the motor windings and the housing in the refrigeration apparatus. This has the additional advantages of providing a long wearing, acid-resisting insulation for the electrical system of the refrigeration apparatus. Also, the polymeric materials may be attached to the walls of the containers for the lubricant and the refrigerant. When used as coatings or linings for parts subject to corrosion, they also protect such parts from

corrosion. Further, the lubricant, or the refrigerant, or both can be passed through an absorption apparatus or filter containing the polymeric material. Still other methods of obtaining contact of the lubricant and the refrigerant with the polymeric material during operation of the refrigeration system will be apparent to those skilled in the art.

A specific embodiment of the present invention in a hermetic refrigeration system is set forth in the accompanying drawing wherein Figure I depicts such a system in which the motor is encased with oil. The compressor reacts on the gaseous refrigerant, pushing it through line A to the condenser where it becomes a liquid. The liquid is allowed to pass through the capillary into the evaporator where the liquid evaporates and in so doing reduces the temperature of the area around the evaporator coils. The gaseous refrigerant then passes through line B into the motor housing and then to the compressor where the cycle is repeated.

Figure II is an enlargement of the motor stator used in the motor of Figure I. This cut-away figure shows the use of polyacrylonitrile fabric as a slot liner and as a phase separator in the stator; said arrangement provides adequate contact of the polyacrylonitrile with the refrigerant and lubricant to effectively reduce copper plating and the formation of gum deposits.

While a detectable decrease in copper plating can be observed when the polymeric material is present in a proportion of only 0.1% by weight based on the refrigerant, at least 0.3% by weight will be required for practicably significant results. Preferably, the polymeric material will be employed in a proportion of at least 2% by weight based on the refrigerant, and most usually about 3%. The maximum proportions of the polymeric material will be dictated solely by considerations of convenience, practicability and economy, since excessive proportions thereof are not harmful.

The refrigerants, which may be employed, are the chloroalkanes, the fluorochloroalkanes and the bromofluoroalkanes. Such refrigerants are represented by methyl chloride, methylene chloride, dichlorodifluoromethane, tetrafluorodichloroethane, fluorotrichloromethane, chlorotrifluoromethane, mono chlorodifluoromethane and bromotrifluoromethane. The process is especially adapted for use with the chlorofluoroalkanes and is preferably used with dichlorodifluoromethane.

The lubricant, which can be employed, may be any hydrocarbon lubricating oil having the viscosity and other charatceristics required by the particular refrigeration apparatus employed. Usually, the lubricant will be a highly refined petroleum oil, but it may be composed, in whole or in part, of synthetic hydrocarbons, such as polyisobutylenes. Also, the amount of the lubricant will be that required by the particular apparatus employed.

Because water may be formed during the continued operation of refrigeration systems and also seeps in from outside in some types of systems, an antifreeze agent, such as methanol, is often added to prevent ice formation from blocking the capillary tubes used for the expansion of the refrigerant. Such antifreeze agents appear to accelerate copper plating in such systems. However, I have found that the polymeric materials, employed in my process, are also effective to materially inhibit copper plating in the presence of such antifreeze agents and such antifreeze agents can be included in my process.

In order to more clearly illustrate by invention, preferred modes of carrying the same into effect, and the advantageous results to be obtained thereby, the following examples are given:

EXAMPLE 1

A one-eight horsepower electric motor is prepared in which the slot liners, phase separators, and wedges, which are normally made from cellulosic material, are made from polyacrylonitrile cloth. The motor is then used in a hermetic compressor and the system operated at 130° to 135° F. ambient temperature. The compressor unit contains a refrigerant of dichlorodifluoromethane and a naphthenic base refrigerator lubricant (such as Suniso 3G Oil). After two months of continuous operation, the system is turned off, dismantled, and the compressor is examined. Very little copper plating is observed and there is no varnishing (formation of gum deposits).

This same test is applied to two hermetic compressors containing conventional motors, i.e., the slot liners, phase separators, and wedges, and made of cellulosic material. At the end of the two-month operating period at about 130° F. ambient temperature, one unit fails due to seizing of the compressor bearings. On dismantling, an examination of the compressor of both units discloses large amounts of copper plating and varnish formation in the compressor bearings.

EXAMPLE 2

Example 1 is repeated with an electric motor whose slot liners, phase separators and wedges, are of a non-woven mat prepared from polyacrylonitrile fiber and a binder comprising an interpolymer prepared from acrylonitrile, butylacrylate and methacrylic acid in the weight ratio of 63:32:5. After two months of operation at about 130° F. ambient temperature, examination of the compressor discloses only slight discoloration of the metal parts (not copper plating) and the presence of an insignificant amount of gum deposit formation.

EXAMPLE 3

An electric motor is made in the conventional manner (cellulosic slot liners, etc.) except that the wire used in the field coils is enameled with an acrylic wire enamel comprising a phenol-formaldehyde resin (10%) and an interpolymer of acrylonitrile (90%). The interpolymer is prepared from acrylonitrile, butylacrylate and methylacrylic acid in the weight ratio of 63:32:5. This motor is then used in a hermetically sealed compressor system comprising a monochlorodifluoromethane refrigerant and a naphthenic base refrigeration lubricant, such as Suniso 3G Oil. After two months of operation at about 130° F. ambient temperature, the unit is dismantled and examined. There is no evidence of copper plating or the formation of gum deposits.

When this same test is repeated with a motor containing field coils of wire enameled with a polyvinylbutyral resin, the compressor on dismantling, shows appreciable copper plating and gum deposit formation.

EXAMPLE 4

A strip of copper, approximately 2⅜ inches long by ¼ inch wide by 1/16 inch thick, and a strip of low carbon steel of similar size, separated from the copper by a piece of glass at each end, were tied together at each end with copper wire. Test strips, so prepared, were then loaded into glass pressure tubes. Into each tube, 2.5 cc. of a naphthenic base refrigeration lubricating oil and 2.6 g. of dichlorodifluoromethane were added. About 0.05 g. of polyacrylonitrile cloth, whose viscosity average molecular weight was about 33,000 to about 46,500, was introduced. Several tubes had no polyacrylonitrile and these were used for control. The tubes were then frozen in liquid nitrogen and evacuated to a few hundredths of a millimeter of mercury pressure before sealing them off by fusing the glass. The tubes were allowed to warm to room temperature while standing vertically. In this position, the metal strips were ¾ immersed in liquid and the polyacrylonitrile was almost completely immersed in liquid. The tubes were stored in an oven at 120° C., removed, cooled and inspected every few days. It was found that copper plating developed much more slowly

in the tubes containing the polyacrylonitrile than in the controls, as may be seen from the following Table I:

Table I

No.	Sample	Days required to produce copper plating at 120° C.	
		Slight Amount	Heavy Amount
1	Control	16	79
2	do	5	65
3(a)	With Polyacrylonitrile (fabric) made from continuous filament.	48	113
3(b)	do	44	113
4	With Polyacrylonitrile (fabric) made from staple.	42	113

A similar test at 150° C. showed the development of medium copper plating in four days in two control samples as compared to 30 days and 41 days for the tubes containing the polyacrylonitrile.

EXAMPLE 5

Experiments were carried out at 120° C. as described in Example 4, with varying amounts of polyacrylonitrile fiber of the kind used in Example 4 and with other aliphatic halide refrigerants. The results are shown in the following tables:

Table II

[Refrigerant: Dichlorodifluoromethane.]

Amount of Inhibitor, mg.	Days to Detectable Copper Plating	Days to Light Copper Plating
None	7	14
None	7	16
78 (3%)	37	74
26 (1%)	30	37
9 (0.35%)	14	46
3 (0.12%)	9	16

Table III

[Refrigerant: Tetrafluorodichloroethane.]

Amount of Inhibitor, mg.	Days to Detectable Copper Plating	Days to Light Copper Plating
None	7	11
78	74	92
78	60	92

Table IV

[Refrigerant: Bromotrifluoromethane.]

Amount of Inhibitor, mg.	Days to Detectable Copper Plating	Days to Light Copper Plating
None	5	22
None	5	22
75	11	36
80	11	36

EXAMPLE 6

Experiments were carried out at 120° C. in the manner described in Example 4 with the following polymeric materials:

(A) Copolymer of acrylonitrile with 5% of vinyl pyridine, having a viscosity average molecular weight of at least 20,000;

(B) Copolymer of acrylonitrile with 5% of 2-methyl-5-vinyl-pridine, having a viscosity average molecular weight of at least 20,000;

(C) A commercial product sold under the trade name "Acrilan" which is believed to be a terpolymer of 85% acrylonitrile and 15% of a mixture of 2-methyl-5-vinyl pyridine and a methylacrylate and to have a viscosity average molecular weight of about 20,000 or more;

(D) A commercial product sold under the trade name "Dynel" which is believed to be a copolymer of 40% acrylonitrile and 60% vinyl chloride and to have a viscosity average molecular weight of about 20,000 or more. (This product is included solely for purpose of comparison.)

The results of the tests are shown in the following Table V:

Table V

[Refrigerant: Dichlorodifluoromethane.]

Inhibitor	Amount of Inhibitor, mg.	Days for Detectable Copper Plating	Days for Light Copper Plating
None		7	13
D	78	11	16
D	78	9	16
A	78	37	46
A	78	46	53
B	79	37	53
B	78	46	53
C	80	30	53
C	79	30	60

It is apparent that polymeric material D, which contains vinyl chloride and less than 50% acrylonitrile, has but little effect, insufficient for practical use in my process.

EXAMPLE 7

78 mg. of polyacrylonitrile fiber like that of Example 5 were added to 2.6 g. of dichlorodifluoromethane containing 0.5 cc. of anhydrous methanol, and the test carried out at 120° C. in the presence of steel and copper strips as described in Example 4. A control test was carried out similarly. After 1 day, copper plating was observed in the control containing no inhibitor, whereas it required 9 days and 16 days in duplicate tests to obtain observable copper plating when the polyacrylonitrile fiber was present.

Similar results were obtained when tetrafluorodichloroethane and monochlorodifluoromethane were similarly tested.

The following Examples 8 and 9 are given for purposes of comparison:

EXAMPLE 8

0.08 gram each of glutaronitrile, adiponitrile, succinonitrile, propionitrile, and benzonitrile were added to 2.6 grams of dichlorodifluoromethane and 2.5 cc. of refrigeration oil. Each mixture was then added to copper and steel strips as described in Example 4 and the system was heated overnight above 250° C. (The heating oven accidentally got out of control and an accurate temperature measurement could not be obtained.) In the morning, all of the test specimens showed extreme decomposition and showed considerably more copper plating than controls which did not contain any nitrile.

EXAMPLE 9

An experiment with phthalonitrile was run as described in Example 8 but at 120° C. At the end of 7 days, heavy copper plating had developed, whereas a control at the end of this time showed only a slight tarnish.

Examples 8 and 9 show that the property of inhibiting copper plating is not common to nitriles, but that the lower nitriles particularly are inoperative for such purpose.

The naphthenic base refrigeration lubricant utilized in Examples 1, 2 and 3 is Suniso 3G Oil which has a flash point ASTM open cup 330–340° F.; a pour point ASTM —35° F. maximum; Sligh oxidation 10–20; floc test —70° F. maximum; a density of 7.75 lbs. per gal. and an SUS viscosity at 100° F. of 150 to 160. For the other examples, the naphthenic base refrigeration lubricant utilized

was Suniso 4G Oil which has a flash point ASTM open cup 350°–360° F.; a pour point ASTM —35° F. maximum; Sligh oxidation 10–20; floc text —50° F. maximum; a density of 7.627 lbs. per gal. and an SUS viscosity at 100° F. of 280 to 300.

It will be understood that the preceding Examples 1 to 7 are given for illustrative purposes solely, and that my invention is not limited to the specific embodiments disclosed therein. On the other hand, it is apparent that many variations and modifications can be made therein, particularly in the refrigerants, the polymeric materials and the proportions thereof and in the techniques employed, within the scope of the general description without departing from the spirit or scope of my invention.

It will be apparent that my invention provides a novel process for operating refrigeration systems employing halogenated hydrocarbon refrigerants, and materially inhibiting copper plating normally occurring therein. It involves novel materials for inhibiting such copper plating, which matetrials are not objectionable in such systems and do not react to produce objectionable substances; said materials are beneficial in that longer motor life is obtained. Mechanical failures of the refrigeration apparatus are thus greately decreased, maintenance costs are materially lowered, and the service lives of the refrigeration systems are considerably prolonged. Therefore, it is apparent that my invention constitutes an important advance in and contribution to the art.

This application is a continuation-in-part application of copending application Serial No. 351,739, filed April 28, 1953, and now abandoned.

I claim:

1. A process for inhibiting copper plating in a closed refrigeration system containing steel and copper wherein said metals are contacted with a mixture of a hydrocarbon lubricating oil and a halogenated hydrocarbon refrigerant in the presence of at least 0.3% by weight, based on the refrigerant, of a polymeric material which is solid at 300° F., said polymeric material being positioned in contact with said mixture, and has a viscosity average molecular weight of at least 20,000, said polymeric material being taken from the class consisting of polyacrylonitriles, copolymers, terpolymers and interpolymers of acrylonitrile, the acrylonitrile component predominating in said copolymers, terpolymers and interpolymers, and, said polymeric material being substantially insoluble in said refrigeration system.

2. The process of claim 1 wherein the halogenated hydrocarbon refrigerant is a chlorofluoroalkane.

3. The process of claim 1 wherein the acrylonitrile component forms about 85% of the polymeric material.

4. The process of claim 1 wherein the polymeric material is polyacrylonitrile.

5. The process of claim 1 wherein the polymeric material is a copolymer of acrylonitrile and a vinyl pyridine.

6. The process of claim 1 wherein said polymeric material is an interpolymer of acrylonitrile, a butyl acrylate and methacrylic acid, said interpolymer being present as a binder with polyacrylonitrile fibers.

7. The process of claim 1 wherein said solid polymeric material is an interpolymer of acrylonitrile, a butyl acrylate and methacrylic acid, said interpolymer being present as a component of an acrylic enamel containing a phenol-formaldehyde resin.

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