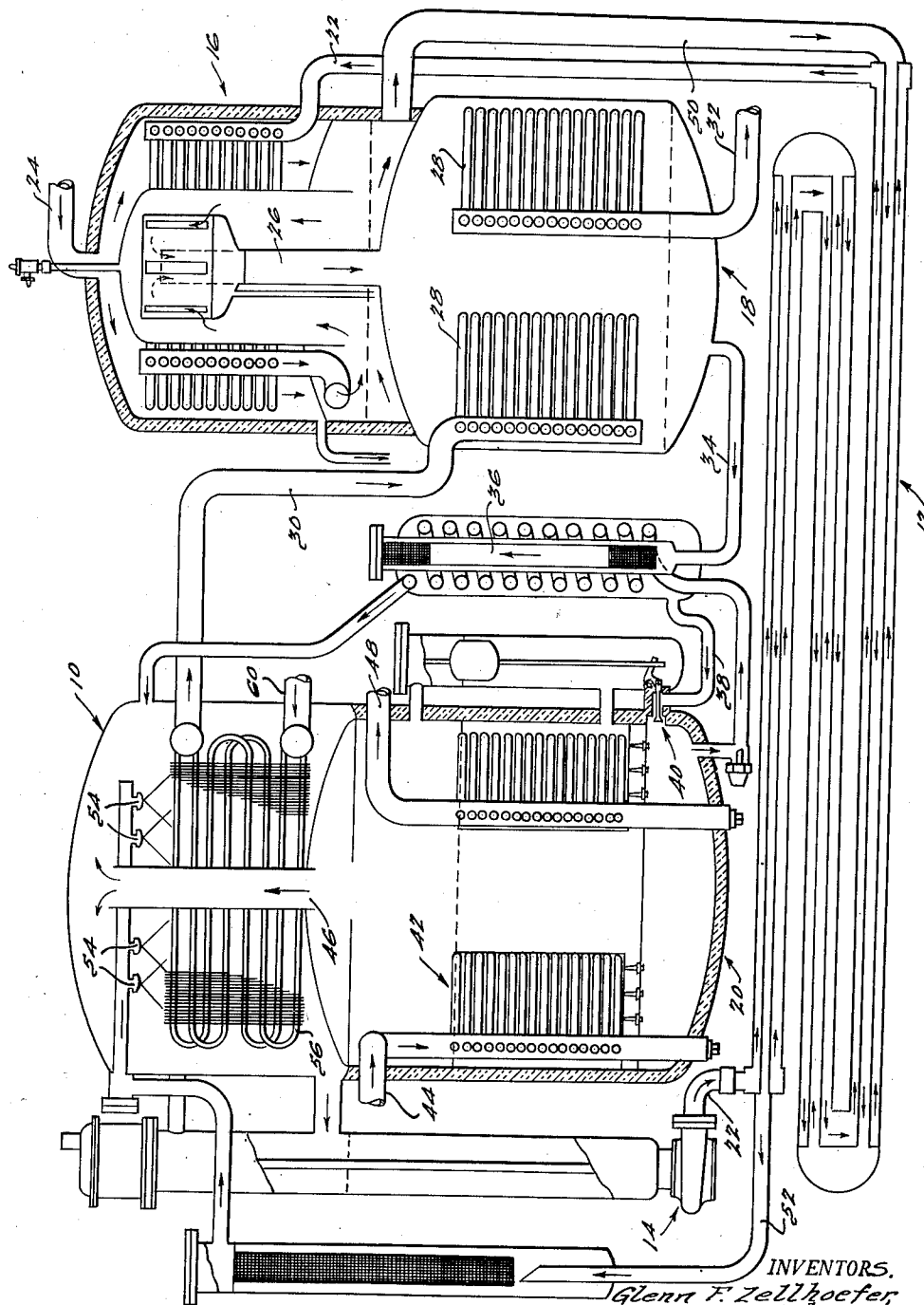


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WORKING FLUID FOR USE IN REFRIGERATING SYSTEMS
AND METHOD OF PREVENTING CORROSION IN
REFRIGERATING SYSTEMS
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WORKING FLUID FOR USE IN REFRIGERATING SYSTEMS AND METHOD OF PREVENTING CORROSION IN REFRIGERATING SYSTEMS

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This invention relates to the art of refrigeration and in particular has reference to working fluids for use in refrigerating apparatus of the absorption type.

Such types of systems employ a working fluid consisting of a suitable absorbent and a suitable volatile refrigerant. Many combinations of absorbents and refrigerants have heretofore been suggested. One particularly efficient working fluid is that disclosed in Zellhoefer Patent No. 2,149,947, issued March 7, 1939, for "Refrigeration," and which working fluid consists of a refrigerant comprising methylene chloride and an absorbent comprising a liquid di-substituted polyglycol derivative such as a diether thereof, and more particularly a dialkyl ether, such for example as tetraethylene glycol dimethyl ether. This latter substance may be properly described as dimethoxy-tetraethyleneglycol or dimethoxy-tetraglycol.

It has been found that working fluids for absorption type refrigerating systems under some circumstances exert undesirable corrosive action upon the metals of which parts of the system are constructed, particularly such parts made of iron and steel. Corrosion has been found in such systems even though the system and the working fluid originally were not contaminated and the refrigerant for the system was carefully prepared and was initially substantially free of acid-reacting materials, and even in cases where the absorbent was itself non-corrosive, yet during the operation of the system corrosion of metal parts of the system, particularly ferrous metal parts, has sometimes occurred.

The corrosive difficulty is believed to be due to the presence in the working fluid of certain organic and inorganic materials, the precise natures of which have not been determined, but which appear to be principally chlorides developed by the decomposition of the chlorine-containing constituents of the working fluid.

As disclosed in the aforesaid patent, the chlorine compounds of the general type exemplified by those containing the dichloromethyl group or radical ($-\text{CHCl}_2$) are capable of forming a thermally unstable loose molecular type of compound with the glycol ether absorbents, and for such reasons are considered to be desirable as a working fluid for an absorption system.

Of these glycol ethers, the following are considered as being within the scope of the present invention, to-wit: Diethylene glycol diethylether, triethylene glycol dimethylether, tetraethylene glycol dimethylether, pentaethylene glycol dimethylether, hexaethylene glycol dimethylether, diethylene glycol ditetrahydrofurfuryl ether, ethylene glycol mono-n-butyl mono-tetrahydrofurfuryl ether, and the like. It is intended to cover the above materials by the term "glycol ether" in the subjoined claims.

We have discovered that the corrosion difficul-

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ties heretofore encountered with such working fluids can be substantially eliminated and the working fluid stabilized by using with such working fluid copper and/or cuprous oxide, preferably in a finely divided state. The invention thus contemplates a non-corrosive, stabilized working fluid consisting of suitable combinations of absorbents and refrigerants of the types previously mentioned containing copper and/or cuprous oxide, preferably in a finely divided state. The invention also contemplates a technique for eliminating corrosion in refrigerating systems using such working fluids by adding to the fluid in the system copper and/or cuprous oxide, preferably in a finely divided state, or replacement of the contaminated working fluid in the system by a non-corrosive mixture including copper and/or cuprous oxide, preferably in a finely divided state.

A principal object of the invention, therefore, is to provide a non-corrosive, stabilized working fluid useful in a refrigerating system, particularly one of the absorption type.

Another object of the invention is to provide a technique for eliminating and/or preventing corrosion in a system in which corrosion has already occurred by the use of a working fluid of the type previously discussed containing copper and/or cuprous oxide, preferably in a finely divided state.

Other objects and advantages of the invention will be apparent from a consideration of the following specification taken in conjunction with the accompanying drawing, of which there is one sheet and wherein:

The sole figure is a schematic drawing of a refrigerating system of the type in which a working fluid embodying the invention may be employed.

As illustrated in the drawing, an absorption type refrigerating system in which working fluid embodying the invention may be employed consists in general of an absorber 10, a heat exchanger 12, a solution pump and motor assembly 14, a heater or still 16, a condenser 18, and a water chiller or cooler 20. When the solution pump 14 operates, strong solution from the absorber 10 flows through the outer passages of the heat exchanger 12 to the heater 16 through the conduit 22. Steam for operating the heater is supplied through the conduit 24. In the heater the solution absorbs heat from the steam, causing the distillation of the major portion of the refrigerant from the solvent. The refrigerant vapor released in the heater flows to the condenser 18 through the conduit 26. Water is supplied to cooling conduits 28 in the condenser 18 through the conduits 30 for condensing the refrigerant in the condenser 18, and the water is carried away from the condenser 18 by conduit 32. Liquid refrigerant flows from the condenser through conduit 34 and dehydrator 36 and con-

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duit 38 to the water chiller, a float controlled valve 40 metering the flow of the liquid refrigerant into the chiller 20 in accordance with the liquid level therein.

Water to be cooled flows into the coils 42 of the heat exchanger in the chiller 20 through conduit 44, and heat absorbed by the liquid refrigerant in the chiller 20 causes such refrigerant to vaporize under the low pressure in the chiller, and the refrigerant vapor then flows through conduit 46 to the absorber 10. The water after being cooled in the heat exchanger 42 is conducted away from the chiller through conduit 48.

While the refrigerant is following the foregoing cycle from the heater to the absorber, the weak solution in the heater flows through the conduit 50, the inner passages of the heat exchanger 12, and the conduit 52 to the absorber 10, and such solution is discharged through nozzles 54 under a pressure differential of the order of 3 to 4 pounds in the form of a fine spray which impinges upon the absorber coil 56 and then flows downwardly over the fins of the coil in a thin film, absorbing the refrigerant vapor that enters the absorber through the conduit 45.

The coil 56 is supplied with water 60 whereby to absorb heat from the absorber, and the water after flowing through the coil 56 may be conducted by conduit 30 to the heat absorbing coil 28 in the condenser. The strong solution formed in the absorber by the absorption of the refrigerant vapor by the weak solution flows by gravity to the suction side of the solution pump 14 and is thereby returned through the conduit 22 to the heater previously described.

The foregoing cycles of the refrigerant and the solution continue as long as the pump 14 remains in operation, thereby continuously absorbing heat from the current of water in the chiller 20. When the solution pump 14 is stopped, the solution from the heater 16 flows into the absorber 10 and an equilibrium is established between the high and low sides of the system. Upon starting the pump operation again, the discharge of the strong solution into the heater will generate the necessary head pressures to effect the circulation of the weak solution from the heater to the absorber.

As previously indicated, it has sometimes been

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it was found that the corrosion difficulties could be substantially eliminated by adding to such working fluid mixture from .1% to 5% by weight of copper and/or cuprous oxide, preferably in a finely divided state. It has also been found that the addition of such an amount of copper and/or cuprous oxide, preferably in a finely divided state, to a working solution mixture in a machine in which corrosion has occurred will not only prevent further corrosion, but will also convert the working solution mixture into a non-corrosive, stabilized working fluid. The corrosion has been found to occur principally in the ferrous metal parts of the system exposed to high temperatures, such for instance as the heater which is subjected to the steam temperature of the order of 240° F. and the heat exchanger 12 through which the hot weak liquor is returned to the absorber.

It has also been found that such addition of such an amount of copper and/or cuprous oxide, preferably in a finely divided state, will thermally and otherwise stabilize the solution against deterioration. Table I, hereinafter set forth, is a comparison of the results obtained by a number of tests made of working mixtures in the presence of a standard steel-copper couple, some with and some without copper or cuprous oxide in a finely divided state, in a glass bomb. The standard couple used in all tests herein referred to is a cold rolled steel rod 1" long, 1/8" diameter, around which is wrapped a copper wire .040 in. diameter, 3" long. The original acidity of the freshly prepared mixtures in test No. 5619.4—1 was .015% or less calculated as HCl which is commercially satisfactory and substantially free of acid reacting materials from a commercial standpoint. The deteriorated solutions referred to in the tests are a composite of sample solutions taken from a number of machines after considerable use in actual service, and analysis after makeup of these solutions indicated that they contained objectionable amounts of iron chloride, iron oxide, HCl and iron organic complexes. These deteriorated solutions originally when introduced in the machines were substantially free of acid reacting materials and the systems of the machines in which such original solutions were originally introduced were not contaminated.

Table I

[Table showing effectiveness of copper or cuprous oxide for stabilizing working mixtures and suppressing corrosiveness of dimethoxytetraglycolmethylene chloride solution in presence of standard steel-copper couple.]

Test No.	Content of Glass Bomb	Time, days	Temp., °C.	Acidity as Per Cent HCl	Cl Ion, Per Cent	Wt. of Couple, gms	Change in Wt. of Couple, Per Cent
5619.4-1-----	90% Solvent, 20% Refrigerant-Standard Couple.	3	125	0.55	0.55	2.3590	-2.52
5636.1-----	Deteriorated solution with acidity 0.13% calc. as HCl-Standard Couple.	3	125	0.59	0.54	2.4350	-2.66
5637.1-1-----	Deteriorated solution with acidity 0.13% calc. as HCl-Cu-Standard Couple.	3	125	0.06	0.08	2.4991	+0.192
5637.3-2-----	Deteriorated solution with acidity 0.13% calc. as HCl-Cu ₂ O Standard Couple.	3	125	0.04	0.07	2.4542	+0.465

found that combinations of refrigerants and absorbents of the kind heretofore referred to cause an undesirable corrosive action upon the ferrous metal parts of the apparatus which causes a gradual deterioration in the efficiency of the machine, resulting in an eventual breakdown thereof. The solution may comprise from 40-90% by weight of solvent, and from 10-60% by weight of refrigerant.

After an extensive period of research and tests

For satisfactory commercial operation of refrigerating machines of the foregoing type, the acidity of the working fluid must be maintained at or below a percentage of .015% determined as HCl.

Table II, hereinafter set forth, is a comparison of the results obtained by a number of tests made of working mixtures in copper and steel bombs, some with and some without copper and/or cuprous oxide in a finely divided state.

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Table II

[Table showing effectiveness of copper and/or cuprous oxide for stabilizing working mixtures and suppressing corrosiveness of dimethoxytetra-glycol-methylene chloride solutions in both copper and steel bombs]

Test No.	Content of Bomb	Original Acidity of Solution Calc. as Per Cent HCl	Acidity of Solution Calc. as Per Cent HCl—After 4 days	Acidity of Solution Calc. as Per Cent HCl—After 8 days
925-1	80% Solvent, 20% Refrigerant in copper bomb	0.00936	0.0054	0.0072
925-2	80% Solvent, 20% Refrigerant in Cu bomb with finely divided Cu powder	0.00936	0.0072	0.0079
925-3	80% Solvent, 20% Refrigerant in Cu bomb with finely divided Cu and Cu ₂ O Powder	0.00936	0.0072	0.0072
925-4	80% Solvent, 20% Refrigerant in steel bomb with Cu powder (finely divided)	0.00936	0.00612	0.00756
925-5	80% Solvent, 20% Refrigerant in steel bomb with Cu ₂ O (finely divided)	0.00936	0.00648	0.00792
925-6	80% Solvent, 20% Refrigerant in steel bomb with finely divided Cu and Cu ₂ O	0.00936	0.0072	0.0090

Table III

[This table shows the effectiveness of powdered copper, finely divided cuprous oxide, mixture of powdered copper and finely divided cuprous oxide and copper tubing in adsorbing products of corrosion from a composite sample of deteriorated solutions taken from machines in the field.]

Test No.	Original Solution Acidity as Per Cent HCl	Acidity as Per Cent HCl—After 24 hours	Acidity as Per Cent HCl—After 72 hours
Cu, 1 200° F., #923-1	0.1530	0.0072	0.0054
Cu, 1 200° F., #923-2	0.1530	0.0126	0.0072
Cu, 1 90° F., #923-3	0.1530	0.0108	0.0036
Cu ₂ O, 1 200° F., #923-4	0.1530	0.0108	0.0108
Cu ₂ O, 1 200° F., #923-5	0.1530	0.0117	0.0108
Cu ₂ O, 1 90° F., #923-6	0.1530	0.0126	0.0108
Cu ₂ O, Cu, 1 200° F., #923-7	0.1530	0.0099	0.0072
Cu ₂ O, Cu, 1 200° F., #923-8	0.1530	0.0099	0.0072
Cu ₂ O, Cu, 1 90° F., #923-9	0.1530	0.0135	0.0090
Cu Bomb, 1 200° F., #923-10	0.1530	0.0252	0.0252
Cu Bomb, 1 90° F., #923-11	0.1530	0.0270	0.0270

1 "Cu" indicates tests in copper bombs with 5 gm. of precipitated copper powder in 70 cc. of solution, "Cu₂O" indicates tests in copper bombs with 5 gm. of finely divided cuprous oxide in 70 cc. of solution, "Cu₂O-Cu" indicates tests in copper bombs with 2.5 gm. precipitated copper powder and 2.5 gm. finely divided cuprous oxide in 70 cc. of solution, and "Cu Bomb" indicates tests in copper bomb with 70 cc. of solution and no Cu₂O or Cu in addition to that of the walls of the bomb.

Table IV

[This table shows selective adsorption properties of powdered copper and cuprous oxide for six different acids in three different solvents.]

Solvent, 50 Gram	Acid	Inhibitor		Original Acidity as percent HCl	Acidity After 16-18 hours as percent HCl
H ₂ O	HCl	Cu (5 gram)	Cu ₂ O (5 gram)	0.216	0.024
Do.	Acetic	do.	do.	0.216	0.206
Do.	H ₂ SO ₄	do.	do.	0.432	0.351
Do.	HNO ₃	do.	do.	0.324	0.320
Do.	FeCl ₃	do.	do.	0.216	0.050
Do.	Oxalic	do.	do.	0.500	0.004
Dimethoxytetra glycol	HCl	do.	do.	0.252	0.020
Do.	Acetic	do.	do.	0.216	0.204
Do.	H ₂ SO ₄	do.	do.	0.347	0.082
Do.	HNO ₃	do.	do.	0.345	0.288
Do.	FeCl ₃	do.	do.	0.108	0.009
Do.	Oxalic	do.	do.	0.435	0.003
Acetone	HCl	do.	do.	0.274	0.0003
Do.	Acetic	do.	do.	0.212	0.191
Do.	H ₂ SO ₄	do.	do.	0.396	0.004
Do.	HNO ₃	do.	do.	0.306	0.160
Do.	FeCl ₃	do.	do.	0.151	0.0007
Do.	Oxalic	do.	do.	0.430	0.0007

From the foregoing tests and from tests made in systems of machines in actual service it has been definitely established that the addition of copper and/or cuprous oxide in the amounts indicated and preferably in a finely divided form will stabilize such working fluids against deterioration and will render such working fluids non-corrosive to the metal parts of such systems.

While we have illustrated and described a preferred embodiment of our invention, it is understood that this is capable of modification, and we therefore do not wish to be limited to the precise details set forth, but desire to avail ourselves of such changes and alterations as fall within the purview of the following claims.

We claim:

1. A stabilized working fluid for use in a refrigeration system of the absorption type consisting of a mixture of the following ingredients: 40% to 90% of a glycol ether, .1% to 5% of copper and 10% to 60% of a highly volatile aliphatic halide containing at least one hydrogen atom.

2. A stabilized working fluid for use in a refrigeration system of the absorption type consisting of a mixture of the following ingredients: 40% to 90% of a glycol ether, .1% to 5% of cuprous oxide and 10% to 60% of a highly volatile aliphatic halide containing at least one hydrogen atom.

3. A stabilized working fluid for use in a refrigeration system of the absorption type consisting of a mixture of the following ingredients: 40% to 90% of a glycol ether, .1% to 5% of copper and cuprous oxide in a finely divided form, and 10% to 60% of a highly volatile aliphatic halide containing at least one hydrogen atom.

4. In a refrigerating system of the absorption type employing a volatile organic halide as the refrigerant and a glycol ether as the absorbent, the process of preventing corrosion of the ferrous metal portions of the system by such fluids and stabilizing the mixture of such fluids which comprises using with the refrigerant and absorbent mixture, .1% to 5% of copper in a finely divided form.

5. In a refrigerating system of the absorption type employing a volatile organic halide as the refrigerant and a glycol ether as the absorbent, the process of preventing corrosion of the ferrous metal portions of the system by such fluids and stabilizing the mixture of such fluids which comprises using with the refrigerant and absorb-

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ent mixture .1% to 5% of cuprous oxide in a finely divided form.

6. In a refrigerating system of the absorption type employing a volatile organic halide as the refrigerant and a glycol ether as the absorbent, the process of preventing corrosion of the ferrous metal portions of the system by such fluids and stabilizing the mixture of such fluids which comprises using with the refrigerant and absorbent mixture, .1% to 5% of copper and cuprous oxide in a finely divided form.

7. A mixture suitable for use as a working fluid for a refrigerating system of the absorption type consisting of from 40 to 90 per cent by weight of dimethoxy-tetraethyleneglycol and from 10 to 60 per cent by weight of methylene chloride, and of from .1 to 5 per cent by weight of copper in a finely divided form.

8. A mixture suitable for use as a working fluid for a refrigerating system of the absorption type consisting of from 40 to 90 per cent by weight of dimethoxy-tetraethyleneglycol and from 10 to 60 per cent by weight of methylene chloride, and of from .1 to 5 per cent by weight of cuprous oxide in a finely divided form.

9. A mixture suitable for use as a working fluid for a refrigerating system of the absorption type consisting of from 40 to 90 per cent by weight of dimethoxy-tetraethyleneglycol and from 10 to 60 per cent by weight of methylene chloride, and of from .1 to 5 per cent by weight of copper and cuprous oxide in a finely divided form.

10. A mixture of dimethoxy-tetraethyleneglycol and methylene chloride containing .1% to 5% by weight of material from the group consisting of copper and cuprous oxide.

11. A stabilized working fluid for use in a refrigerating system of the absorption type con-

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sisting of a mixture of a glycol ether, a highly volatile aliphatic halide containing at least one hydrogen atom and .1% to 5% by weight of material selected from the group consisting of copper and cuprous oxide.

12. A working fluid for use in a refrigerating system of the absorption type consisting of a glycol ether and a highly volatile aliphatic halide containing at least one hydrogen atom stabilized and made non-corrosive to ferrous metals by the presence of .1% to 5% by weight of material selected from the group consisting of copper and cuprous oxide in a finely divided form.

13. A method of preventing corrosion of ferrous metals by and stabilizing a mixture of dimethoxy-tetraethyleneglycol and a methylene chloride which comprises using with such mixture, .1% to 5% by weight of material selected from the group consisting of copper and cuprous oxide.

14. A method of preventing corrosion of ferrous metals by and stabilizing a mixture of dimethoxy-tetraethyleneglycol and a methylene chloride which comprises adding to such mixture, .1% to 5% of copper.

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