1990

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ABSTRACT

HFC134a(CH_2FCF_3) is primarily developed as an alternative to the ozone depleting refrigerant CFC12(CCl_2F_2). In the case of the substitution of refrigerants for home refrigerators, a test, which is aimed at the evaluation of the influences on the material in the refrigerant in cycle, is necessary as well as thermodynamic characteristic test. The testing required includes both laboratory and system work. In order to make judgements about the reliability and performance of proposed new system, laboratory data are to be used. Therefore the laboratory testing has to simulate system work. This paper presents some laboratory data that may be needed in this effort.

(1)The stability of HFC134a and polyalkylen glycols(PAG), which are the leading candidate for lubrication of HFC134a, is discussed by using sealed glass tubes. After the test , gas analysis usig the gas chromatograph is used in order to know the decomposition mechanism of HFC134a/PAG mixturers. Further, in order to determine the effect of water and molecular sieve on stability we tested.

(2)The heat resistance of PAG is studied by new method called Chemiluminescence(to be referred to as CL).

(3)The effectiveness of lubrication is tested by HAYAMA wear tester and MAX-WEILAND method. In addition,the effect of water on lubrication is further discussed.

(4)The compatibility of the HFC134a/PAG mixtures with magnetic wire is discussed by autoclave method in consideration of the influence of the water.

(5)The compatibility of the HFC134a/PAG mixtures with insulation film is also discussed by autoclave method in consideration of the influence of the water.

INTRODUCTION

In 1974, Rowland and Molina published their hypothesis that the atmospheric ozone was being depleted by chlorofluorocarbon compounds(CFCs 11,12,113,114, and 115), leading to international agreement to reduce CFC prduction. The 1987 Montoreal Protocol, under the auspices of the United Nations Environmental Programme(UNEP), established a plan to reduce CFC production to 50% of 1986 levels by mid-1998, beginning with a return to 1986 levels in mid-1989. Subsequent scientific information on ozone level reductions greater than expected provided the impetus for a reassessment of the adequency of the Montreal Protocol , resulting in recommendations in September 1989 for a complete CFC production phase-out by the year 2000. The recommendation will be considered by the second meeting of Parties to the Montreal Protocol in June 1990 in London.

The leading candidate for CFC12 subsitution is HFC134a, a material that contains no ozone-depleting chlorine. Besides, its thermodynamic properties are similar to those of CFC12.

But when we use HFC134a, having application as the refrigerant for home refrigerators, as the subsitute for CFC12, we have to pay attention the following characteristics of HFC134a which has the influences on the material in the refrigerant in cycle.[1,2] The moleculor of HFC134a (CH_2FCF_3) is relatively polar compared to CFC12(CCl_2CF_2) and HCFC22($CHClF_2$) as revealed by dipol moments for these substance. The higher polarity of HFC134a contributes to low solubility in non-polar lubricants such as the mineral oils and synthetic hydrocarbons presently used as refrigeration compressor lubricant. Thereby requiring the use of a higher polarity synthetic oil family:polyalkylen glycols(PAG). The moleculor structure of PAG(ex. R-{O-(CH_2-C(R)H-O)n-H}m) has a ether linkage(-O-) and hydroxyl terminal group(-OH), taking the form of hydrogen bond , water is more soluble than mineral oils and synthetic hydrocarbons. It is well-known that the water causes the hydrolysis of organic insulation materials such as magnetic wire and insulation film which are used in motor.

We have conducted the following test with paying attention to the above-mentioned characteristics.

(1)The stability of HFC134a and PAG is discussed by using sealed glass tests.

(2)The heat resistance of PAG is studied by CL. We studied it in the air , because , in the CFC12 refrigerantin cycle, we often had known by experience the oxidative deterioration with refrigerating machine oil caused by extremely little oxygen.

The above-mentioned two experiments were carried out in attempt to define the chemical stability of HFC134a and PAG.

(3)The effectiveness of lubrication is tested by HAYAMA wear tester and MAX-WEILAND method. HAYAMA wear tester is simulated the behavior of the slide between vane point and rolling piston in rotary compressor. And MAX-WEILAND method also simulated the behavior of slide between axis and bearing.

(4),(5)The compatibility of the HFC134a/PAG mixtures with magnetic wire and insulation film are tested by autoclave method. Autoclave method bears remembrance to the atmosphere of the compressor, we can know the influence of HFC134a/PAG mixtures to them at accelerated conditions with temperature and pressure.

As the result of this study,

(1)① In general HFC134a/PAG mixtures were more stable than CFC12/mineral oil mixtures. But even HFC134a/PAG mixtures were observed some decomposition and copper plating phenomena on steel. ② Further the influence of water was

concerned with stability and copper plating phenomena. Concerning with this work we observed water had the bad effect of stability rather than in the case of no water.
③The effect of molecular sieve desiccant made good influence of the stability of HFC134a/PAG mixtures than no addition. But we didn't recognize the difference of the effect of stability between commercial molecular sieve and developmental molecular sieve.
(2)The heat resistance of PAG ranked according to increasing reactivity were as follows : alkylbenzene and synthetic parafinic oil mixture < PAGs < (naphthenic)mineral oil.
(3)Lubricity was different to each other. In addition, the effect of water was not good for lubricity.
(4)We will be able to use ester-imide/amide-imide(EI/AI) double coated magnetic wire in less than 0.5%-water-dissolved PAG.
(5)Similarly we will be able to use polyethlene terephthalate(PET) film for insulation film in less than 0.1%-water-dissoloved PAG.

Experimental

Materials

(1)Refrigerating machine oils
Six refrigerating machine oils,Oil A,Oil B,Oil C,Oil D, Oil E and Oil F,were used. The colors,specific gravities, viscosities,miscibilities,pour points,water contents and compositional features of oils are summarized in Table 1.

Table 1. Properties of the Oils.

oil	color ASTM	Sp. Gr. g/cm³	Viscosity (37.8℃) cSt	miscibility U-CST(℃)*	miscibility L-CST(℃)*	pour point ℃	water contents ppm	compositional featurs
A	L1.0	0.9143	30.03	none	none	<-40	20	naphthenic, mineral
B	L0.5	0.8724	34.58	none	none	<-45	≤30	alkylbenzen paraffinic mixture
C	L0.5	0.9568	24.59	—**	<-60	<-50.0	300	polyalkylen glycol
D	L0.5	0.9595	24.1	>90	<-40	<-52.5	500	polyalkylen glycol
E	L0.5	—**	22.5	>90	<-70	<-50.0	100	polyalkylen glycol
F	L0.5	0.989	32.5	>85	<-70	<-50.0	20	polyalkylen glycol

* U-CST : Upper-Critical Solution Temperature
L-CST : Lower-Critical Solution Temperature
Oil A & B were measured with CFC12
Oil c ~ E were measured with HFC134a
** not measured

(2)Refrigerant
We used commercial refrigerant CFC12 and HFC134a aimed for study as they were. Their purities were severally 99.99%

and 99.9%.

(3)Molecular sieve desiccant

Two types of molecular sieve desiccants were used. One (to be referred to as A molecular) was commercial molecular sieve desiccant of 4 Angstrom pore size for CFC12, another (B molecular)was developmental molecular sieve of 3 Angstrom pore size for HFC134a.

(4)Magnetic wire

We used two types of commercial magnetic wires (Nominal diameter of conductor 1.0 mm), one was polyester which is used for CFC12 at present, another was polyester-imide/amide-imide(to be referred to as EI/AI) which was used for HCFC22 Air Conditioner at present.

(5)Insulation film

One commercial PET film were used for insulation film.

The Method for the evaluation of the influences on the material in the refrigerant in cycle.

(1)Stability

Fig.1 shows the sealed-glass-tube test which is useful in determining stability: oil and refrigerant are added to a glass tube with test materials such as steel, copper, aluminum. Subscribing for a purpose, we added water and molecular sieve desiccant still more. And we placed in an oven for 56days at 175°C. After aging gas samples from sealed tubes were analyzed by a Shimadzu GC-4A gas chromatography (GC) with a flame ionization detector (FID) and a Porapak Q column to indicate HFC134a decomposition or reaction. In addition the behavior of a system to copper plating on the surface of steel was measured by JEOL JXA-840 Electoron Probe Micro Analyzer(EPMA).

(2)Heat resistance

The heat resistance of refrigerating machine oils were studied by chemiluminescence(to be referred as CL)analyzer[3] (Tohoku Denshi Sangyo Model CLD100). Fig.2 shows a schematic diagram of its apparatus. Generally we use Fig.3 to explain the very faint light emission-mechanism in the reaction of "$A+B \rightarrow [E] \rightarrow P$".

Chemical species in excited states($P*$) which is produced by chemical reactions fall to ground state(P) emitting visible light, and this is called "CL".The photomultiplier having high sensitivity makes it possible to catch a very first stage of oxidation of organic compounds by counting this extremely weak luminescence($\sim 10^{-15}$W). On the other hand, it shoud be recognized that the stability of polymers basically depends upon the chemical changes in structure caused by degradation. Then, the structure of polymer is one of the important factor concerning the stability. From these points of view, we have studied of the CL phenomenon in refrigerating machine oils induced by heat.

(3)Lubricity

Fig.4 and Fig.5 show the schematic diagram of apparatus used for study of lubrication. They call HAYAMA wear tester (ISHIHARA SEISAKUJYO) and MAX-WIELAND method. The test condition are shown in Table 2.

Table 2 The wear test condition.

	HAYAMA	MAX-WIELAND
TEST PIECE	VANE : steel (HRC 58) R/PISTON : FC (HRC 45)	PIN : steel (HRC 4) BUSH : FC (HRC 20)
Load	15 Kgf	300 Kgf
Sliding speed	3 m/s.	0.065 m/s.
Sliding length	65000 m	712 m
Oil volume	800 cc	30 cc
Oil temperature	about 60℃	about 60℃
Water content in oils	Initial water content (about 500ppm)	
	0.1, 0.5 and 1.0%	

After the test, by means of measurment of wear volume we can anticipate the differences in performance arising from the effect of the new refrigerant/new oil mixtures.

(4)Compatibility of Magnetic Wire

Fig.6 shows the schematic diagram of apparatus used for study of compatibility of the HFC134a/PAG mixtures with magnetic wire. The test condition are summarized as Table 3.

Table 3 The test condition of compatibility of the HFC 134a/PAG mixture with magnet wire.

Samples	Polyester-wire EI/AI-wire
Figure of samples	Twist pair
Refrigerating machine oil volume	380 cc
Autoclave volume	1900 cc
Water content in oil	initial(about 500ppm), 0.5% and 1%
Aging condition	175℃ x 7 days
Pressure (at 175℃)	30 Kgf/cm² G

After aging, magnetic wires were measured break-down-voltage(B.D.V) by B.D.V-measurement-apparatus.

(5)Compatibility of Insulation film

The compatibility of the HFC134a/PAG mixtures with insulation film was also studied by autoclave method. The test condition are summarized as Table 4. After aging we measured the volume of oligomer extraction from PET film with refrigerant/oil mixtures by 0.45 μm pore-sized-membrane filter. And also tensile strength were measured.

Table 4 The test condition of compatibility of the HFC 134a/PAG mixture with insulation film.

Sample	PET-film
Figure of sample	Shape of dumbbell
Sample volume	50 g
Refrigerating machine oil volume	800 cc
Autoclave volume	2000 cc
Water content in oil	initial(about 500ppm), 0.2%, 0.5% and 1%
Aging condition	150℃ x 7 days
Pressure (at 175℃)	30 Kgf/cm² G

RESULTS & DISCUSSION

(1)The stability of HFC134a/PAG mixtures

①Fig.7 shows the stability of HFC134a/PAG mixtures compared to CFC12/oil mixtures. In general HFC134a/PAG mixtures were more stable than CFC12/oil mixtures. But after aging we analyzed the gas by GC and analyzed catalysts such as steel by EPMA. Table 5 shows the results of GC analysis.

Table 5 The results of GC analysis.

SGTT condition				Result of gas analysis (area%)	
Refrigerant	oil	M/S	Water content in oil.	HFC134a	CFC12
CFC12(in.)	–		–	–	99.996
CFC12	A	none	about 30ppm	–	79.861
CFC12	B	none	about 30ppm	–	99.080
HFC134a(in.)	–	–	–	99.932	–
HFC134a	C	none	about 500ppm	99.925	–
HFC134a	D	none	about 500ppm	99.924	–
HFC134a	D	none	1%	99.872	–
HFC134a	D	A	about 500ppm	99.924	–
HFC134a	D	B	about 500ppm	99.917	–

Analysis condition
(GC-FID)
Column Porapac Q Injection Temp. 200 ℃
Column Temperature 150 ℃ Carrier gas rate 20ml/min.

Fig.8 shows the results of element analysis on the surface of the steel by EPMA. From Table 5 and Fig.8 we recognized the decomposition of refrigerant and copper plating phenomena on steel were occured. Generally copper plating is induced by chlorine ion[4] which is decomposition of CFC12 (CCl_2F_2). Similarly the extremely little contamination of chlorine compounds in HFC134a induced copper plating in

HFC134a/PAG mixtures we considered.

② Fig.9 and Table 5 show the influence of water. 1% water content system produced more copper plating and less stability than no water content system.

③ Similarly Table 5 shows the effect of molecular sieve desiccant. In addition, it made good influence of the stability, but we didn't recognize the difference of the effect of stability between A molecular and B molecular.

(2) The heat resistance of PAG

Fig.10 and Table 6 are the results of the heat resistance measured by CL anlyzer. The heat resistance of PAG ranked according to increasing reactivity were as follows :

OIL B < OIL C < OIL D << OIL F << OIL E < OIL A

(alkylbenzen / parafinic oil / mixture) (PAGs) (mineral oil)

This method is very useful to evaluate the stability of oxidation deterioration of refrigerating machine oil under extreme little oxygen such as in the refrigerant in cycle. Still more the moleculor structure of PAG has especially a ether linkage and hydroxyl terminal group, in the process of heat decomposition at local hot spot such as between bearing surface, it might produce alkoxy radicals(RO・) and/or alkyl peroxy radicals(ROO・) by itself. So this method is useful to know the resistance of oxidation deterioration under extreme little oxygan and decomposition of PAG by itself.

The different behavior of CL intensity, which was observed in PAGs in this work, came from the difference of molecular structure and additives.

Table 6 Temperature dependence of increment CL from oils.

oil \ Temp.	20℃	50℃	100℃	150℃
A	399112	1078535	7656891	70238904
B	22833	24680	61646	267111
C	25615	27192	82894	695255
D	24977	27453	91206	859280
E	355019	1030926	8254648	62758616
F	29531	42333	712965	6053329

(3) The effectiveness of lubricity

Oil E and oil F indicated the similar wear volume to oil A and oil B, but oil C and oil D indicated 2 ~ 3 times wear volume(Fig.12). And Fig.11 shows the less water content in PAG, the smaller wear volume were indicated, especially oil C and oil D were rather influenced. These behavior of lubrication mainly depend on not refrigerant (it means lubricity effect of refrigerant, ex.chlorine ion) but on the molecure structure of refrigerating machine oil and additives.

Compared Fig.11 with Fig.12, we didn't recognize the clear difference of wear volume of initial water content in various oils by HAYAMA wear test(Fig.11). The reason is a point of the way of oil feed. In real rotary compressor, the motion of slide between vane point and rolling piston were used under the condition of boundary lubrication. But when enough oil was supplied in HAYAMA wear test, the condition of lubrication were occured not under boundary lubrication but closely under hydrodynamic lubrication.

(4)The compatibility of HFC134a/PAG mixture with magnetic wire

Fig.13 shows the influence of water on two types of magnetic wire. A matter of course EI/AI wire was hardly caused the hydrolysis by in less than 0.5%-water-dissolved PAG. On the side of heat resistance, polyester wire was damaged under every conditions.

(5)The compatibility of HFC134a/PAG mixture with insulation film

Similar to above-mentioned polyester wire, PET film for insulation film was easily caused the hydrolyis under law temperature and law content of water in PAG. In less than 0.1%-water-dissoloved PAG(Fig.14) and considering its heat resistance, we can use it for insulation film in HFC134a/PAG mixtures system.

CONCLUSION

This paper presents some evaluation data that should be useful to those who are developing HFC134a with polyglycols as the lubricant in refrigerator. We have discussed the chemical stability,heat resistance,lubrication,magnetic wire compatibility and insulation film compatibility for the HFC134a/PAG mixtures comparing CFC12/mineral oil mixture.

These results lead to the conclusion that:

(1)In general, HFC134a/PAG mixtures were more stable than CFC12/mineral oil mixture. But some decomposition and copper plating phnomena on steel were observed.
Water had the bad effect of the stability and copper plating.
Molecular sieve desiccant had the good effect of the stability, but we didn't recognize the difference between 4Å moleclar and 3Å moleclar.

(2)The heat resistance of PAG ranked according to increasing reactivity were as follows:
alkylbenzen and parafinic oil mixture < PAGs < mineral oil

(3)Lubricity was different to each other. In addition, the effect of water was not good for lubricity.

(4)We will be able to use ester-imide/amide-imide(EI/AI) double coated magnetic wire in less than 0.5%-water-dissolved PAG.

(5)Similarly, we will be able to use polyethylene terephthalate(PET) film for insulation film in less than 0.1%-water-dissoloved PAG and considering its heat resistance.

ACKNOWLEDGEMENT

The technical assistance of S.Aoki and S.Ogasawara are greatly acknowledged and the encouragement and support of J.Enomoto,K.Shimamura and A.Katata are greatly appreciated.

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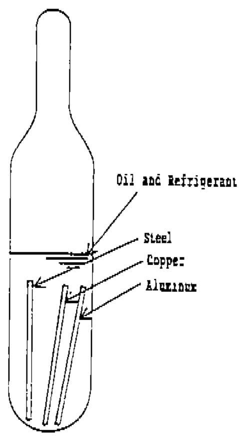


Fig.1 Experimental arrangement of sealed-glass-tube (substitute for apurpose,we add water and molecular seave desiccant.)

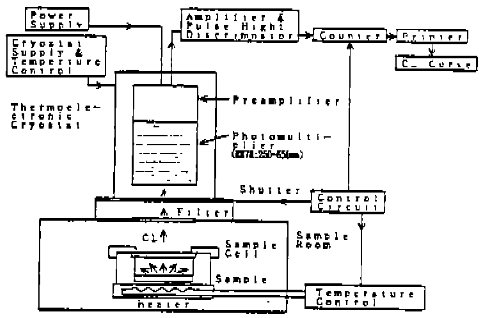
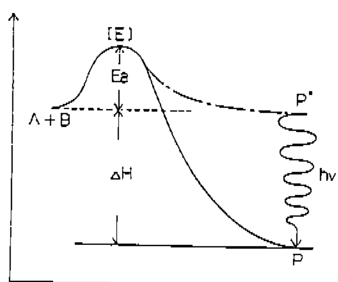


Fig.2 Schematic representation of a chemilunescence analyzer.A sample placing in the sample cell inside a light-tight box can be heated to a desired temperature,and resulting emission of light is detected with photomultiplier being cooled.



Explanation of code;
A+B:reaction of A+B
P* :the molecular which has excitation energy
P :stable compound
[E] :transition state
Ea :activation energy
ΔH :enthalpy
hv :faint light (which is occured by energy discharged)

Fig.3 Faint light mission-mechanism is the reaction of "A+B→[E]→P*".

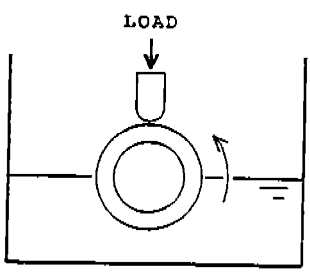


Fig.4 Schematic diagram of HAYAMA wear tester.

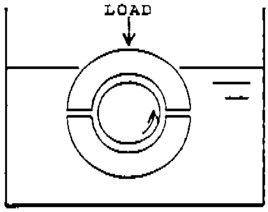


Fig.5 Schematic diagram of MAX-WIELAND wear tester.

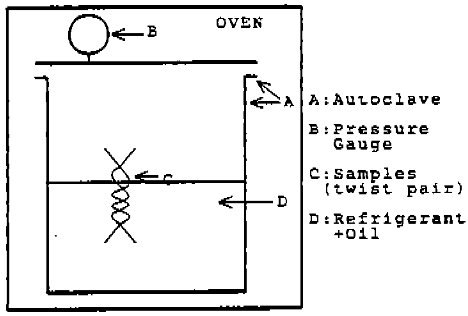


Fig.6 The schematic diagram of apparatus used for study of compatibility of the HFC134a/PAG mixture with magnet wire.

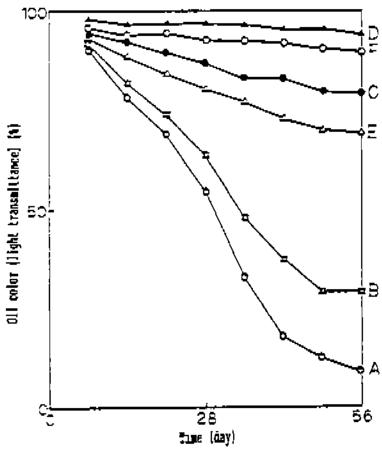


Fig.7 Oil color in Sealed Tube vs. time.
(oil color were measured by light transmittance at 540 nm.)

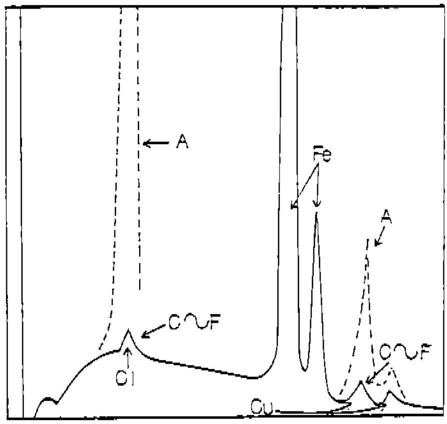


Fig.8 Elemental analysis on the surface of the steel compared with HFC134a/PAG and CFC12/oil.

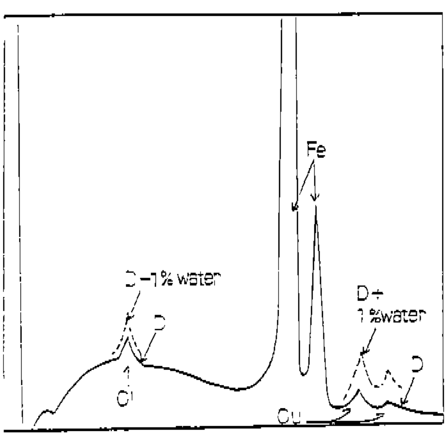


Fig.9 Elemental analysis on the surface of the steel compared with D and D+1%water.

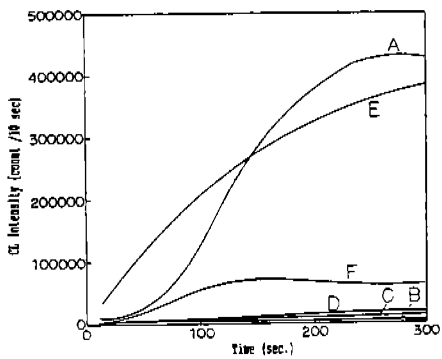


Fig.10 Charge in the chemiluminescence intensity of oils at 100℃

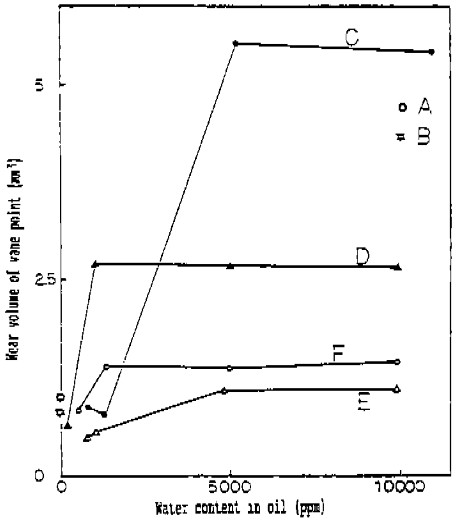


Fig.11 Wear volume vs. water content in oils by HAYAMA.

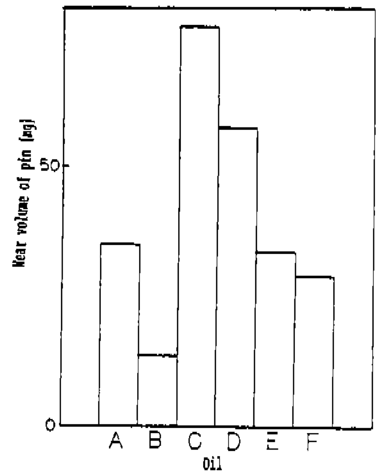


Fig.12 Wear volume in various oils by MAX-WIELAND.

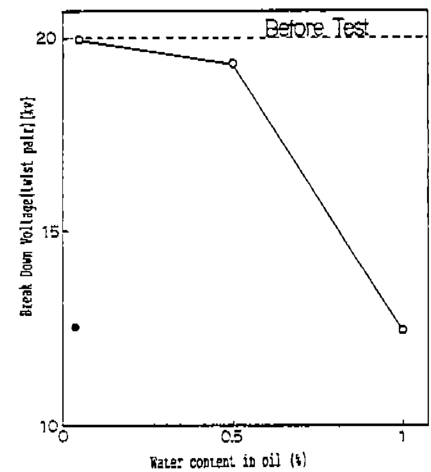


Fig.13 The compatibility of magnet wire vs. water in PAG.

Explanation of code;

—○— : EI/AI wire

● : polyester wire

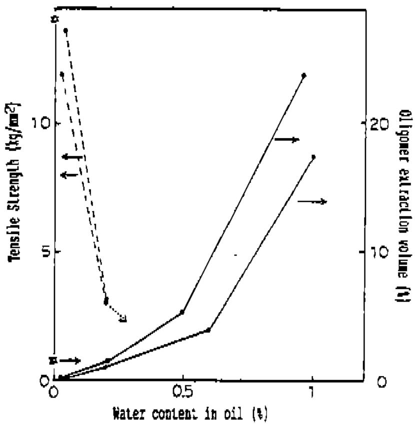


Fig.14 The compatibility of PET-film vs. water in PAC.

Explanation of code;

—●— : oil C × HFC134a

—○— : oil D × HFC134a

▫ : oil B × CFC12