1996

New Type Lubricant for Ammonia Refrigerating Systems

H. Takahashi
Japan Energy Corporation

T. Kaimai
Japan Energy Corporation

NEW TYPE LUBRICANT FOR AMMONIA REFRIGERATING SYSTEMS

Hitoshi Takahashi and Takashi Kaimai
Petroleum Products Laboratory
Japan Energy Corporation

ABSTRACT

New lubricant which can dissolve with ammonia refrigerant was developed. PAG based oil was found to be dissolved with ammonia and to have fine stability. It contributes to realize maintenance-free refrigerating system because oil returning are possible. It also helps to reduce refrigerant amount because of improvement of thermal conductivity. Ammonia refrigerant will be focused more as an alternative for HCFCs.

INTRODUCTION

Ammonia is known as high efficient refrigerant,[1] and now, it is focused again because of its environmental safety properties, ODP-free and GWP-free. But, ammonia has several unfavorable properties, such as smell, toxicity, flammability, corrosivity, and so on. The most unfavorable property on the view of operating ammonia refrigeration systems is immiscibility with mineral oil.

Immiscible oil has possibility to be left inside a evaporator and reduces the efficiency. Once oil is discharged with refrigerant, It could hardly return to a compressor, then the compressor with few oil will result in failure. To prevent these troubles, refrigeration equipment needs an oil separator, interval oil removal from the evaporator inside and oil replenishment into the compressor. For the spread of wide applications including alternation of HCFCs with ammonia refrigerant, it is indispensable to realize a compact, maintenance-free and direct evaporation system. And development of new oil which has miscibility with ammonia refrigerant will realize a such new easy-operation refrigerating system with environmental-friendly refrigerant.

INVESTIGATION OF MISCIBLE LUBRICANT

Search for Miscible Base Oil

The first step to develop new miscible refrigerating oil was finding out miscible base oil. In this investigation, It was very useful that know-hows which were found out in the investigation to develop new refrigerating oil for HFC refrigerants. HFCs also do not dissolve with mineral oil. This phenomenon

is understood by polarity of compounds.[2] Base oil must have polarity to dissolve with such high polar compounds, HFCs. So that oxygen containing compounds, such as esters or PAGs were selected as base oils for HFC refrigerants. Ammonia is a polar compound, thus it was predictable that there were several candidates in esters and PAGs.

Fluidity test with ammonia at low temperature, shown in Table-1, was performed with several kinds of oil. Miscibility of each oil was measured by phase separation temperature of oil / ammonia mixture (Oil / R717 = 5 / 1 by weight). Fluidity was measured following method. Sealed glass tube within oil / ammonia mixture was cooled down to -30℃ or -50℃. Then glass tube was reversed and the time taken for 50mm movement of mixture or oil was measured. Mineral oil and alkylbenzens were immiscible with ammonia, and they solidified at low temperature below -30℃ with no fluidization. On the other hand, all PAGs selected were miscible even at -50℃ with good fluidity. in the case of esters, though they could not dissolve with ammonia at room temperature, they had fluidity. So, new refrigerating oil should be selected from these oxygen containing organic compounds.

Stability with Ammonia

The second step was checking stability with ammonia, because ammonia with moisture has remarkable reactivity. Autoclave test, shown in Table-2, was performed for selected synthetic oils which had good fluidity with ammonia. Both esters indicated much sediment after test, and PAG which has -OH in its end also indicated sediment. The amounts of sediment were related with TAN of oils, thus it was clear that sediment made from reaction of acid and ammonia. With moisture, ester decomposes to alcohol and acid by hydrolysis reaction, then acid reacts with ammonia and acid-amide is produced which is observed as sediment. Alcohol which has -OH becomes acid easily by mild oxidation, so that alcohol type compounds also result in sediment. Through this autoclave test, It was found that capped-PAG which was alkylated both ends was the best compound as base oil for ammonia refrigerant. It has good miscibility and stability with ammonia.

Lubricity Improvement

The next step was investigation of lubricity. The priority of new oil is miscibility with ammonia, but, concerning about lubricity, miscibility works as a negative factor. When ammonia dissolves with oil, viscosity of mixture becomes lower than that of oil itself. Ammonia dissolution to oil can be regarded as oil dilution by ammonia, thus new refrigerating oil must have excellent lubricity even in diluted condition.

Additive is one choice to improve the lubricity. Esters or alcohols as oiliness reagents and

phosphates as extreme pressure agents are famous anti-wear agents. Although, they have possibility to result in sediment, because of generated acid by hydrolysis or mild oxidation of additives It will be hard work to improve lubricity with additives, and it seemed only way that finding out the best structure of base oil to have enough lubricity without additives. Of cause, structure affects not only lubricity but also other important properties, such as stability, miscibility, and fluidity. As a result of investigation, it was found that block copolymer type PAG had desired property; miscibility, good stability and superior lubricity. Finally, block copolymer PAG with both alkylated ends was selected as base oil for ammonia refrigerating system. This base oil has good miscibility with ammonia, fine stability in ammonia atmosphere and superior lubricity without additives.

Specific property of new oil is shown in Table-3, and stability examined by sealed tube test is shown in Table-4. Superior stability of ammonia miscible oil compared to that of mineral oil was found. Both PAG and mineral oil indicate no sediment, however, while color of PAG was permissible level, that of mineral oil became worst level.

PRACTICALITY OF MISCIBLE LUBRICANT

In laboratory tests, new PAG oil for ammonia refrigerant indicated its superior properties. Then practical performance tests have been done in collaboration with an ammonia refrigerating machine maker. Fluidizing test was also done in actual refrigerating equipment. In a special refrigerating machine with sight glasses, fluidity of oil was observed. While mineral oil could not flow because of solidification, new PAG oil was observed to flow with ammonia refrigerant. Self-oil-returning was confirmed exactly.[3),4)]

Up to now, practical performance of new PAG oil have been confirmed successfully with actual refrigerating machines. Table-5 shows two examples which were sampled after 2,000 hours running. each sample did not indicated any evidences of oil inferior. Each oil still would be enough performance and in good condition.

NEW AMMONIA REFRIGERATING SYSTEM

Development of ammonia miscible oil could make ammonia direct evaporation system practical. In this system, miscible oil and hermetic compressor with canned motor were applied, and it was achieved that ammonia leak prevention and refrigerant amount reduction. Especially, amount of ammonia refrigerant could be reduced remarkably to about a tenth of amount for equivalent flooded type evaporator equipment. Furthermore, there is another merit which contribute to thermal conductivity. It was confirmed that thermal conductivity improved 60% in the case of using new PAG oil compare to

mineral oil system.[3),4)] Refrigerant amount reduction and thermal conductivity improvement will make ammonia refrigerating equipment down-sized and risk-free.

SUMMARY

New ammonia miscible refrigerating oil was developed. Its practicality have been confirmed by laboratory tests and actual equipments. This oil contributes to make ammonia refrigerating equipment maintenance-free, compact and high-efficient one. And it also contributes to develop new market for ammonia refrigerating system.

Reference

1) S. Senrui and T. Takaichi, Refrigeration, Vol. 70, pp507-517, Japanese Association of Refrigeration (1995)
2) T. Kaimai, Petrotech, Vol. 18, pp1053-1059, The Japan Petroleum Institute (1995)
3) K. Kawamura, Proceedings of 1992 JAR Annual Conference, pp193-203, Japanese Association of Refrigeration (1992)
4) H. Namiki, Proceedings of the International Symposium on R22 & R502 Alternative Refrigerant '94, pp57-62, The Japan Refrigeration and Air Conditioning Industry Association (1994)
5) H. Takahashi, Refrigeration, Vol. 70, pp518-523, Japanese Association of Refrigeration (1995)

Table 1 Fluidity Test[5]

Oil \ Item		Miscibility	Fluidity (sec)	
		Phase Seperation Temp. (℃)	@−30℃	@−50℃
Naphthenic Mineral Oil		Separated at R. T.	103	>300
Alkylbenzene	Hard Type	Separated at R. T.	201	>300
	Soft Type	Separated at R. T.	7	>300
PAG	Mono-ol Type	−50	<1	4.5
	Dialkyl Type	<−50	<1	1.5
POE	Hindered Type	Separated at R. T.	<1	3
	Complex Type	Separated at R. T.	<1	3

Oil / R717 = 5 / 1 (by Weight)

Fluidity was measured by the time taken 50mm movement of liquid

Table 2 Stability Test (1)[5]

Item \ Oil		PAG		POE	
		Dialkyl Type	Mono-ol Type	Hindered Type	Complex Type
Color	(ASTM)	L3.0	L3.0	L1.5	L1.5
Total Acid Number	mgKOH/g	0.03	0.05	0.17	0.61
Sediment		No Detected	Few Amount	Medium Amount	Much Amount

Autoclave Test

Oil : 50g, R717 : 0.059MPaG { 0.6kgf/cm²G }, N_2 : 0.56MPaG { 5.7kgf/cm²G }

Cat. : Fe Wire (3m), 150℃×30days

Table 3 Specific property of Ammonia Miscible Oil[5]

Item		Specific Property
Color	(ASTM)	L0.5
Flash Point	℃	240
Pour Point	℃	−40
Kinematic Viscosity (@40℃)	mm^2/s	47.2
Total Acid Number	mgKOH/g	0.01
Phase Separation Temp. Oil / R717 = 5 / 1	℃	−45
Falex Extreme Pressure (@40℃)	N {Lbf}	3114 {700}

Table 4 Stability Test (2)[5]

Item \ Oil	Ammonia Miscible Oil	Naphthenic Mineral Oil
Color (ASTM)	L1.5	L8.0
Sediment	No Detected	No Detected

Sealed Tube Test

Oil / R717 = 3ml / 7ml, Cat. : Fe Wire, 150℃×14days

Table 5 Property of Oil Sampled from Practical System[5]

Item		Sample 1	Sample 2
Running Time	hrs	2000	2000
Color	(ASTM)	L1.0	L1.5
Total Acid Number	mgKOH/g	<0.01	<0.01
Peroxide Number	ppm	<1	<1
Fe Dissolved in Oil	ppm	1	2