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Decomposition of Refrigerants in Household Refrigerators

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DECOMPOSITION OF REFRIGERANTS IN HOUSEHOLD REFRIGFRATORS

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ABSTRACT

The purpose of this paper is to report about the chemical reaction between oil and freon during the formation of oil-coke and other halogenated gases. Through the years we have collected data concerning this reaction in refrigeration systems.
Some of the parameters influencing the reaction rate are described.

OIL AND FREON REACTIONS IN LAB-TEST

Laboratory analyses carried out by Spauschus (ref1) 15 years ago and more recent analyses carried out by Borchard (ref2) have shown that oil and freons can, at sufficiently high temperatures, be made to react during the formation of halogenated gases and oil-coke.
Such laboratory tests are made under batch-reactor conditions, i.e. oil and freon are mixed in a pressure container of a given volume with the addition of metal as a catalyst.
The container is maintained at a constant temperature for a certain number of days, after which the oil and gas phase are analysed.
In this way the volume and type of breakdown products can be determined and it becomes possible to determine the type and order of reaction that has taken place.
Laboratory tests are well-suited to reveal how willing oils and freon are to react, but they cannot be used to determine the rate at which the substances will consequently react when they work together in a compressor.
The characteristics of such laboratory tests are:

- The system is static - contact time and reaction conditions are well known
- The reactants are completely mixed
- There is an unlimited amount of both reactants

OIL AND FREON REACTIONS IN COMPRESSORS

In a refrigeration system and, more precisely, in a compressor, oil and freon work together under flow-reactor conditions:
Briefly, oil and freon flow through the compressor with widely different velocities and are exposed to different and at times very high temperatures.
This means:

- The system is dynamic - contact time and conditions vary
- The raectants are not completely mixed
- An excess of one component can occur

In refrigeration compressors used in household appliances the occurrence of high and for the reaction critical temperatures can be assumed:

- In and around the valve system under certain load conditions
- In the bearings under metal-metal friction
- In the motor - from motor defect or overload

Naturally, the wish is that such reactions will not occur in the compressors.
The quality of a compressor is determined partly by its performance data and partly by how long it will yield that performance.
Temperatures inside a compressor depend on the loading it is subjected to, i.e. ambient temperature, suction gas temperature and pressure, parameters which to a certain extent are outside the responsibilities of the compressor manufacturer and which depend on the dimensions and application of the refrigerating system.

COMPRESSOR LIFE TESTING

The compressor manufacturer can build in thermal protection systems and set application limits on the various sizes of compressor, and in this way prevent indirectly, the occurrence of undesirable oil-freon reactions.
The aid the compressor manufacture has to set relevant application ranges for a given compressor design is derived from the carrying out of accelerated life tests and at the same time following freon-decomposition gases development.
The principle of ours tests and the associated analyses can be briefly described as follows:
When a certain compressor model is to be tested a number of units are taken for building into a hot gas system, i.e. a gas circuit where the pressure and temperature of the suction gas, and the pressure of the discharge gas can be regulated with suitable regulating valves (see fig. 1).
The hot gas system is charged with a known amount of freon and the compressor is installed observing the normal rules for refrigerating system build-up, without air, water, flux residue, etc.

The difference between a hot gas system and an ordinary refrigerating system is that with the former the refrigerant is held in the gas phase during the test.
Under test a set of operating conditions are maintained, there value depending on what is to be tested and the level of acceleration required.
Occasionally a sample of the gas phase is extracted. This is done using the analysis container which is evacuated beforehand. During sample extraction the system is pressure equalized.
After extraction the sample is analysed using a gas chromatograph - the qualitive and quantitive composition of the refrigerant is determined.
An example of a typical gas analysis after 2ooo hrs stressed test shows the results given in fig.2 . The system was charged with freon 12.

REACTION PRODUCTS

Products from the reaction between oil and the most commonly used refrigerant freon 12 in a batch process are identified as freon 22, HCl and oil-coke.
In the main, the formation of the same products has shown itself when the reaction occurs in a refrigeration compressor.
Freon 22 formed in a freon 12 refrigerating system can be used as a measure of to what extent a high temperature situation has occured.
Freon 22 is in itself quite unharmful but the fact that it does occur shows that an undesirable reaction has happened. The reason for this reaction or the reaction product like oil-coke will sooner or later lead to compressor breakdown.
This means that the rate of formation of freon 22 can be used to establish the life time for a compressor.

EVALUATION OF LIFE TESTS

The composition of the refrigerant gas as a function of time, and the compressor condition after test form the basis for assessing the application range for the compressor design, or whatever the test was intended to reveal.
If the life tests have been performed at different stress levels it becomes possible to calculate the time or stresses neede before reaching i.e. a certain degree of freon-oil reaction.

EXAMPLES OF FACTORS THAT CAN AFFECT OIL-FREON 12 REACTION RATE IN COMPRESSORS

In the section which follows the described tests are performed at only one stress-level - since the intension was to mention some of the parameters which influence the reaction rate.
The results shown are individual measurements which are taken as being representative of the experiments they are meant to illustrate.
The reported life tests are carried out with compressors that yield 125-175 kcal/h at normal load i.e. $-25^{o}C/+55^{o}C$ and $+32^{o}C$ ambient temperature.
Results of the gas analyses are given in vol% and in all cases the total freon charge has been 40 g.
Fig.2 shows the previously mentioned results of a normal gas analysis:

Gases CO and CO_2 stem from the insulation materials - and the formation of these gases are not mentioned more -. Freon 22 stems from the oil-freon 12 reaction in the bearings or around the valves.

EXAMPLE 1: ELECTRICAL FAILURE

Fig.3 shows the composition of the refrigerant gas after the motor in a compressor has burnt out because of short-circuiting.
Note especially the decomposition gas products like freon 22, freon 23, methane etc.

EXAMPLE 2: HIGH TEMPERATURE CAUSED BY FRICTION- AND COMPRESSION HEAT

Fig.4 shows decomposition gas freon 22 as a function of time for two compressors whose performance are identical but whose bearing systems are different:
fig.4a represents a design incorporating a dry-lubricated bearing, e.g. a pivot bearing or ball joint
fig.4b is from a design where all bearings are hydrodynamically lubricated, e.g. the scotch yoke design.

We think the results should be interpreted as follows:
The design represented by fig.4a has a running in period when metal-metal friction occurs until the dry-lubricated bearing is worn in.
This produces the high temperature conditions in which oil and freon 12 can react.
Such a running in period does not occur in the design fig.4b refers to.
The sequence of freon 22 formation is othervise the same for both designs, and this is bound up with the oil-freon 12 reaction in the valve system - the only other region with high temperature.
Both decomposition gas sequences - based on highly accelerated test - are considered as being normal and after operating for 6000 hours such compressors are in full working order.

Fig.4c shows the sequence of freon 22 formation when a defective bearing leads to insufficient lubrication and an increasing level of metal-metal friction.
The result of course is completely unsatisfactory and after the test the compressor has lost some of the performance.
By using the gas analysis it was possible to predict these results before 1000 hours operation.

EXAMPLE 3: MATERIALS REACTIVITY

Fig.5a and 5b show the sequence of freon 22 formation in six mechanically and thermally identical compressors, but with two different oils.
Fig.5a is based on the reaction between a well refined mineral oil and freon 12. Fig.5b is based on the reaction between alkyl benzene based oil and freon 12. All other test parameters being held identical.

These figs. illustrate the difference between oils. Compressors with alkyl benzene oils are better suited to a stress situation than compressors with mineral oils - other features identical.

This conclusion is also based on the fact that the rate of reaction always varies with temperature and we have performed the tests also at other temperatures to insure that the reaction rate is still lower for the alkyl benzene based oil than it is for mineral oil.

The investigations behind fig.5c are based on both the compressor designs mentioned before.
The thermal and mechanical load was also the same, but the test was conducted with freon 502 instead of freon 12.
After 2000 hours test it has not been possible to detect any halogenated gas decomposition products.
After the test the compressors were working with complete performance and no discolouring was seen on the valves.
The fig. shows that freon 502 is much more stable than freon 12 in a refrigeration system. There is absolutely no formation of decomposition gas and no other sign of a freon-oil reaction.
This test has also been performed at various stress levels - still with the same result.

INFORMATION FROM THE MARKET ON OIL-FREON 12 REACTIONS IN REFRIGERATING SYSTEMS

Through the years we have of course kept track of our compressors on the market, partly through close contact with our customers and partly through our own analyses of defects and rejects.
We have therefore an excellent record of reject percentages and reject causes for appliances and the associated compressors up to 5 years old.
In any event reject causes is due to 'defects' of one form or another: a life of 5 years is not satisfactory.
In Europe most refrigerators become much older and to learn more about the extent of oil-freon 12 reaction in aged systems we set out to analyse some old refrigeration appliances.

REFRIGERATOR APPLIANCES ANALYSED

In Denmark it is normal to trade-in ones old refriferator for a new one. The dealer will sometimes recondition the old appliance and sell it at a special bargain price, at other times he will sell it for scrap.
It was from such a dealer we bought the stock of used appliances: 15o old refrigeration appliances.
These appliances had been in service for 5-22 years and the wiew was that there life must in the main be considered as satisfactory and an analysis of freon 22 content in the refrigerating systems should give an indication of the rate for oil-freon 12 reaction in a household refrigerator.

The features of these appliances were as follows:

- 150 appliances, 15 without charge or with burnt motor. Both defects influence the composition of the refrigerant gas and therefore make the appliances unusable as far as an oil-freon 12 reaction analysis is concerned
- 135 refrigerating systems still performed quite well. Most were equipped with Danfoss type PW compressors.
  Compressor size distribution was:

1/12 hp :	28 pcs.
1/10 hp :	35 —
1/8 hp :	57 —
1/6 hp :	8 —

- The refrigerating systems were representative of many different producers and were of different types:
  - Deep freezers
  - Combined refrigerator/freezers
  - Refrigerators
- It was assumed that all the appliances had been used in identical geografic and climatic area.

DESCRIPTION OF ANALYSES

We took a sample of the refrigerant gas from all 135 refrigeration systems. This was done after 24 hours pressure- and temperature equalizing.
During extraction, equalizing pressure is also measured.
The sample itself is extracted using a special tapping valve which is connected to an evacuated analysis container and a pressure gauge.

The gas sample is completely analysed using gas chromatography and, among other things, the content of freon 22 in vol% is determined.
Since the freon charge, equalizing pressure, etc. was not the same in all systems examined, the vol% is not particularly significant.
Much more important is wether freon 22 is present or not.
With the experience we have in analysis accuracy, refrigerant purity, etc. our assessment is that only where the content is 0.1 vol% is it certain that the product is formed by oil-freon 12 reaction in the refrigerating system.
Figs.7 and 8 show the analysis results in diagrams: Only in 21 of the 135 systems there was more than 0.1 vol% freon 22.

INTERPRETATION OF RESULTS

The most important reult is that decomposition gas freon 22 is found in some systems but not in others and that no decomposition gases were found to originate from refrigerants other than freon 22.
This corresponds very well with lab test and life test.

Fig.7a and b show age and number distribution of the appliances not containing decomposition gas and appliances containing decomposition gas.
It would appear that there is no difference regarding the age distribution in the two categories.

Figs.8 show the corresponding distribution according to refrigerating system type.
This reveals that:

- 30% of used deep frezers contained decomposition gas freon 22
- 20% of used refrigerator/freezers contained freon 22
- 0% of used refrigerators contained freon 22

The influence of a series of parameters on oil-freon 12 reaction rate were also tested using our analysis material, but apart from the application dependence

no significant correlations were found.
To illustrate this, it could be mentioned that decomposition gas formation neither depends on the content of noncondensible gases, the appliance manufacturer, electric motor insulation material, filter drier type, nor, as previously mantioned, the operating time.

The conclusions we draw are:

- There is a significant connection between the application of a refrigerating system and the reaction rate for the chemical reaction between oil-freon 12 in that system.
- The risk of ageing of refrigeration systems due to oil-freon reactions seem to be very, very small.

CONCLUSION

Some factors affecting the reaction rate for the chemical reaction between oil and freon working together in a compressor have been illustrated by results from life tests.
Allthough exact figurs for the reaction rate are not calculated it becomes significant that a change from freon 12 to freon 502 will reduce the risk for oil-coke formation on valve and widen the application area for a certain compressor design.
It has been illustrated by analysis of old refrigeration appliances that aged appliances very selldom mean that the refrigeration system itself is aged.
It was also shown that risk of reaction between oil-freon depend on the type of appliance.

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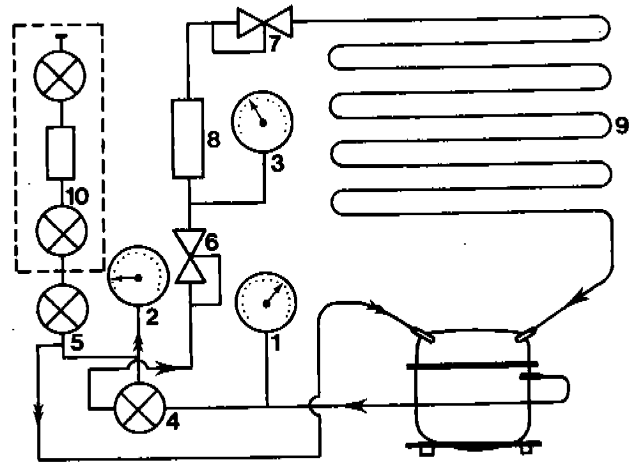
1. Spauschuss, H.O. and Doderer, G.C.:
   Reaction of refrigerant 12 with petroleum oils
   ASHRAE meeting Febr. 13-16 1961
2. Borchardt, Hans J.:
   New findings shed light on reactions of flourcarbon refrigerants.
   DuPont Innovation Vol. 6, 2, 1975

Fig. 1



1, 2 and 3 - Manometers.
4 - T-valve.
5 - Valve.
6 - Discharge pressure regulator.
7 - Suction pressure regulator.
8 - Extra volume.
9 - Cooling grille.
10 - Sample holder.

Fig. 2

Normal gasanalysis after 2000 hours test:

- 0.61 vol% freon 22
- 0.54 vol% CO_2
- 0.22 vol% CO

Rest: freon 12 and 0.12 vol% NC-gas

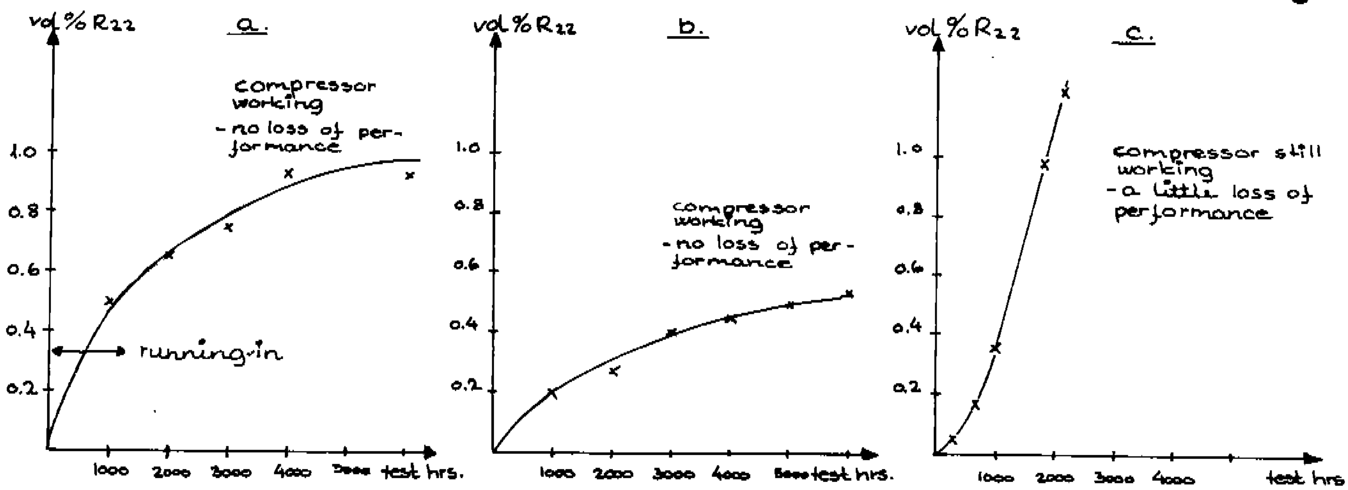
Fig. 3

Gas analysis after short-circuiting:

- 0.43 vol% freon 22
- 0.04 vol% freon 23
- 0.19 vol% C_2H_2
- 0.ol vol% C_2H_4
- 0.14 vol% CH_4
- 0.07 vol% CO

Rest: freon 12 and 2.0 vol% NC-gas

Fig. 4



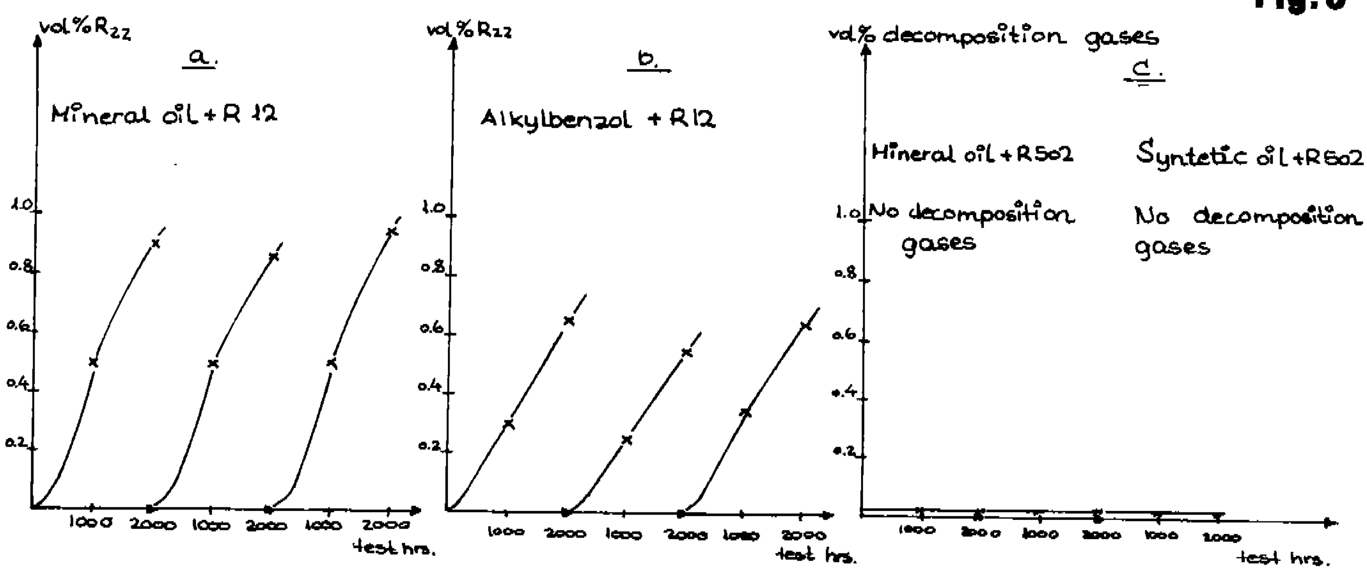
nr. 3388 FR — One bearing: dry friction

nr. 3391 PW — All bearings: oil lubricated

nr. 3696 — All bearings oil lubricated, mechanicall failure in one bearing

Formation of freon 22 during accelerated lifetimetest
Testconditions: Δ tw : + 20°C , - 5°C / +70°C
Influence of mechanical parameters.

Fig. 5



FR nr. 1, 2 and 3
Sag nr. HG-ER 76/083

FR nr. 4, 5 and 6
Sag nr. HG-ER 76/083

SC nr. 1, 2 and 3 Sag nr. HG-ER 77/124
PW nr. 5 Sag nr. HG-ER 2996

Formation of freon 22 or other decomposition products during accelerated lifetimetest
Testconditions : Δ tw : + 20°C , - 5°C / +70°C
Influence of chemical parameters

Fig. 7a

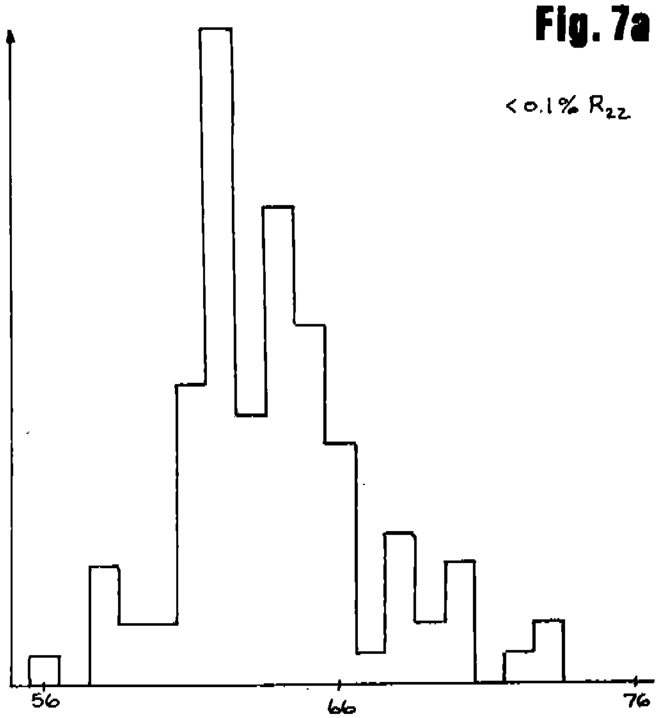


Fig. 7b

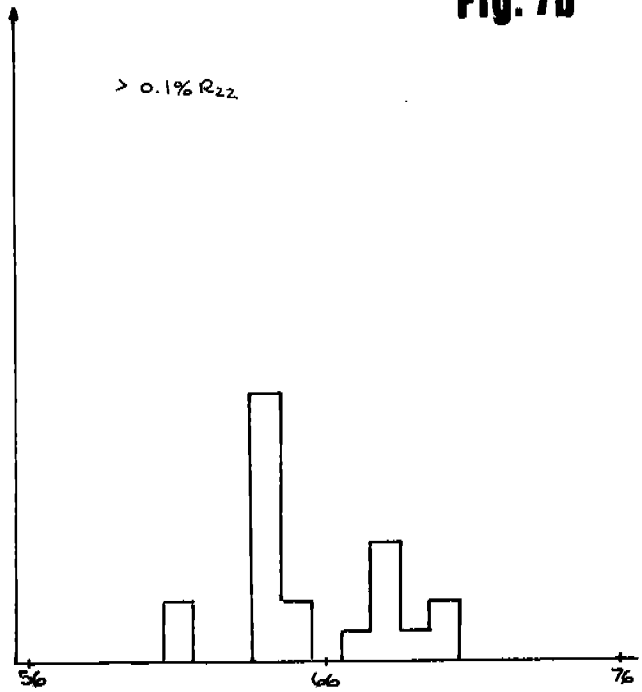


Fig. 8a

Homefreezers

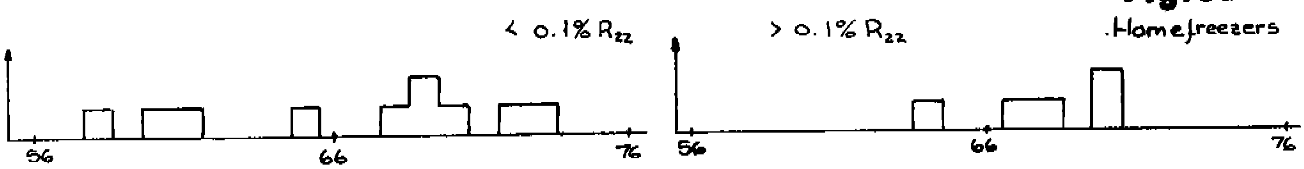


Fig. 8b

Household refrigerators with speciel low-temperature compartment

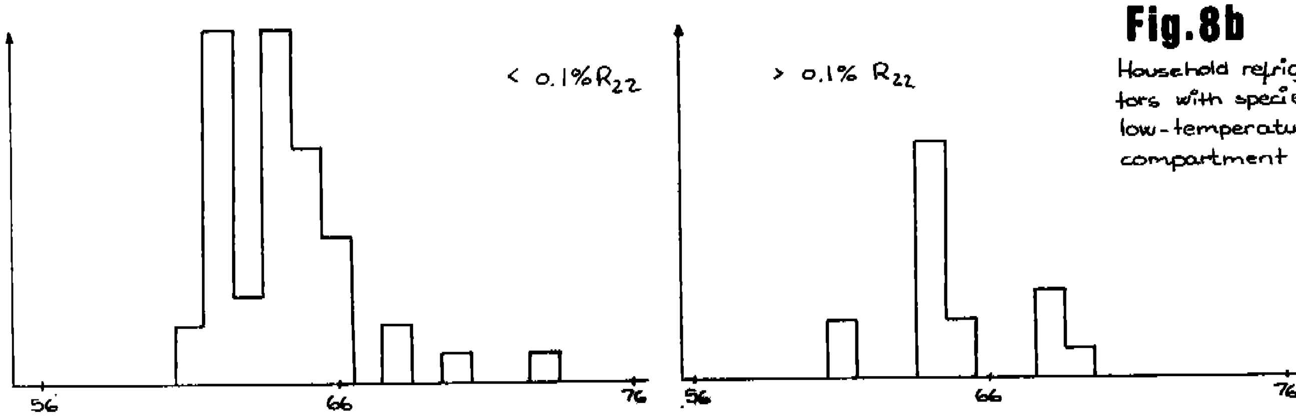


Fig. 8c

Household refrigerators.