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Project Summary

Evaluation of Refrigerant from Mobile Air Conditioners

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This project was initiated to provide a scientific basis for choosing a reasonable standard of purity for recycled chloroflurocarbon (CFC) refrigerant in operating automobile air conditioners. It evaluated the quality of the refrigerant from air conditioners in automobiles of different makes, ages, and mileages, from different parts of the country, and with both failed and properly working air conditioners. The refrigerant, CFC-12, was tested for water content, acidity, residue quantity, refrigerant purity, residue purity, inorganic chloride, and inorganic fluoride. This work will be the basis for programs to reduce CFC emissions from the servicing of automotive air conditioners.

Of the 227 cars sampled, neither the compressor oil nor the refrigerant showed any measurable levels of acid (to 1 ppm), inorganic chlorides (to 0.1 ppm), or inorganic fluorides (to 0.1 ppm). The gaseous refrigerant, in all but two samples was of higher purity than the specification for new CFC-12.

The amount of residue measured in the CFC-12 was simply the compressor oil which was carried over into the sampling container by the refrigerant. The amount of residue in each sample depended on the amount of refrigerant in the air conditioner, the rate at which the sample was removed (the sampling rate), and on how soon after the air conditioner was used the sample was taken.

The residue (compressor oil) was also tested for purity. It was found to be very pure (>99% in all but one or two samples). That impurity was found to consist of very small amounts (<1 ppm) of a large number of different organic compounds. There was no statistically significant correlation between residue purity and car mileage, whether the car's compressor was functioning, or with the area of the U.S. where the sample was taken.

Traces of water were found in the refrigerant. The mean for all of the samples was found to be 56 ppm. No statistical correlation was found between the water content of the refrigerant and whether the compressor was working or failed nor with the area where the sample was taken; however, a statistically significant correlation was found between the odometer reading of the car and the water content. The mean water content for odometers registering up to 18,000 mi (29,000 km) was 34 ppm. At higher mileage ranges, the mean moisture content of the refrigerant was in the 56- to 94-ppm range.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Approximately 25% of all domestically consumed chlorofluorocarbons (CFC or CFCs) are currently used in automobile air conditioners, the single largest use of these chemicals. Moreover, current servicing practices result in substantial but unnecessary emissions of CFC-12 (dichlorodifluoromethane). During typical servicing, any CFC-12 remaining in the automobile air conditioner is first vented to the air, a new charge of CFC-12 is sometimes used to test the system and locate the leak, and finally the system is recharged with CFC-12 after repair. The release of CFC to the atmosphere could be reduced by requiring the recovery and reuse of the refrigerant from all automobile air conditioners serviced; however, there has been little information available on the level of contamination in operating automobile air conditioners and the ability of equipment to satisfactorily clean the CFC for reuse.

This project to evaluate CFC refrigerant from automobile air conditioners was initiated in response to these questions. The quality of refrigerant present in vehicles of different makes, ages, and mileages and from different parts of the country has now been assessed. The refrigerant from 227 vehicles with both failed and properly working air conditioners was collected and tested. The results of the program have provided an understanding of not only the quality of the refrigerant found in automobiles but also of how failure of the compressors and other equipment affects its contamination.

The work was guided by and performed in cooperation with an ad hoc industry group comprised of representatives of interested parties. The ad hoc industry group agreed that the following parameters would fully describe possible refrigerant contaminants: water content, acidity, residue, chloride ion, purity of the liquid phase, purity of the gas phase

The group also determined that the recycled refrigerant would be considered satisfactory for reuse if recycling equipment could achieve a standard of purity comparable to that of the refrigerant in properly working air conditioners in automobiles that have been driven for 15,000 ± 3,000 miles (25,000 ± 5,000 km). Thus, the two main aims of the program were: (1) to determine the purity of CFC using the six parameters listed above for properly working air conditioners in cars at 15,000 ± 3,000 miles, and (2) to determine the maximum CFC contamination for cars that will seek service due to major component failure.

In response to the objectives, refrigerant in 227 vehicles from different parts of the U.S. with a variety of mileages and automobile air conditioners was evaluated.

Sampling Procedure

The equipment used for sampling the automobile air conditioners consisted of a sampling cylinder, sampling line, and a manifold gauge set and vacuum pump (furnished by the shop at the sampling site).

Three hundred sampling containers that were manufactured specifically for this purpose were used for this program. Each container is an (approximately) 1-gal. (3.8 L) steel vessel equipped with a 2-way valve suitable for CFC-12. One sampling line was made for each container and packed with it. Before being shipped to the sampling sites, all sampling containers and sampling lines were cleaned, dried and tested to ensure that they were clean and capable of holding pressure.

At the sampling site, the sampling containers were filled with refrigerant from the automobiles by placing the sampling container into a pan of dry ice and evacuating the line and container. The sample was then drawn from the air conditioning system at the high pressure side so that lubricant would be withdrawn with the refrigerant. Once the sampling was completed, the air conditioning system was serviced, if needed, and then recharged by service center personnel following normal procedures. For each vehicle, the model, year, type of engine and air conditioner, and other information were recorded on a Vehicle Information Form prepared for the purpose.

Analytical Procedures

The contents of each sample container were analyzed as received by the method indicated for the following:

1. Moisture content: Karl Fischer titration
2. Acidity or acid number: KOH titration
3. High boiling residue or oil content: Gravimetric analysis
4. Cleanliness or purity of the refrigerant: GC/FID.
5. Purity of the residue: GC/FID.
6. Free halides: Ion chromatography

Results

This sampling and analytical program showed that the refrigerant in operating air conditioners is very pure. Acids do not accumulate in the refrigerant. Any impurities that accumulate in the air conditioning system are concentrated in the compressor oil. They are dissolved by the liquid phase of the refrigerant but d not get carried over into the gas phas The gas phase proved to be free (contaminants and equivalent in purity t new CFC-12.

Water content was the only paramete which was highly dependent on vehicl mileage. In more than 95% of th samples analyzed, moisture was preser at above the specification for new CFC 12. Table 1 summarizes the results fc water as well as for residue purity. Th water content of the refrigerant tended t be greater in vehicles with highe mileage. However, even refrigerant i new vehicles had a moisture level greate than the 10-ppm specification on ne CFC-12. This may be due to the sma amount of moisture that is present on a manufactured parts (e.g., as th compressor, expansion valve, and hoses and to the migration of moisture throug hose material. As illustrated by th relatively small standard deviation shown in Table 1, the moisture in th lower mileage ranges does not vary a much as it does in the higher mileag ranges. The moisture level in th refrigerant did not show any correlatio with geographic location or vehicle make

The mean for all of the samples wa found to be 56 ppm. No correlation wa found between the water content of th refrigerant and the area of the U.S. wher the sample was taken; however, correlation was found between th odometer reading of the car and th water content. The mean water conter for cars up to 18,000 mi (29,000 km) wa 34 ppm. Above this mileage, the mea moisture content of the refrigerant i different mileage ranges remained in th 56- to 94-ppm range.

Contamination of the CFC-12 wit HCFC-22 is not widespread. Only tw cars out of more than 200 teste contained more than the limit for ne CFC-12 of 0.5%. Even if it occurs, it effect is limited since it quickly leaks ou of the system through the hoses and ha a very limited effect on the ai conditioner's performance.

Neither the refrigerant nor the residu (compressor oil) which came with during the sampling showed an measurable level of acid (to 1 ppm inorganic chlorides (to 0.1 ppm), c inorganic fluorides (to 0.1 ppm). Th refrigerant in all the samples was bett than the purity requirement for new CFC 12 by these criteria.

Table 1. Summary of Results (ppm)

Good Compressors (miles)[a]	Moisture				Residue Purity			
	No.	Maximum	Mean	SD[b]	No.	Maximum	Mean	SD[b]
0-12,000	15	207	34	50	16	7,600	1,841	2,300
12,000-18,000	49	127	34	28	47	9,900	1,969	2,353
18,000-40,000	39	1,002	73	189	39	10,600	1,656	2,327
40,000-60,000	25	413	56	77	23	6,600	1,246	1,558
60,000-90,000	41	224	49	36	41	9,700	1,230	2,277
>90,000	23	755	94	147	22	4,700	785	1,232
Subtotal	192				188			
Failed Compressors	24	515	58	100	26	5,700	852	1,208
Total	216				214			
Blanks	21	65	15	16	20	2,100	313	504

[a]1 mi = 1.6 km
[b]Standard deviation

One possible explanation of the absence of acid is that an automobile air conditioner is a relatively benign environment for a material as chemically stable as CFC-12. A second explanation is that the acids that might form are fully contained in the lubricant or are neutralized by the metal content of the air conditioner components. There was evidence that free acid reacted with the material of the sampling system. This chemical reaction would result in deterioration of metal, but would not degrade refrigerant.

The finding on the lack of acid is good news for the program. Because the sampling system was selected to closely duplicate the recovery system that will be used to recycle the refrigerant, there is every reason to believe that no significant quantity of acid will be removed from the unit during recycling/servicing. Furthermore, any acid present during normal capture and recycling of the refrigerant can be removed by the recycling equipment. Laboratory tests indicate that acid can be neutralized by contact with special metal compounds that can be incorporated in the recycling equipment. The acid is neutralized within a few minutes of contact. Based on this laboratory analysis, acidity in recycled refrigerants will not be a problem if recycling equipment is properly designed.

The level of residue in each sample depended on the amount of refrigerant in the air conditioner, the rate at which the sample was removed (the sampling rate), and on how soon after the air conditioner was used before the sample was taken. The residue detected in the samples is primarily the compressor oil which was carried over into the sampling container by the refrigerant. No significant contamination, other than oil, was found in the CFC.

The residue (compressor oil) was also tested for purity. The results are summarized in Table 1. It was found to be very pure (>99% in all but one or two samples). The impurity was found to consist of very small amounts (<1 ppm) of a large number of different organic compounds. The concentration of any one compound was too low to allow identification. The residue turned out to be a reasonably good quality compressor oil. Attempts were made to correlate the residue purity with car mileage, with whether the compressor had failed or not, and with the part of the country where the sample was taken. No correlation was found with any of these three parameters.

The purity of the refrigerant itself was tested by withdrawing a sample of the gas phase from the sampling container and analyzing it with a gas chromatograph/flame ionization detector. The purpose of this test was to determine whether any of the refrigerant samples had been contaminated with other CFCs such as HCFC-22. The test could also identify any gaseous products of decomposition of the refrigerant or of the compressor oil. Except for two samples that showed some HCFC-22, no measurable extraneous materials were found in the gas phase of the refrigerant.

Trace quantities of other CFCs and HCFCs are common contaminants in CFC-12 and are allowed by the specifications for new CFC-12 to compose up to 0.5% of the product. Samples of new CFC-12 from several suppliers were analyzed as part of this program and were found to contain up to 0.1% HCFC-22 as well as of other volatile components. HCFC-22 contamination in operating automobile air conditioners cannot remain very high because it quickly leaks out through the rubber hose materials.

Only two samples of refrigerant out of the 227 automobiles tested were found to contain more than 0.5% HCFC-22 in the CFC-12; one contained 2% and the second 5% HCFC-22. In neither case did the level of contamination make that air conditioner's performance deteriorate to the point where the owner chose to have it repaired.

Conclusion

This sampling and analytical program showed that the refrigerant in operating air conditioners is very pure. Acids do not accumulate in the refrigerant. Any impurities that accumulate in the air conditioning system are concentrated in the compressor oil. They are dissolved by the liquid phase of the refrigerant but do not get carried over into the gas phase. The gas phase proved to be free of contaminants and equivalent in purity (as measured by a gas chromatograph with a flame ionization detector) to new CFC-12. The moisture level in the refrigerant did not show any correlation with geographic location or vehicle make.

The finding on the lack of acid is good news for the program. Because the sampling system was selected to closely duplicate the recovery system that will be used to recycle the refrigerant, there is every reason to believe that no significant quantity of acid will be removed from the unit during recycling/servicing. Furthermore, any acid present during normal capture and recycling of the refrigerant can be removed by the recycling equipment. Laboratory tests indicate that acid can be neutralized by contact with special metal compounds that can be incorporated in the recycling equipment. The acid is neutralized within a few minutes of contact. Based on this laboratory analysis, acidity in recycled refrigerants will not be a problem if recycling equipment is properly designed.

The lack of chloride or fluoride ions in the samples further reinforces the above conclusion. These ions would typically form by hydrolysis of the CFC-12, forming hydrochloric or hydrofluoric acid. The lack of these ions, coupled with the high purity seen in the CFC-12 itself, indicates that refrigerant breakdown does not occur under the conditions encountered in an automobile air conditioner.

In summary, the data gathered he indicate that the CFC-12 refrigerant do not degrade significantly with us Furthermore, while small amounts of cc taminant are removed with the refrigera during servicing, the bulk of tl contaminants remain with the compress oil. Current servicing practices do r require that the compressor oil l changed unless the compressor is r placed. The presence of HCFC-22 concentrations above the specification i new CFC-12 is rare, less than 1% of t cars tested. HCFC-22 contaminant quic ly leaks out of the automotive air con tioner through hoses and, does n appear to cause operational problen while in the system.

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***Dale L. Harmon** is the EPA Project Officer (see below).*
The complete report, entitled "Evaluation of Refrigerant from Mobile Air Conditioners," (Order No. PB 89-169 882/AS; Cost: $15.95, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
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