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ACCELERATED SEALED TUBE TEST PROCEDURE FOR REFRIGERANT 22 REACTIONS

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INTRODUCTION

Laboratory evaluations of the chemical stability properties of many air conditioning compressor and system components have presented somewhat of a dilemma to the investigator. This is due to the excellent chemical stability of Refrigerant 22 in the range of normal systems operating temperatures. With the more reactive Refrigerant 12 one can study its interaction with other hermetic system components by quantitatively measuring the conversion of R12 to R22 in sealed tubes after short exposures to reasonable temperatures.[1] Typically, such tests are performed by aging the test system for 14 days at 175°C (347°F). Similar tests with R22 have to be conducted at temperatures of at least 250°C (480°F) to obtain equivalent levels of refrigerant conversion.[2] Such temperatures, however, will oftentimes exceed the inherent thermal capabilities of many organic materials, and test results obtained at these extreme temperature accelerations may or may not be relevant to material performance in air conditioning compressors.

An alternate method is to conduct tests with R22 systems at some lower temperature, say 150°C, for long time periods in the order of several hundred days. Much of the data reported in the literature on the effects of metals and metal alloys on R22 decomposition has been obtained in this fashion.[3] While this approach is feasible for long range material studies it is of little value in situations where quick answers are needed in support of engineering and manufacturing decisions.

Our laboratory has in recent years used a compromise of sorts for sealed tube tests with R22. Materials to be tested are usually aged for 30 days at 150°C after which time the tube contents are compared visually to a standard consisting of presently used system components. If the test materials show more change than the standard they are judged to be more reactive and hence undesirable for use in our R22 systems. Test materials appearing as stable or better than the standard are considered suitable for our purposes. This procedure, as all compromises, is not always entirely satisfactory.

In order to obtain more quantitative data after short term tests at lower temperatures correlations have been established between R22 and R12.[4] Here, sealed tube test data are obtained in R12 and these results are then used to predict material compatibility in R22. This approach is based on the assumption that the very same reactive chemical entities which interact with R12 will also interact with R22 though at much slower rates for a given temperature. It has not been accepted universally.

The 30 days at 150°C test method for R22 systems has a potentially dangerous shortcoming. There are many chemical reactions that do not proceed at uniform rates with time. In some instances potential reactants do not react with each other for a finite period of time - the induction period. After this induction period reaction proceeds readily. This behavior is due to inhibiting effects of certain system components, for example, protective coatings on metal surfaces, naturally occurring inhibitors in petroleum lubricants, and others.

Another case involves reactions which will proceed for a period of time at a uniform and oftentimes quite slow pace until suddenly reaction rates increase rapidly. Such reactions sometimes exhibit run-away rates leading to rapid destruction of the initial reactants. Causes for this behavior are depletion of natural inhibitor systems or a build-up of very reactive reaction products from the slow primary reaction. The latter phenomenon has been observed in sealed tube tests involving both R12 and R22 and aluminum alloys.[5] To protect ourselves against the possibility of such run-away reactions we have frequently conducted sealed tube evaluations of metals in R22 at temperatures higher than the usual 150°C test. This procedure has been generally accepted especially in those instances where the high temperature tube test showed no increase in reactivity over the comparison standards. However, in cases where test metal specimens showed substantially increased reactivity questions have been raised about the validity of such high temperature tests for the evaluation of materials destined for much lower use temperatures in compressors.

Recently we conducted an evaluation of a zinc die cast material at both 150°C and at 200°C. Tube tests were carried out long enough at both temperature levels to allow gas chromatographic and hence quantitative analyses of the reaction products. The results of these tests and their inference on the validity of temperature acceleration in sealed tube tests with R22 are discussed in this paper.

TEST PROCEDURES

The sealed tube tests were conducted in heavy-walled glass tubes of 8mm ID, 13mm OD and an approximate internal volume of 7cc when sealed. Sealed into these tubes were a small piece of the test metal approximately 1/16 x 1/4 x 1" in size, 1.0cc of compressor oil where indicated, and 0.45g of R22. Using above quantities assured that with oil containing tubes one-half of the metal specimen was submerged in oil-refrigerant solution while the remainder was exposed to refrigerant gas. In tubes containing only R22, all of the metal specimen was exposed to refrigerant gas at aging temperatures.

Aging of the sealed tubes was carried out at 150°C (302°F) and at 200°C (392°F). The tubes were examined visually about once a week. At the end of the aging periods (530 days at 150°C and 30 and 91 days at 200°C respectively) the tubes were subjected to gas chromatographic analysis using previously reported procedures.[2]

TEST RESULTS AND DISCUSSION

Zinc die cast specimens were aged in compressor oil and R22 at 150°C without any changes observable after 30 days of aging. These results were identical to those obtained on valve steel containing test standards, i.e. no difference in behavior between the zinc alloy and the valve steel.

Concurrently identical sets of tubes were aged at 200°C. At this higher temperature we observed darkening of the oil-refrigerant solution and pitting of zinc die cast metal at the 14-day inspection. Again no changes were observed on valve steel containing tubes, indicating that at 200°C the zinc alloy is apparently more reactive than valve steel. The aging of these 200°C tubes was continued to an accumulated total of 91 days. At that point the steel containing tubes began to visually show attack on the metal specimens. The zinc alloy containing tubes, after 91 days, had been subject to considerable chemical changes as evidenced by pitting and darkening of the metal specimens, darkening of the oil, and heavy tube wall deposits.

Meanwhile, we had continued the aging of the 150°C tubes with the idea to extend aging until such time that visual evidence of zinc die cast reactivity could be observed. From the observed onset of zinc die cast R22-oil interaction after 14 days at 200°C we speculated that this would occur after about 450-500 days of aging at 150°C. This estimate was derived from the Arrhenius reaction rate theory which states that reaction rates increase by a factor of approximately 2 or 3 for each 10 centigrade degree rise in temperature. The zinc die cast specimens did actually show the first visual evidence of reaction at 150°C after aging for 472 days.

This observation provided us with qualitative evidence that the reaction of the zinc die cast metal with R22 and compressor oil proceeds at theoretically predictable rates at least over the cited temperature range. From a practical point of view this lends justification to the use of temperature accelerated data for the prediction of oil-metal-R22 interactions at lower temperatures. Subsequent gas analysis of these sealed tubes yielded additional support to this finding.

Table I summarizes the gas chromatographic data obtained from the zinc alloy containing tubes aged at both 150°C and at 200°C. The primary gaseous reaction product identified in these tubes was R23. This is the product of R22 disproportionation as identified several years ago by Spauschus and Doderer[2]:

$$\underset{\text{R22}}{2\ CHClF_2} \xrightarrow[\text{Catalyst}]{\text{Metal}} \underset{\text{R23}}{CHF_3} + CO + \text{other products} \quad (1)$$

A second recognized mechanism of R22 decomposition is the reduction reaction where R32 is the indicator gas[2]:

$$\underset{\text{R22}}{CHClF_2} + \text{Oil} \xrightarrow[\text{Catalyst}]{\text{Metal}} \underset{\text{R32}}{CH_2F_2} + \text{other products} \quad (2)$$

No R32 was found in the zinc alloy tubes.

The last column in Table I lists the mole percent of R22 decomposed. This number is the sum of the identified R22 decomposition products adjusted to account for the correct molar ratios of reactants to products as required to satisfy equations 1 and 2 above. That is, one mole percent R23 found corresponds to two mole percent R22 decomposed, whereas one mole percent R32 found corresponds to one mole percent R22 decomposed. This last column then permits a direct comparison of R22 sealed tube test results, regardless of the mode of refrigerant decomposition.

Interesting to note is the effect of oil on R22 decomposition in the presence of the zinc alloy. The quoted earlier work[2] on R22 decomposition had shown that in the absence of oil R22 disproportionates to R23 with iron, copper and aluminum catalysts. When oil was added to these systems both reduction and disproportionation took place. In the present instant oil did not cause R22 reduction to occur but rather increased the rate of disproportionation by more than one order of magnitude.

Reasons for this behavior of the zinc alloy system are not apparent at the present time though it is well to point out that the experimental conditions were not identical in the two studies. The present data were obtained at 150°C and at 200°C while the earlier results stem from 250°C aging tests.

An examination of reaction rates for the zinc-R22-oil system confirmed the earlier qualitative observation that this system obeys the general statement of the Arrhenius reaction rate theory. Aging times at 200°C were converted to equivalent aging times at 150°C by doubling the time for each ten centigrade degree difference in temperature. Thus, 30 days at 200°C are equivalent to 960 days at 150°C, and 91 days at 200°C becomes 2912 equivalent days at 150°C. A semilog plot of percent R22 decomposed against aging time at 150°C gives a nearly linear relationship as shown in Figure 1. Calculations show that a factor of 1.87 for each 10 degree temperature difference (instead of 2.0 as used in the conversion of the 200°C data) would more correctly fit the data obtained in our experiments. Additional calculations based on the data in Table I show that the activation energy for the reaction between zinc alloy and oil-R22 is about 25,000 calories/mole - a reasonable figure for this type of chemical reaction.

The 200°C compatibility test method described in detail for the zinc-R22-oil interaction has since been used to determine the effects on system stability of a few other metallic compressor construction materials. Table 2 lists tube test data obtained with lead, a brass alloy, two steel alloys and a zinc chromate plated steel. Note that the lead gave rise to both R23 (disproportionation of R22) and R32 (reduction of R22) under the conditions of these experiments. A more ready comparison of the relative effects of these metals on system stability is provided by the block diagram displayed in Figure 2.

The data summarized in Figure 2 allow us qualitative judgement about the relative reactivity of the materials listed. Not provided is quantitative information as to the degree of liability the designer would incur if one substituted one metal for another. Figure 3 attempts to provide quantitative estimates of this type.

In Figure 3 mole percent R22 decomposed per <u>day</u> is plotted against reaction temperatures. The line for zinc alloy is derived from data points at 150°C and 200°C. The plots for the other metals are based on the 200°C experiments only, with the corresponding lines drawn parallel to the zinc alloy line. This, of course, assumes that the zinc reaction proceeds by the same mechanism as that of the other metal - R22 - oil reactions.

The following examples will illustrate the use of Figure 3. Let us say we want to replace a compressor part currently fabricated from a ferrous alloy (either carbon steel or something similar in chemical composition) with one made from the zinc die cast alloy. The part in question is exposed normally to oil and Refrigerant 22 at a temperature of 175°F. The normal running time per year for the unit is 2400 hours. What will be the effect of this material change on the chemical stability of the system over a ten year period?

Extrapolation of the line for carbon steel in Figure 3 indicates a decomposition rate of 7×10^{-8} mole percent R22 per 24 hour operation period or 7×10^{-5} mole percent per 10 years of service. For zinc alloy the corresponding rate is 2×10^{-2} mole percent R22 decomposition for a 10 year period. In either case the accumulated R22 decomposition is quite small and in all probability the zinc die cast will not present any significant problems in terms of the overall chemical stability of the air conditioning system.

On the other hand, if above material substitution were to be made for a part exposed during operation to temperatures in the 250°F range, (for example near the exhaust valve) the R22 decomposition rate will change from 4×10^{-3} mole percent for the ferrous alloy to 1 mole percent for the zinc alloy over the 10 year service period. While there are no hard and fast rules about the amounts of refrigerant decomposition that can be safely tolerated in a system, an estimated refrigerant decomposition of 1 percent due to one system component tells us that at a minimum great care should be exercised prior to instituting the proposed material substitution.

SUMMARY

A sealed tube test procedure has been described for quantitative evaluation of the chemical compatibility of compressor components in Refrigerant 22 systems. To permit test completion within a reasonable length of time testsare conducted at temperatures significantly higher than those encountered in actual service. A test period of 30 days at 200°C (392°F) yields quantitative information about interaction of metals with Refrigerant 22 and compressor oil. Justification for the extrapolation of the 200°C reaction data to lower temperatures is demonstrated by reaction rate data obtained with a zinc die cast alloy.

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Compression Refrigeration Systems", Proceedings of the XI International Congress of Refrigeration, Munich, Germany, September 1963, pg. 685-691.

TABLE 1

SEALED TUBE TEST DATA FOR REACTION OF
ZINC DIE CAST ALLOY WITH R22/OIL AND WITH R22

REACTION SYSTEM ZINC ALLOY PLUS	AGING TEMPERATURE	AGING TIME	VISUAL APPEARANCE AFTER AGING	GAS CHROMATOGRAPHIC ANALYSIS % NONCONDENSABLES (CO, N_2, CH_4)	% R23	% R32	MOLE % R22 DECOMPOSED (REF. 2)
R22 and Oil	200°C	91 days	Liquid pale yellow; metal black & pitted wall deposits	3.32	5.93	-- *	11.86
R22 only	200°C	91 days	No visual changes	0.03	0.39	--	0.78
R22 and Oil	200°C	30 days	Liquid pale yellow; metal black; wall deposits	0.12 0.16 0.12	2.20 2.36 1.75	--	4.40 4.72 3.50
R22 and Oil	150°C	530 days	Liquid very pale yellow; Metal black; Wall deposits	0.08 0.06	1.8 1.3	--	3.6 2.6
R22 only	150°C	530 days	No visual changes	0.02	0.008	--	0.016

* Also found in this tube were CO_2, C_2H_6 (ethane), and R12.

TABLE 2

SEALED TUBE TEST DATA FOR REACTION OF
METALS WITH R22 AND OIL

Tube charges: Metal Sample 1/16 x 1/4 x 1", 0.45g R22, 1cc of Compressor Oil (where indicated).
Test Conditions: 30 days at 200°C

TEST METAL	OIL PRESENT	VISUAL APPEARANCE AFTER AGING	GAS CHROMATOGRAPHIC ANALYSIS % NONCONDENSABLES	% R23	% R32	% R22 DECOMPOSED
Valve Steel	Yes	Metal lightly tarnished	NIL	0.01	N.D.	0.02 max.
Carbon Steel	Yes	Metal lightly tarnished	0.06	0.04	N.D.	0.08
Zinc Chromate Plated Carbon Steel	Yes	Metal blackened; Wall deposits; liquid from water-white to light tan	1.08	0.89	0.09	1.87
Brass	Yes	No visual changes	NIL	0.01	N.D.	0.02 max.
Brass	No	No visual changes	NIL	0.01	N.D.	0.02 max.
Zinc Die Cast Alloy	Yes	Metal blackened; Wall deposits; liquid yellow	0.13	2.10	N.D.	4.20
Lead	Yes	Liquid phase pale yellow	0.08	0.07	0.33	0.47
Lead	No	Liquid phase pale yellow	0.11	0.04	0.14	0.22

FIGURE 1

RATE FOR R22 DECOMPOSITION FOR THE REACTION SYSTEM ZINC DIE CAST ALLOY-R22-OIL

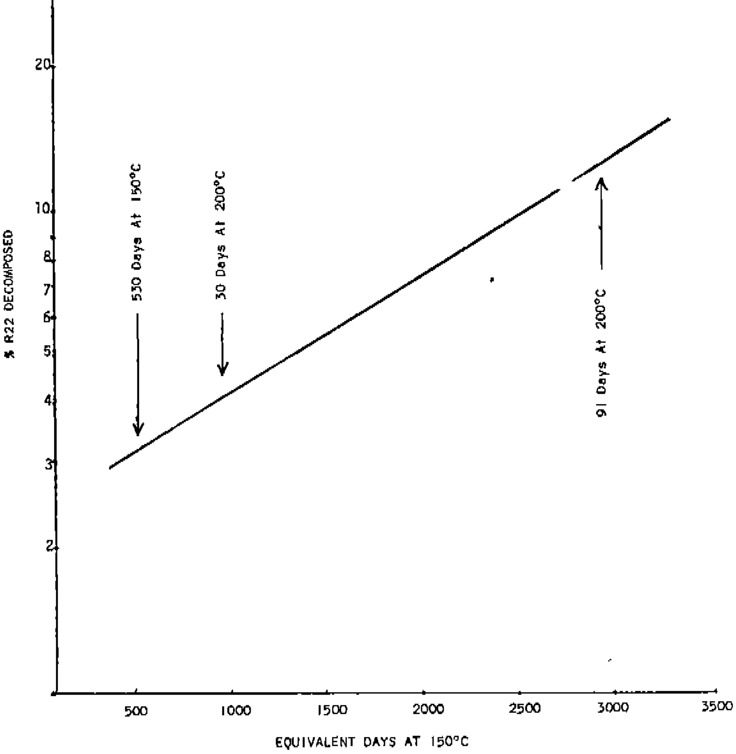
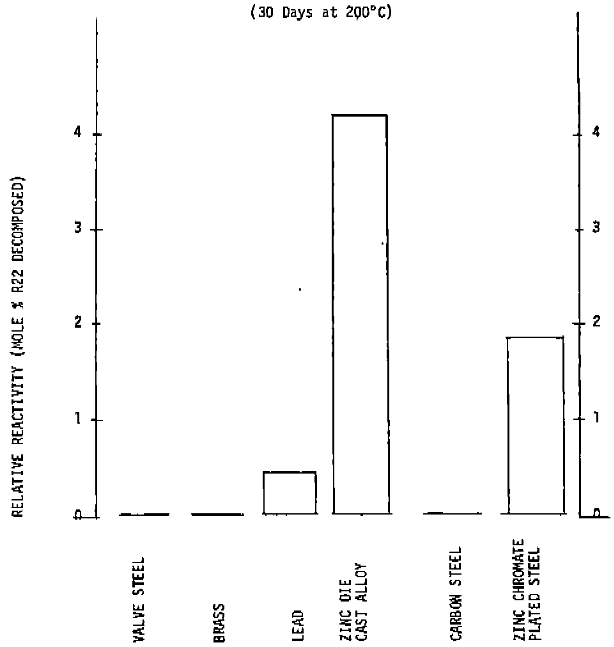


FIGURE 2

RELATIVE REACTIVITY OF METALS WITH R22-OIL

(30 Days at 200°C)



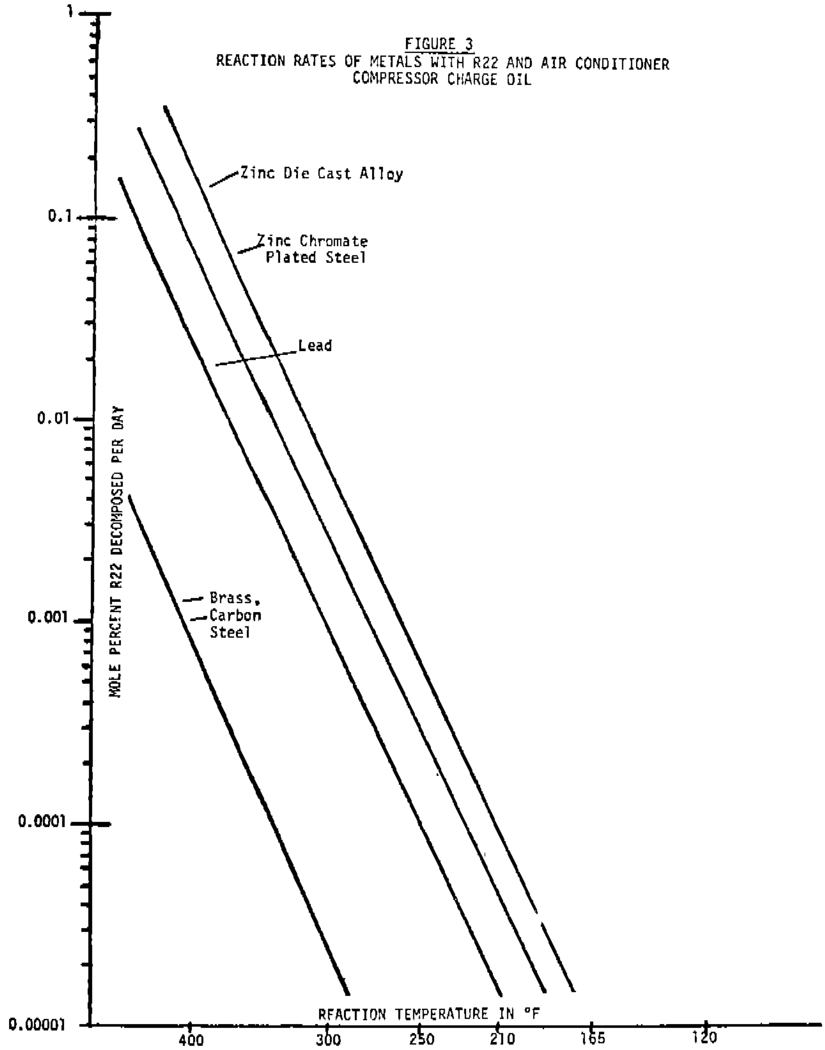


FIGURE 3
REACTION RATES OF METALS WITH R22 AND AIR CONDITIONER COMPRESSOR CHARGE OIL
Zinc Die Cast Alloy
Zinc Chromate Plated Steel
Lead
Brass, Carbon Steel
MOLE PERCENT R22 DECOMPOSED PER DAY
1
0.1
0.01
0.001
0.0001
0.00001
REACTION TEMPERATURE IN °F
400
300
250
210
165
120